Some electrochemical papers: Department of Chemical Engineering, 1906-1935. 1936

[s.l.]: [s.n.], 1936

These papers in Applied Electrochemistry are placed in the Library of the Chemical Engineering Department for the convenience of our students in electrochemistry.

Oliver P. Watts.

Oct. 2. 1939.

SOME

ELECTROCHEMICAL PAPERS

DEPARTMENT OF CHEMICAL ENGINEERING

1906 - 1935

CONTENTS

ELECTROPLATING.

18. Addition Agents in Deposition of Iron.

19. Cleaning and Plating in the Same Solution.

20. Rapid Nickel Plating.

21. Progress of the Hot Nickel Solution.

22. Protection of Iron by Electroplating.

23. Evolution of Hydrogen from Cyanide Plating Solutions.

24. Remarkable Pitting of Electroplating.

25. Plating Iron from Copper Sulphate Solution.

26. Diffusion of Electroplate into Zinc.

27. Effect of Nitrates on Current Efficiency of Plating Solutions.

28. Anodes for Chromium Plating.

29. The Plating on Radiator Shells.

30. New Bath for Direct Nickeling of Zinc.

31. Throwing Power and Current Efficiency of Nickel Plating Solutions at Low and at High pH.

REPORT OF COMMITTEE ON TEACHING OF ELECTROCHEMISTRY

AMERICAN ELECTROCHEMICAL SOCIETY

The undersigned were appointed as a committee to answer the following three questions addressed to the American Electrochemical Society by Mr. W. E. Wickenden, director of the investigation of engineering education, now being conducted by the Society for Promotion of Engineering Education.

1. How many graduates of engineering schools should be definitely pointed to your special field each year to meet reasonable demands without overcrowding?
2. What specific training, in addition to the foundation subjects common to practically all engineering courses, should the above-mentioned group receive?
3. What training bearing directly upon your field should be offered the general body of students in the electrical and chemical or other courses?

As a first step, all available college and university catalogues were examined to learn to whom letters of inquiry should be sent. Although the questions above were limited to engineering schools, other schools were included in the list to whom letters were sent, because the Round Table Discussion is not to be limited to the teaching of electrochemistry in engineering schools.

In one hundred and twenty colleges of the United States and Canada, forty-nine gave no instruction in electrochemistry; fifteen devoted one semester or more of physical chemistry to electrochemistry, while sixty-four catalogued courses in electrochemistry.

Sixty-seven letters brought twenty-nine replies. Ten of these were from the East, ten from the Middle West, five from the Far West, and four from Canada. The failure to receive replies from teachers of electrochemistry who have been or are now prominent in this society, and a half dozen of the largest and most important of the endowed and state universities in which electrochemistry is taught, is disappointing, to say the least.

In all but one of the twenty-nine schools, instruction in electrochemistry is given as a part of the student's general education in connection with some special course, either as a required or elective subject.

	Required.	Optional.
Chemistry Course	6	4
Chemical Engineering Course	18	2
Electrical Engineering Course	5	4
Metallurgy	3	0

Optional means that electrochemistry is reported as frequently elected by students in the course specified.

An attempt has been made to classify instruction in electrochemistry as "theoretical"—confined to the ionic theory, conductivity, etc.—and "applied,"—dealing with the application of electrochemical principles to industry. So far as could be determined from the replies the actual hours given to electrochemical instruction are as follows:

	Lecture or recitation.			Laboratory.		
	Min.	Max.	Average.	Min.	Max.	Average.
Theoretical	12	75	54	20	88	60
Applied	20	108	55	0	144	59

Two schools specialize in electrochemistry to the extent of giving a four-year course leading to the degree of B.S. in electrochemistry; a reply was received from but one of these two.

Regarding the specific instruction which should be given in electrochemistry, only eight answered the question. One considered electro-analysis sufficient. Others say "the fundamentals," or specify some particular text book. Electrolysis, plating, corrosion, the refining and recovery of metals, organic and inorganic preparations by electrolysis are mentioned.

As specific subjects in addition to those common to all engineering courses, which the student of electrochemistry should take, are the following: direct and alternating current machinery, power transmission, physical chemistry and metallography.

The recommendation of the course or courses in which instruction in electrochemistry should be given follows closely the practice of each school.

Several schools are graduating twenty to thirty men annually who have had instruction in electrochemistry, none of whom are employed in electrochemical work. Four schools report the total of graduates for a dozen years or more who have been instructed in electrochemistry as follows:

Graduate	In Elect. Chem. work.	Per cent.
244	Half (estimated)	50
169	8	4.7
114	16	14
238	8	3.5

Eleven schools report a demand for graduates because of their instruction in electrochemistry; fourteen find no such demand. Nineteen report as the number of men which they can place because of their electrochemical training, none; the remaining ten report a total of twenty-six.

Judging from the replies of the schools, the demand for technical men with some instruction in electrochemistry is confined mainly to the East, is very slight in the Middle West, shrinks to zero on the Pacific coast and Canada, with the South not heard from.

THE ELECTROCHEMICAL INDUSTRIES

Although it was thought that the electric steel industry and manufacturers of electric furnaces would have little or no use for men instructed in electrochemistry as at present taught, they were included among the industries to whom letters were sent. For convenience the industries were classified as follows:

	Letters.	Replies.	Yield.
Industrial Research Laboratories	10	5	50%
Refineries	11	2	18%
Special Furnace Industries SiC, A_2O_3, P, CaC_2, etc.	12	1	8.3%
Caustic & Chlorine	6	1	16%
Special Electrolytic Al, $KClO_3$, CCl_4, etc.	6	3	50%
Electric Steel	12	2	17%
Electric Furnace Mfgrs.	66	1	17%
	63	15	24%

Sixty-three letters elicited fifteen replies. Outside of electric steel and furnace manufacturers, twelve companies with a total of six hundred and thirty technical men, employ sixty-five of these because of their electrochemical knowledge. Eleven companies express a preference that either a few or all of their technical employees shall have studied electrochemistry. Eight prefer that these men get their electrochemical instruction in a course in chemistry, three in chemical engineering, and four in metallurgy. Only six companies have any annual requirement for graduates with training in electrochemistry, and their requirement totals fourteen.

The following comments are from two different electrolytic industries:

"We would be glad to have them have a little general knowledge of electrochemical theory, in a few cases. It is my personal opinion that such instruction can best be given in connection with the courses in chemistry. In explanation of the above answers, I may say that in employing a man for a position we expect him to have a good fundamental training in chemistry or some branch of engineering which particularly fits him for the position which he is to fill. Aside from this fundamental training we consider the most important qualifications to lie along the lines of character, personality, energy and ability. Naturally for certain positions, such as the higher positions in chemical laboratory work for example, a considerable amount of previous experience in the practice of his profession is required of the applicant. As far as his schooling goes, however, we feel that a thorough fundamental training in his profession is of more importance than any course which he may or may not have had in electrochemistry as such."

"In answering your whole topic very generally, we would say that we have need for men who have pursued mechanical courses, metallurgical courses, and chemical courses. For laboratory work the more chemistry a man has had, the better will be his usefulness here. For our mechanical and construction work we need men strongly specialized along mechanical lines, while for our more general work a metallurgical training is desirable, because this plant is especially a metallurgical plant. We find that men coming to us have frequently very strongly specialized. The chemists know very little of metallurgy, less of electrical engineering, and nothing about mechanical engineering, and you might apply a similar classification to each of the other several lines. Rather than specializing in electrochemistry, I should think that metallurgical students should be given a basic training in electrical and mechanical fundamentals. This certainly applies to undergraduate work, and, in my opinion, also to graduate or other courses of longer duration. The electrometallurgical knowledge of the kind required in our business can be acquired by continuation of study after entering into the practical operation, and we believe that the larger basic education is an advantage."

From the director of a great research laboratory: "It seems to me that you ought to add electrical engineering to the courses in which instruction in electrochemistry should be given. I believe that all courses would be improved by the addition of electrochemistry."

If the few replies received may be taken as representative of the electrochemical industry, both schools and industry agree that specialized education in electrochemistry should not be undertaken as a part of the four years study for the bachelor's degree. The fact that in so many schools electrochemistry is a required study shows a belief in its value as a part of the education of the technical graduate.

The specific training which should accompany electrochemistry is indicated by the courses in which it is recommended, the schools placing chemical engineering first and chemistry second, while the industries prefer that electrochemistry should be an accompaniment of a chemical course, with metallurgy and chemical engineering following in order of preference.

From the time devoted to electrochemistry it is evident that some schools are giving to this subject quite all the attention which, as a mere part of some broader course, it deserves; others are giving so little time to it that their students can know little more than that there is a field of organized knowledge called electrochemistry. The subject matter of electrochemical instruction varies nearly as greatly as the time given to it. Catalogues show that what different colleges teach under the name of electrochemistry may be any of the following:

(a) A semester of electro-analysis.

(b) A term or semester of lectures on the ionic theory, with or without laboratory work.

(c) Lectures or recitations on the electrochemical industries, with or without laboratory practice.

(d) A semester or more of both class and laboratory work on the ionic theory and its applications, followed by an equal time on industrial electrochemistry, and sometimes an additional year's work on some special problem as a graduate thesis.

With such a wide variation in the extent and content of what the schools are teaching under the name of electrochemistry, it is little wonder that the electrochemical industries are not wildly enthusiastic that their technical men shall have taken a course in this uncertain quantity. Two reasons for this unsatisfactory condition in electrochemical instruction are probably,

(a) Its newness,—electrochemistry has had a place in most schools for less than ten years.

(b) No attempt has ever been made by the teachers of electrochemistry, by this society, or by the electrochemical industries to define or determine either the content or extent of what might be accepted as reasonable instruction in electrochemistry.

Where electrochemistry is taught only for its general value in some specific course, as is almost universally the case at present, the time available will not permit going deeply into both the theory and industrial applications, and one of these must be stressed to the relative neglect of the other. This difficulty is likely to increase rather than to diminish, for the engineer and technical man is coming to appreciate more and more the value of such studies as economics and business administration, and some of the long-established subjects of technical courses will, in the near future, have to show cause why they should not be thrown out to make room for these newcomers. Besides furnishing the basis for an understanding of a wide variety of phenomena encountered in living as well as in industry, it should not be overlooked that electrochemistry is an admirable subject for developing the student's powers of observation and reasoning.

The Committee,
O. P. Watts, *Chairman*
L. Kahlenberg
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American Electrochemical Society,
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New York City.

A paper presented at the Nineteenth General Meeting of the American Electrochemical Society, in New York City, April 7, 1911, President Wm. H. Walker in the Chair.

POLARIZATION IN ITS RELATION TO THE DECOMPOSITION PRESSURE OF ELECTROLYTES.

By OLIVER P. WATTS.

One of the properties which distinguishes electrolytic from metallic conductors is the relation between the impressed electromotive force and the current which is produced thereby. In a metallic wire, the resistance of which is known, the current may be calculated by an application of Ohm's law. This is not so for electrolytes when "direct current" is used, except for a few combinations of special electrodes and a particular electrolyte.

If a gradually increasing E. M. F. is applied to the ends of a wire and simultaneous readings of the current and pressure are made, the current increases in the same ratio as the E. M. F.

When an electrolytic conductor with electrodes of platinum, carbon, or some other material, insoluble in the particular electrolyte chosen, is substituted for the wire, it is found that for small values of pressure no permanent current flows. The E. M. F. must exceed a certain minimum value before a permanent current is obtained. This minimum value is the so-called decomposition pressure.

In Table I are given the values of current corresponding to the indicated E. M. F. applied to two feet of No. 26 "ni-chrome" wire.

TABLE I.

Impressed E. M. F. Volts	Current Milli-amperes	Impressed E. M. F. Volts	Current Milli-amperes
0.25	48	1.75	344
.50	95	2.	390
.75	143	2.50	490
1.00	190	3.	586
1.25	242	3.50	680
1.50	292	4.	775

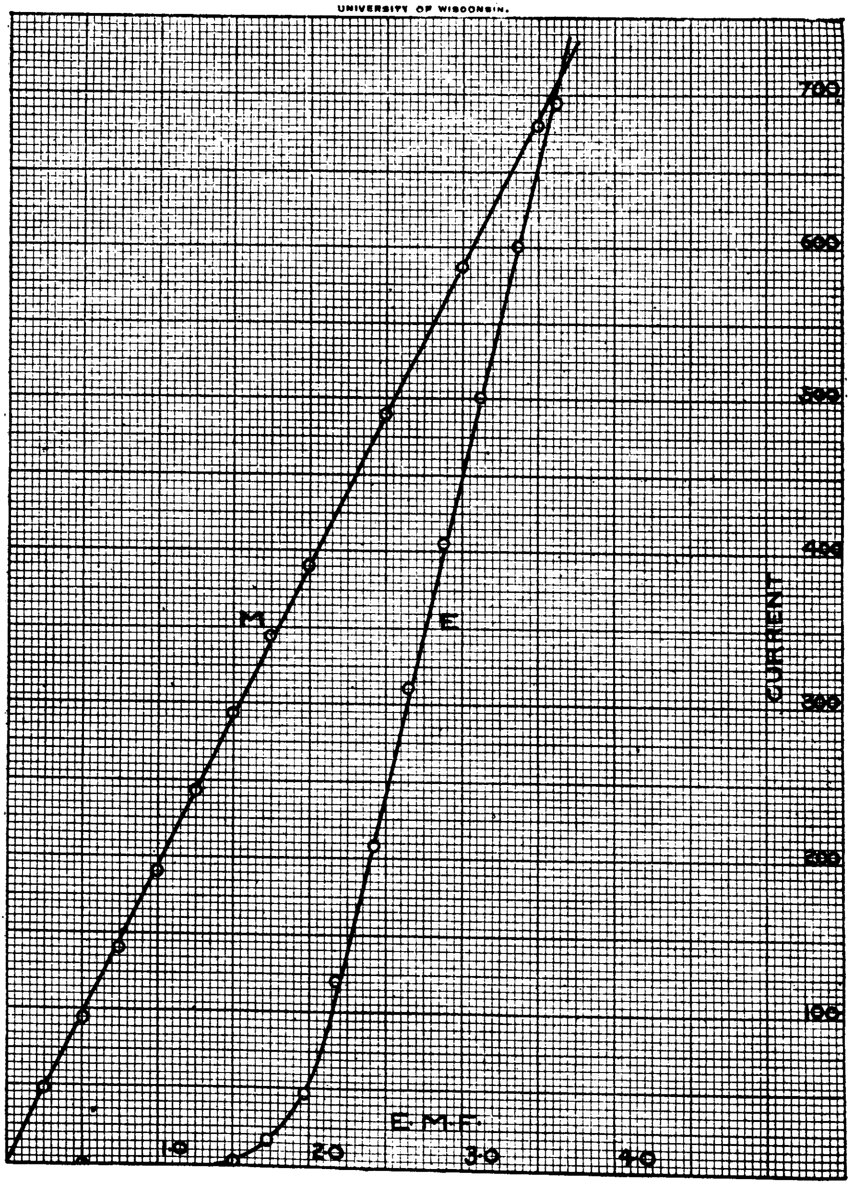

FIG. 1. Current-E. M. F. Curves for a Metallic (M) and for an Electrolytic (E) Conductor.

Figure I shows graphically the relation between current and E. M. F. for the wire, and for a 10 percent solution of zinc bromide with carbon electrodes. The numerical data for the latter are given in Table VI.

It is of interest to review the explanations which have been offered for this peculiar behavior of electrolytes. First in point of time was Grotthus' hypothesis, which was proposed in 1820. According to this, the reason why any pressure, however small, does not send a current through an electrolyte as it does through a metal is because a definite E. M. F. is required to break up the molecules of each particular compound, and therefore no current can pass below that E. M. F. These "decomposition pressures" have been determined experimentally for many different solutions, and it has been found that the more stable a chemical compound is, the greater its decomposition pressure. From the values of the heats of formation and of solution of compounds, it has been found possible to compute values for the decomposition pressures, which agree closely with those obtained experimentally.

Into this seemingly satisfactory agreement of theory with experimental observation, there was projected a disturbing fact. It is possible for an E. M. F. far below the decomposition pressure to produce a considerable momentary current, or a very minute steady current in an electrolyte. To harmonize theory and fact, Clausius, in 1856, suggested that the molecules of a dissolved compound which is capable of conducting an electric current are not firmly locked together, but that the atoms are continually changing partners with their neighbors, and that the E. M. F. is not called upon to disrupt molecules, but only to give direction to the movements of the atoms or radicals during their moments of freedom. It should thus be possible for any E. M. F., however small, to produce a flow of current in an electrolyte.

In the more recent theory of "electrolytic dissociation," advanced by Arrhenius in 1887, it is assumed that by the mere act of dissolving, a large proportion of the molecules of all dissolved substances which yield conducting solutions are broken up into two or more parts.

Thus each of the later theories of the mechanism of the process of electrolysis has been formulated in such a way as to eliminate any "decomposition pressure," yet in every case of electrolysis with insoluble electrodes no permanent current of any magnitude is obtained until a certain voltage has been exceeded. Theoretically the phenomenon of the decomposition pressure has been eliminated; practically, it is still with us.

Although the cause of this phenomenon has been clearly set forth in some of the texts on electrochemistry, there still seems to be considerable misapprehension upon this point.

One view of the cause of the different behavior of metallic and of electrolytic conductors is indicated in the two following quotations:

[1] "The advantages of soluble anodes over insoluble anodes is that a very much smaller E. M. F. is required to produce the same result. * * * This is due in the two cases to a difference in the contact resistance to the current, as it leaves the electrode and enters the solution, which is sometimes called "transfer resistance." This is undoubtedly a physical effect, which must not be confounded with the phenomena of polarization. With insoluble anodes, *this resistance is said to be largely due to a condensed film of gas,* which is only slightly removed by agitation of the liquid, but it is also accounted for by other actions of a more complex nature."

In a very valuable and suggestive paper[2] upon the corrosion of metals, it is pointed out that the rusting and corrosion of iron is an electrolytic process and that the speed of rusting depends upon the rate of removal of a protective film of hydrogen which forms upon the metal. Thus we find:

"One fact regarding the corrosion of iron appears to be undisputed, *viz.,* that oxygen is necessary for a continued action. This corrosive action can cease from two causes, viz., * * * or the action may be stopped by a film of molecular or gaseous hydrogen upon the metal, which, owing to its resistance, prevents the flow of an appreciable current."

It is the purposes of this paper to show clearly that the principal factor in causing the phenomenon of the decomposition voltage as observed in electrolysis is not the *resistance* of a gas or other film upon either or both electrodes, but that it is due to a counter-electromotive force which is produced at the electrodes as a result of the action of the impressed E. M. F. This counter-E. M. F. will hereafter be referred to as polarization.

Let a voltmeter and a milli-ammeter be suitably connected to two platinum electrodes immersed in dilute sulphuric acid or

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[1] Cyaniding of Gold and Silver Ores. Julian and Smart, p. 137.

[2] Tr. Amer. Electrochem. Soc., **14**, 179 (1908).

sodium chloride, and readings of current made as the impressed E. M. F. is increased. If the circuit is opened from time to time for the purpose of reading the polarization, great difficulty will be experienced, if it be not found utterly impossible, to get satisfactory readings when the electrodes are the small ones of one or two square centimeters area, such as are commonly used for these experiments in the laboratory. The polarization is there, but the voltmeter requires a greater current for its action than this tiny storage cell can furnish.

TABLE II.

Electrolyte, Normal NaCl. Electrodes, carbon.

Impressed E. M F. Volts	Current Milti-amperes	Polarization Volts
0.1	0	0.075
0.2	0	.16
.45	0	.40
.62	0	.58
.84	0	.80
.96	0.25	.88
1.09	0.25	1.03
1.26	0.4	1.18
1.51	1.0	1.38
1.96	5.	1.57
2.21	10.5	1.80
2.51	22.	1.84
2.80	60.	1.84
3.00	105.	1.83

In Table II and Fig. 2 are given the results obtained when the potentiometer is substituted for the voltmeter. The electrolyte was normal sodium chloride and the electrodes were of carbon, 6 x 9 mm., immersed about 37 mm. The curves indicate the reason for no permanent current up to 1.5 volts.. With each increase of applied pressure there is developed a counter-electromotive force equal to it, so that no current can flow, and the only reason there is ever any permanent current through an electrolyte when using insoluble electrodes is because there is a limit beyond which the polarization no longer increases in the same ratio as the impressed E. M. F. At about 1.5 volts the polarization lags behind the impressed E. M. F., and at this point the flow of current begins. At about 2.5 volts the polarization has reached its maximum value, so beyond this pressure the current varies directly as the impressed E. M. F.

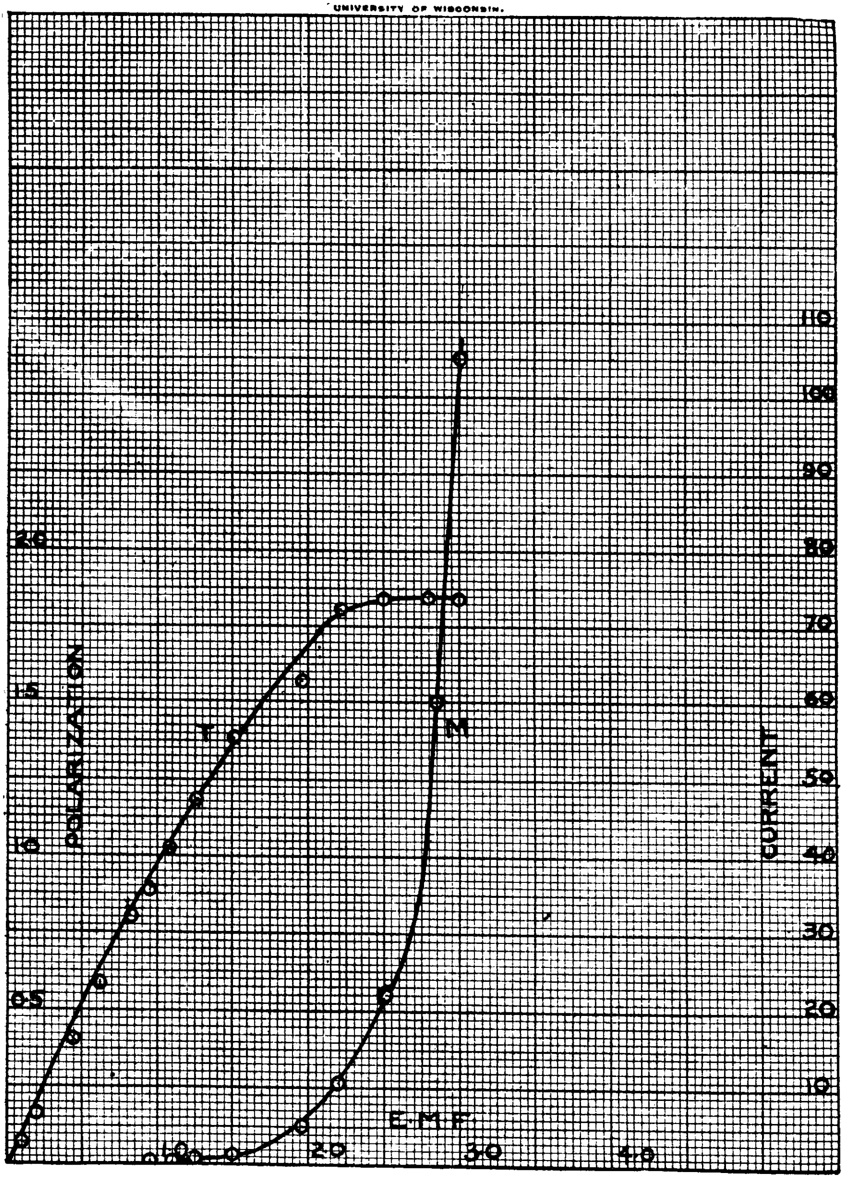

FIG. 2. Electrolysis of n.NaCl.—Carbon Electrodes.

The only possible part that the resistance of a gas film can play is to that small extent by which the polarization falls short of equaling the impressed E. M. F. The method of reading the polarization consisted in opening the line switch with one hand

and afterward closing the key of the galvanometer with the other, so that an appreciable interval elapsed between the breaking of the circuit and the reading of the galvanometer. It is therefore probable that the actual values of the polarization are slightly higher than the values recorded.

TABLE III.

Electrolyte, Normal $CuSO_4$. Electrodes, platinum.

Impressed E. M. F. Volts	Current Milli-amperes	Polarization Volts
0.25	0	0.25
.50	0	.43
.75	0	.71
1.00	0	.90
1.25	0	1.13
1.50	1.	1.30
1.75	7.	1.36
2.0	11.	1.40
2.25	37.	1.40
2.50	53.5	1.40
2.75	70.	1.39
3.00	85.	1.41
3.25	102.	1.41
3.50	119.	1.43
3.75	136.	1.43

Table III and Fig. 3 show similar observations for normal copper sulphate with electrodes of sheet platinum one centimeter square. The general character of the curves is the same as for sodium chloride. It is to be noted that in this case gas is liberated only at the anode, and if it were the resistance of a gas film which prevents the passage of the current below 1.25 volts, this action would be confined to the anode, and the single gas film there would have to be quite as effective as the two films, one at each electrode, in the case of common salt.

The cause of the polarization is indicated by the behavior of the ammeter needle. When the E. M. F. is 0.5 volts, or any other value below the decomposition point, if the circuit be opened for a minute, and then closed again, at the instant of closing there is a considerable rush of current, which in a second or two dies away to zero, the value of the permanent current for the E. M. F. applied. When the circuit was open there was little or no polarization at the electrodes, and on closing the circuit a flow of

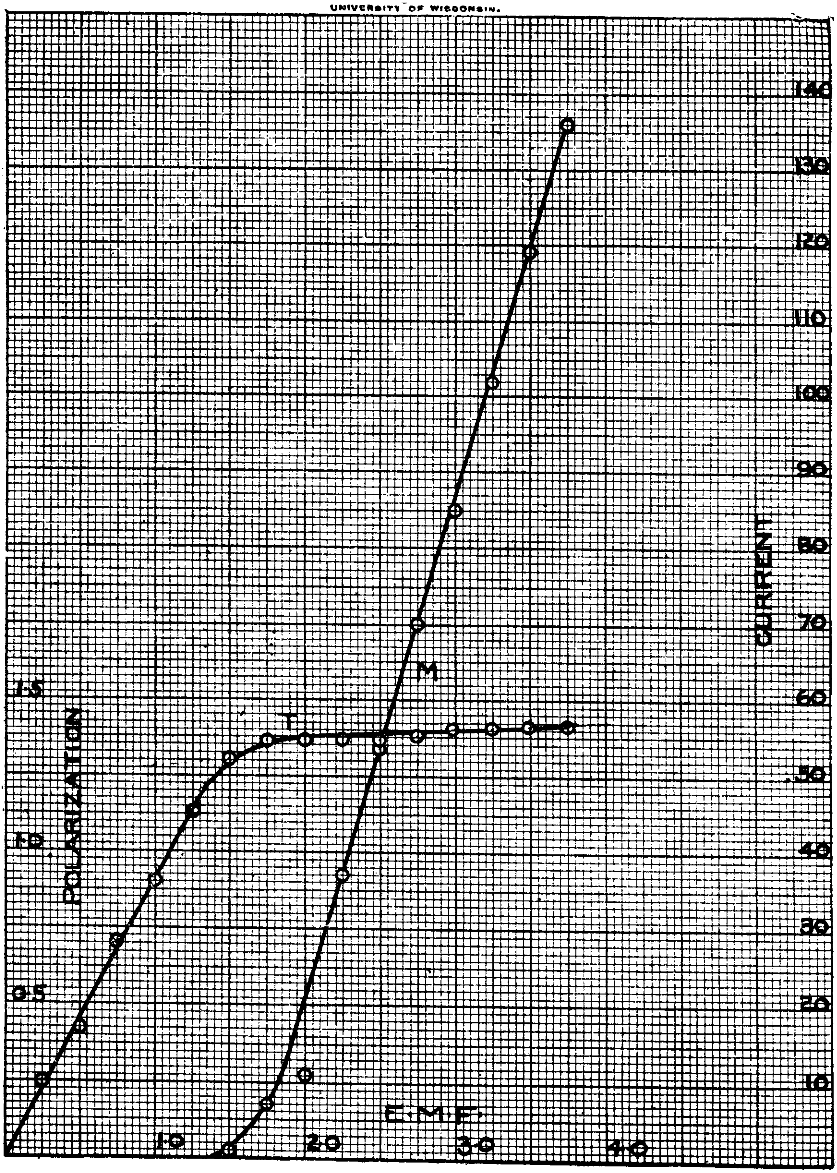

Fig. 3. Electrolysis of n.CuSO$_4$—Platinum Electrodes.

current began according to Ohm's law, just as it would flow through a wire, but, as a result of the deposition of the products of electrolysis at the electrodes, an increasing counter-electromotive force was produced, which finally attained the value of the impressed E. M. F. and stopped the flow of current.

The "residual current," that permanent current, normally so small as to escape notice, which flows through electrolytes at any constant E. M. F. below the decomposition pressure, is only the current required to deposit products of electrolysis equal in amount to those dissolved by the electrolyte or otherwise removed.

By the introduction of a third electrode and the measurement of the differences of potential between this and the anode and cathode, it is possible to ascertain what proportion of the total polarization is contributed by the anode and what by the cathode. The most satisfactory reference electrode to use for this purpose is the "normal calomel electrode," so well known that a description of it is unnecessary.

TABLE IV.

Electrolyte, normal $CuSO_4$. Electrodes, platinum.

Impressed E.M.F. Volts	Current Milli-amperes	Polarization Anode volts	Polarization Cathode volts	Total volts
0.05	0	—0.882	—0.839	0.031
.25	0	—.903	—.689	.236
.48	0	—1.118	—.646	.460
.72	0	—1.355	—.646	.709
.96	0	—1.591	—.642	.962
1.20	0	—1.763	—.581	1.185
1.44	0.5	—1.883	—.560	1.344
1.68	5.	—2.020	—.560	1.460
1.92	18.	—2.012	—.560	1.452
2.17	33.	—2.020	—.560	1.460
2.42	49.5	—2.020	—.560	1.460

Table IV and Fig. 4 show the results of repeating the electrolysis of normal copper sulphate and determining the polarization at each electrode. The current curve, M., and the curve of the total polarization, T, are as in the previous experiment. The curves of polarization of the anode, A, and of the cathode, C, are especially interesting. The initial readings of polarization at anode and cathode, before any external E. M. F. was applied to them, was omitted by the student who performed this experiment, but if curves A and C were extended backward to obtain the value of the polarization at zero E. M. F., both electrodes would show about 0.77 volts, the single potential of platinum in this electrolyte. As the E. M. F. impressed upon the electrodes is increased, the curves A and C separate, the potential of the cathode increasing to

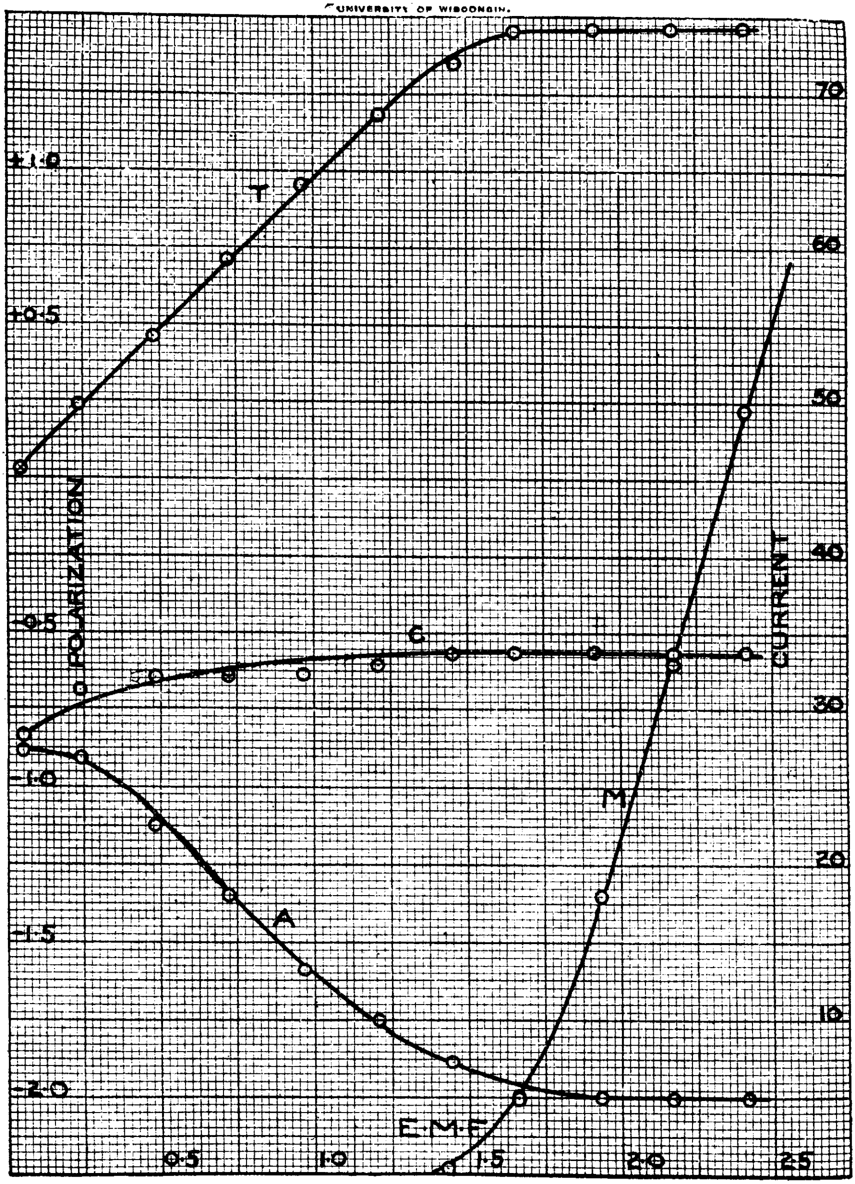

FIG. 4. Electrolysis of n.$CuSO_4$—Platinum Electrodes.

that of copper as its limit, and the potential of the anode diminishing to that of platinum saturated or coated with oxygen. It is seen that the polarization of the cathode quickly reaches a maximum, while that of the anode continues to increase until the impressed

E. M. F. reaches 1.75 volts. The cathode contributes only 22 percent to the total maximum polarization, the remainder being due to the anode. A comparison of the distances between curves A and C at various points, with values shown on curve T for the same E. M. F., shows how closely the separate potentials of anode and cathode agree with measurements of the total polarization.

TABLE V.

Electrolyte, zinc bromide. Electrodes, carbon.

Impressed E. M. F. Volts	Current Milli-amperes	Polarization		
		Anode Volts	Cathode Volts	Total Volts
0	0	—0.995	—0.992	0.009
0.05	0	—1.004	—.960	.037
.15	0	—1.050	—.951	.102
.25	0	—1.137	—.919	.215
.48	0.5	—1.245	—.809	.429
.72	0.7	—1.251	—.575	.667
.96	0.7	—1.253	—.342	.893
1.20	0.8	—1.271	—.148	1.122
1.44	2.5	—1.285	+.026	1.311
1.68	18.	—1.315	+.165	1.479
1.92	43.5	—1.323	+.368	1.654
2.17	119.	—1.362	+.456	1.816
2.42	209.	—1.372	+.461	1.833
2.65	310.	—1.372	+.472	1.845
2.88	405.	—1.372	+.484	1.856
3.13	500.	—1.372	+.484	1.856
3.38	600.	—1.372	+.484	1.856
3.62	695.	—1.401	+.461	1.862
3.86	795.	—1.401	+.461	1.862
4.11	925.	—1.401	+.461	1.862

Table V and Fig. 5 are the results of the electrolysis of a solution of zinc bromide with carbon electrodes. The cathode contributes 78 percent of the 1.86 volts total polarization, while the anode supplies the remaining 22 percent. The electrolysis of zinc bromide effectually disposes of any claim that the failure to obtain a visible current with the first application of E. M. F. to electrolytes is due to the resistance of a gas film at either electrode. No gas is evolved in this case, except that at a very high current density a little hydrogen may be deposited along with the zinc at the cathode.

The curves for the cathode in figures 5 and 6 show a gradual change from electrodes of platinum to copper and zinc, respectively. Similarly, the anode curves represent the change from a

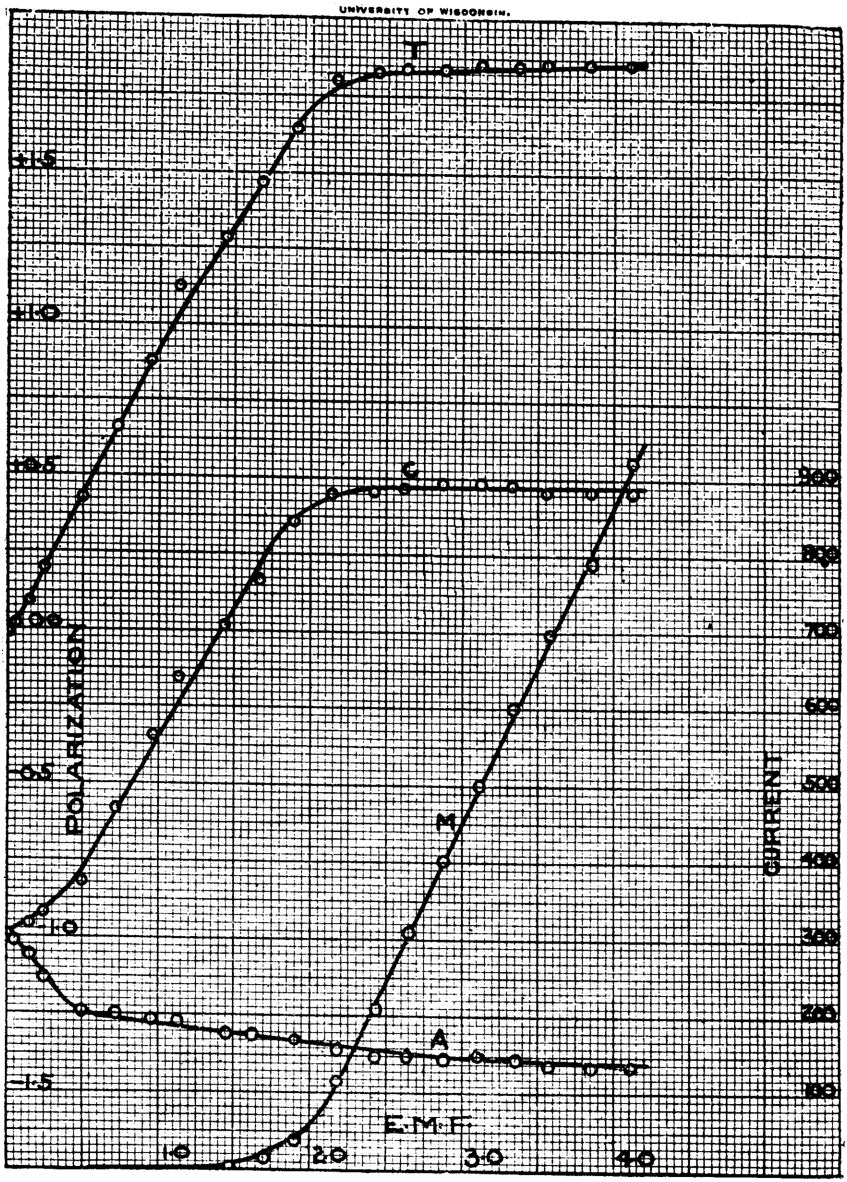

FIG. 5. Electrolysis of $ZnBr_2$—Carbon Electrodes.

platinum electrode making contact with the original solution, to platinum saturated or alloyed with oxygen and with bromine, respectively, making contact with an electrolyte saturated with these products of electrolysis. The source of the counter-electromotive force, then is of the same nature as the E. M. F. of any primary, or storage cell, viz., it is the result of an unsymmetrical electrochemical system, consisting of two electrodes in one or more electrolytes. Before electrolysis the electrolytic cell was symmetrical consisting of like electrodes in an electrolyte of uniform composition, concentration and temperature, and therefore the E. M. F. of the cell was zero. With copper sulphate the application of an E. M. F. causes the system to become unsymmetrical, by the deposition of copper at the cathode and oxygen at the anode. The E. M. F. of this little copper-oxygen storage cell, which, as in all storage cells, is opposite in direction to the charging E. M. F., continues to increase in magnitude, as more and more copper and oxygen are deposited, until its E. M. F. equals the impressed E. M. F., when the flow of current ceases. All this may occupy one or two seconds. With each increase of impressed E. M. F. this process is repeated, until the value of the impressed E. M. F. exceeds that attainable by the little storage cell; then a permanent current flows.

Having considered several cases of electrolysis with insoluble electrodes, it will now be of interest to use a soluble anode.

TABLE VI.

Electrolyte, acid $CuSO_4$. Electrodes, copper.

Impressed E.M.F. Volts	Current Milli-amperes	Polarization		Total Volts
		Anode Volts	Cathode Volts	
0	0	—0.553	—0.563	0.001
0.15	2.9	—.556	—.538	.017
.25	10.7	—.556	—.545	.015
.50	31.	—.560	—.545	.020
.70	50.	—.560	—.545	.017
1.00	82.	—.563	—.543	.022
1.25	105.	—.567	—.538	.025
1.50	130.	—.560	—.531	.030
1.75	152.	—.567	—.531	.032
2.25	182.	—.567	—.519	.045
2.75	232.	—.571	—.512	.060
3.25	295.	—.574	—.502	.076
3.75	350.	—.579	—.499	.087
4.75	325. (*a*)	—.574	—.487	.087
5.00	380.	—.574	—.487	.089

(*a*) The current varies between 250 and 400.

Table VI and Fig. 6 show the action of copper electrodes, 1 x 2 cm., with only one side exposed, in the acid copper sulphate solu-

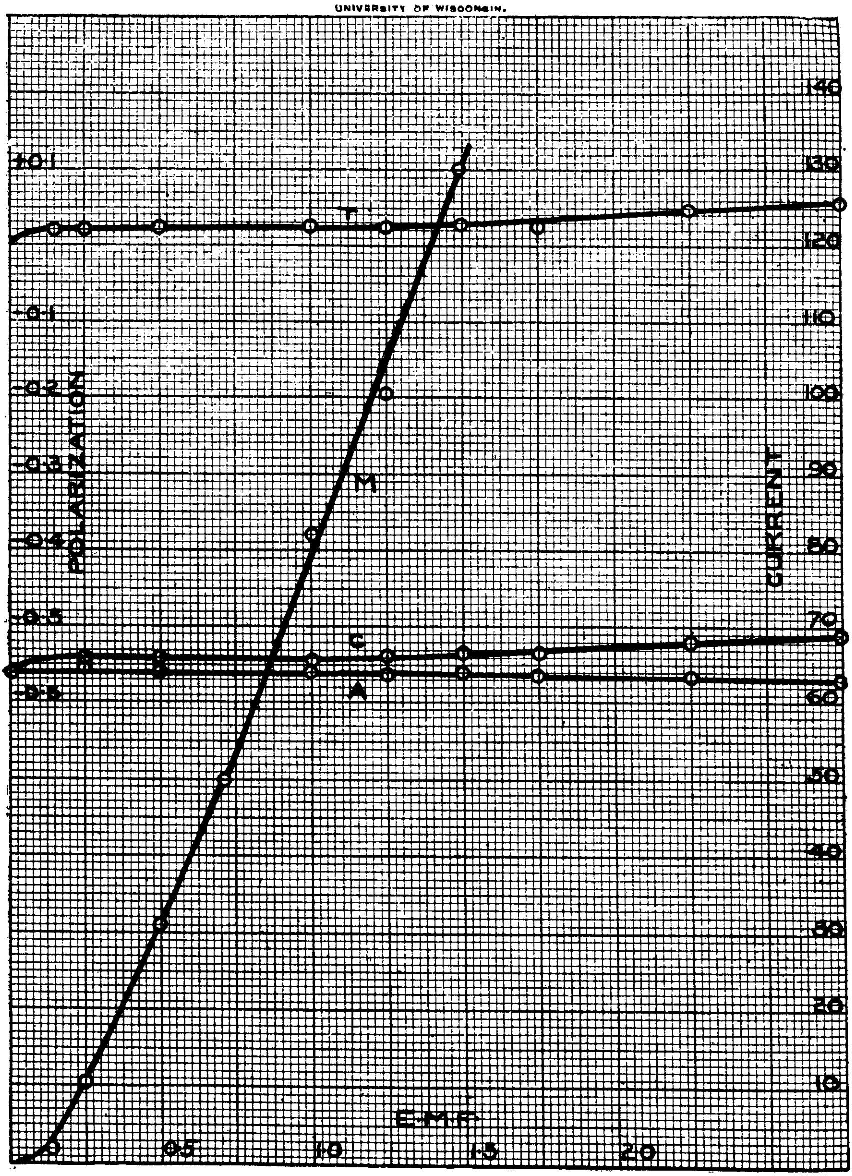

FIG. 6. Electrolysis of Acidified $CuSO_4$, Electrodes Copper, 1 x 2 cm., one side only exposed. Current Density: A. per Sq. foot = milliamperes used ÷ 2.

tion as used for electro-plating. The current-E. M. F. curve is almost like that for a metallic conductor. The reason for this is seen on examining the polarization curves. The greatest value for the total polarization was 0.06 volts instead of 1.46 obtained for copper sulphate when platinum electrodes were used. It is this failure of the polarization to rise to any considerable value, which makes the current-E. M. F. curve so different from those of the other electrolytes. At the lowest E. M. F., 0.15 volt, the total polarization had already attained to 20 per cent. of its highest value. Eighty-five percent of the greatest total polarization is found at the cathode. It is to be noted that the polarization shows no evidence of having reached a maximum, as it did with the insoluble electrodes. It is evident that had a greater E. M. F. been applied, a still larger polarization would have resulted. It might well be asked how there can be any polarization when at the outset, and also at the end, the system consists of two copper electrodes in a solution of copper sulphate. If such an electrolytic cell as this is projected on a screen by means of a stereopticon, the reason for polarization appears. At the cathode there is formed, as a result of the deposition of copper, a layer of dilute solution in contact with the cathode. It is well known that the value of the potential set up by a metal making contact with a solution is affected by the concentration of the solution. Copper in copper sulphate is no exception to this rule. Diffusion and the circulation caused by differences in density tend to destroy this film of dilute electrolyte bathing the cathode, so that the degree of dilution attained may be expressed as a state of dynamic equilibrium here between the electric current which produces it and the above forces which would destroy it. It is evident that the higher the current density at the cathode, the more dilute will be the electrolyte which is in immediate contact with it. The anode, on the other hand, is surrounded by a layer of electrolyte which is more concentrated than the original solution; but as this dense electrolyte rapidly streams down and collects as a layer across the bottom of the cell, it might be expected that increase of current would have less effect upon anode polarization than upon that at the cathode, and this is shown to be the case.

The examples of electrolysis so far considered show that:

1. Polarization is responsible for the phenomenon of decomposition pressure in electrolytes.

2. The total polarization may be resolved into two components, the one at the anode, the other at the cathode.

3. Since it is polarization which prevents the flow of current in accordance with Ohm's law, the residual current is the equivalent in current of the rate of depolarization of the electrodes by the electrolyte.

Moreover, if electrolysis causes a change in the material of an electrode, or of the electrolyte in immediate contact with it, the polarization at the electrode is large. This is the case with an insoluble anode, and usually so for a cathode whose position in the electrochemical series is far from that of the element which is deposited upon it by the current.

If the chemical composition of the electrode and of the electrolyte in contact with it are not changed, the polarization will be small. This occurs with a soluble anode and with a cathode of the same material as that deposited by the current.

The data in the tables was, in the main, secured by students in the regular laboratory experiments in electrochemistry, and this paper is presented with the hope that it may prove useful to students who are engaged in similar work. For the plotting of the curves, the author is indebted to Mr. W. B. Schulte.

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DISCUSSION.

PROF. J. W. RICHARDS: I think this is largely a very careful repetition of work which has already been done, and does not carry with it any disclosures or any new principles. I think, however, that the data and the curves given will furnish a good basis for careful discussions of the phenomena of back-electromotive force.

MR. CARL HERING: It seems to me that Dr. Watts merely gives this phenomenon a name; giving a thing a name is not giving an explanation. It is a fundamental principle that a current multiplied by an electromotive force represents energy. If a current is passed against a counter-electromotive force, it must represent energy, and energy which is not in the form of heat; in an electric motor it is in the form of motion; in a cell it is in the form of chemical energy. It seems to me the explanation of this counter-electromotive force, which the author calls polarization, is simply that some chemical energy is being stored up somewhere; electrical energy is being changed into chemical energy of some kind.

In connection with the latter part of the paper, where Dr. Watts compares the two electrodes with the calomel cell, I recall a method I used a good many years ago in testing accumulators. It consists in having in the cell two other plates, which are exactly like those that you are testing except that they are not in circuit and may be quite small. For instance, I used two small, fully charged accumulator plates, one positive and one negative, which I inserted in the accumulator and then measured the voltage between each of the test plates and the corresponding accumulator plate. In that way I obtained an indication of the condition of the large plates with reference to the normal test plates, which were not in circuit. The results were quite instructive.

In connection with this subject, although not bearing on it directly, I would like again to bring up the question of the origin of the energy of the expansion of the gases set free. When gas is liberated in electrolysis there is an expansion of, I think, about 1,600 times the volume; that is, the gases, oxygen and hydrogen, after they are set free, have a volume about 1,600 times that of the water from which they are formed. Hence there has been a very great expansion against atmospheric pressure, and that requires energy. The question is, where does that energy come from; does it come from the current or from the heat of the liquid? I think an investigation of this question might lead to some interesting results.

PROF. RICHARDS: In most of these tables there is given a statement of the first-applied electromotive force, showing no current in milli-amperes. My experience has been that with almost any applied electromotive force, under similar conditions, you can find a current if you have the ammeter delicate enough to measure it. The fact of "no current" means that the milli-ammeter was not delicate enough to measure the current. With a micro-ammeter Dr. Watts would have gotten readings all the way down to the first-applied electromotive force which could have been put on the cell.

Dr. Watts (*Communicated*): This paper is an attempt to set forth the facts in regard to the relation between current and impressed electromotive force in several different electrolytic cells and to point out that, in those cases in which the flow of current is not in accordance with Ohm's law, there exists a counter-electromotive force which partially or completely, as the case may be, nullifies the impressed e. m. f. and so causes the phenomenon of the decomposition voltage.

While agreeing with Mr. Hering when he says that "giving a thing a name is not giving an explanation," the writer was under the impression that he had included the explanation as well as the name. On pages 94-98, 101, 103, 105 and 106 the cause of the counter-electromotive force is traced to the changes produced in the materials of the electrodes by the passage of current, and it is there stated that "the source of the counter-electromotive force is of the same nature as the e. m. f. of any primary or secondary cell." Since an explanation of any new or imperfectly understood phenomenon in nature consists in showing that it has a definite relation to other and well-known phenomena, it is hoped that the above may be accepted as an explanation of decomposition voltage.

A paper presented at the Twenty-first General Meeting of the American Electrochemical Society, in Boston, Mass., April 20, 1912, President W. R. Whitney in the Chair.

THE EFFECT OF VARIOUS SUBSTANCES ON THE RATE OF CORROSION OF IRON BY SULPHURIC ACID

By Oliver P. Watts.

In Vol. 8 of the transactions of this society, C. F. Burgess called attention to the remarkable reduction in the corrosion of iron by sulphuric acid, brought about by the addition of a small amount of arsenious oxide to the acid. Later[1] he explained the protective action as follows: "The explanation which has been offered for this phenomenon is that the iron receives, by contact with the solution, an extremely thin coat of arsenic which resists the action of the acid and protects the underlying metals." He also gave experimental proof that the iron was coated with arsenic.

It has long been known that by dipping clean iron into solutions of suitable composition and concentration thin coatings of gold, silver, platinum, copper, and several other metals may be deposited on the iron. It is generally conceded that such coatings are not sufficiently continuous and impervious to protect the underlying metal from corrosion, even though the metal forming the coating may itself be thoroughly resistant to the corrosive agent. Instead of being a protection, such coatings are usually considered to be stimulators of corrosion.

Since all metals which thus deposit upon iron when it is immersed in a solution of the metallic salt are electro-negative to iron, a short-circuited voltaic cell is formed, of which the iron is anode and the metal deposit is the cathode. So long as any iron remains in contact with the electrolyte, it would seem, except for certain considerations which will be presented later, that the corrosion of the iron ought to be stimulated by this condition, and that the only way in which such a coating could afford good

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[1] For references see list at end of paper.

protection would be by covering the iron completely, so that no electrolyte could come in contact with it.

Speaking of the effect of other metals in contact with iron, W. H. Walker says,[2] "Tin is a metal which, like copper, accelerates the corrosion of iron by aiding in the oxidation of the hydrogen set free by the reaction." M. P. Wood[3] calls attention to the injurious action of metals, "The use of anti-corrosive, or anti-fouling paints, containing salts of any metal, is attended with the greatest danger to the coated (iron or steel) structure. These pigments are extremely sensitive to the presence of saline elements in moisture, their action being to rapidly dissolve portions of the iron, and to deposit the metal which they contain upon the surface of the plates, and these deposits, exciting energetic galvanic action, cause corrosion and pitting to go on with alarming rapidity. Both mercury and copper salts are offenders in this way."

It appears then, that arsenic is unique among the metals which precipitate themselves upon iron from solution, for arsenic protects iron almost completely from powerful corrosive agents, while the other metals are generally considered to aggravate corrosion and rusting. The protective action of arsenic cannot be due to any superior power of resisting attack by sulphuric acid, for silver, platinum and gold are even more resistant, and yet accelerate the corrosion of iron. It is evident that these other metals do not form continuous and impervious coatings over the iron, else they would protect it. It is difficult, perhaps impossible, even with the aid of the electric current, to deposit from solution a thin coating of one metal upon another so perfectly as to protect the underlying metal from corrosion by an acid ordinarily capable of attacking it. It is almost incredible that a thin yet perfect and non-porous metallic coating should be deposited by a process which depends for its operation upon the dissolving of the underlying metal. The protective action of coatings of copper, silver, etc. thus deposited on iron is about as effective as would be expected from a knowledge of their method of formation. They are continually being undermined by the corroding of the iron anode at points not yet covered, until the copper or silver becomes detached, to have its place taken by a new coating, and so on, as long as any of the salt of the depositing metal remains in the solution. If the coated metal be removed to an acid, the corrosive action is similar, except that the renewal of the coating can take place only at a rate not greater than that at which the detached metal redissolves in the acid.

If the coating of arsenic is so porous and imperfect as the action of acids shows the coating of copper, for example, to be, how can the arsenic protect the iron any better than copper does? It occurred to the writer that the explanation lay in a high overvoltage or excess potential of hydrogen on arsenic, and the experiments which follow were undertaken to discover whether this is the explanation of the singular and mysterious protective action of arsenic. If the above explanation is correct, among the metals which deposit upon iron when it is immersed in a solution of their salts those having a high overvoltage for hydrogen should protect iron, and those of very low overvoltage should aggravate corrosion.

If an electrode of platinum coated with platinum-black be immersed in normal sulphuric acid the electrode will be electronegative to the solution by about 1.14 volts. If now a small but slowly increasing electromotive force be applied between this electrode and an insoluble anode it will be found that the platinized cathode becomes progressively electronegative with regard to the solution. When a certain difference of potential between the cathode and the solution is reached, bubbles of hydrogen begin to appear on the cathode. If a cathode of smooth platinum is used, hydrogen will not appear on this until it has become 0.09 volts more positive than the other cathode was when hydrogen first appeared on it. Similarly zinc must be 0.70 and mercury 0.78 volts more positive than the platinum-black before hydrogen appears upon them. This excess of potential required to cause a visible liberation of hydrogen upon a cathode of any particular metal, over the potential required for the liberation of hydrogen upon platinum coated with platinum-black, is known as the overvoltage of hydrogen upon that metal. In Table I are given the single potentials in normal solutions of the sulphates of the metals, and the overvoltage of hydrogen as stated by different observers.

TABLE I.

		Overvoltage in normal sulphuric acid			In 5 per cent. KOH.
	Single Potential	Caspari[4]	Foerster[5]	Harkins[6]	Nutton and Law[7]
Mercury	—0.98	0.78	0.43	0.74	
Zinc	+0.524	0.70		0.71	0.70
Lead	—0.095	0.64	0.35	0.62	0.57
Tin	—0.085	0.53	0.43	0.55	0.61
Cadmium	+0.162	0.48	0.48		0.52
Arsenic	—0.550			0.39	
Bismuth	—0.490			0.38	
Iron	+0.093				0.15
Copper	—0.515	0.23	0.10	0.25	0.41
Cobalt	—0.019			0.22	
Nickel	—0.022	0.21	0.10	0.15	0.37
Silver	—0.947	0.15		0.13	
Platinum	—1.140	0.09	0.07	0.07	
Gold	—1.356	0.02	0.055		

On the theory that the protection of iron by a deposit of arsenic is due to the high overvoltage of hydrogen on the latter the action would be as follows: Iron dissolves and by so doing deposits arsenic upon the surface of the iron. Since the arsenic is deposited simultaneously with the dissolving of the iron, and only as a result of this dissolving, it is hardly possible that the iron should be perfectly covered by arsenic, but here and there holes will exist, allowing the iron to make contact with the electrolyte. Voltaic cells are thus formed. From the single potentials of iron and of arsenic, + 0.093 and — 0.550, these cells should have an electromotive force of 0.64 volts, and the corrosion of the iron ought to be very vigorous. It is here that the overvoltage of hydrogen comes in play. The iron is anode and the arsenic cathode, and, just as in any other primary cell with sulphuric acid as electrolyte, hydrogen is deposited on the cathode. But when hydrogen is liberated on arsenic the potential of the latter is raised 0.39 volts higher than — 0.277, the potential at which hydrogen is liberated on platinum-black. This would raise the potential of the arsenic to + 0.113 volts, or higher than the potential of the iron anode. This means that in our iron-arsenic cell there can be no visible evolution of hydrogen on the arsenic, for before this can occur the potential of the cathode has become equal to that of the anode, and corrosion of the iron ceases, in other words, this particular primary cell polarizes so badly that after a few seconds of action its electromotive force has fallen to zero.

If the above explanation is correct, protection should be afforded by those metals which plate out on iron by immersion, and whose overvoltage for hydrogen is great enough to raise their potentials to at least equal the single potential of iron. The potentials of the following metals are far enough below that of iron to expect that they will deposit on iron even in moderately strong sulphuric acid: antimony, arsenic, bismuth, gold, lead, mercury, platinum, silver and tin. Potential measurements made by students in the writer's laboratory indicate that chromium should be included in the list. Omitting lead, on account of the insolubility of its sulphate, mercury, tin, and arsenic show the highest overvoltage; compounds of these metals were therefore used in a preliminary experiment, by A. C. Shape.

Specimens of mild sheet steel of 22 gauge, 5 centimeters square, were pickled in sulphuric acid to remove the scale, dried, weighed, and corroded in sulphuric acid to which three volumes of water had been added. The amounts of the reagents added were 4 c.c. of twice normal stannous chloride, the same volume of twice normal sodium arsenate, and 16 c.c. of half normal mercuric chloride. The results are shown under Test 1.

Test 1.

Specimen	Reagent Added	Original Weight	LOSS	
			In 24 Hours	In 48½ Hours
A	None	16.38 g.	6.64 g.	10.32 g.
B	$SnCl_2$	16.53	0.09	0.11
C	$HgCl_2$	16.48	0.42	1.37
D	Na_3AsO_4	16.93	0.07	0.10

Tin and arsenic gave equal and excellent protection, but the action of mercury was not so satisfactory. The failure of the mercury may have been due to its gathering in drops and leaving exposed considerable areas of the iron. It has been pointed out by Cushman[8] that the protective action of a piece of zinc in contact with an iron surface extends but a very short distance from the zinc. The corrosion of specimen *C* was very peculiar, and was confined to deep pits about the diameter of a pin. The pitting was especially noticeable upon the edges of the sheet. In view of these facts, the writer did not consider the imperfect protection afforded by mercury to be fatal to his theory as to the nature of the protective action, and he decided to investigate the matter more fully.

The specimens used were as previously described. Corrosion was carried out in covered glass tumblers containing 200 c.c. of solution. The acids used in the following tests were sulphuric acid of specific gravity 1.140 at 15°C. corresponding to 19.6 percent acid, and of specific gravity 1.072 or 10.48 percent acid, hydrochloric acid of specific gravity 1.095 or 18.8 percent and hydrobromic acid of specific gravity 1.145 or 18 percent acid. In future these acids will be referred to by their approximate percentage composition.

In Test 2 the reagents added were in such amount as to make the solutions one hundredth normal with regard to the reagents. Since antimony is closely related chemically to arsenic, it was hoped that this might give the same degree of protection, and, on account of its less poisonous nature, prove useful commercially for this purpose.

Test 2.

For 21 h. 45 m. at room temperature (21°C.)

Specimen	34.9 per cent. H_2SO_4	Reagent Added	Weight	Loss
1	"	None	16.08	11.50
2	"	$Ni(NH_4)_2(SO_4)_2$	16.42	12.25
3	"	$CuSO_4$	16.12	11.36
4	"	$AgNO_3$	16.59	11.37
5	"	$Sb_2(SO_4)_3$	16.44	12.15

On examining the specimens at the end of the time specified they were all found to be covered with crystals of ferrous sulphate to such an extent that further corrosion was prevented. To avoid this difficulty weaker acids were used in all other tests.

Test 3.

In 19 percent sulphuric acid for 24 hours.

Specimen	Reagent Added		Weight	Loss
6	None		16.13 g.	5.47 g.
7	0.75gNa_3AsO_4	=0.20g.As	16.52	0.08
8	$As_2(SO_4)_3$	=0.20g.As	16.61	0.02
9	$SnCl_2$	=0.47g.Sn	15.92	0.02
10	0.678g.$HgCl_2$	=0.50g.Hg	16.14	1.40

The results of this test in the more dilute acid confirmed those of the previous test, except that the mercuric chloride showed less protective action.

In Test 4 various additions were made to the acid. As in Test 3 the various solutions were one twenty-fifth normal as regards the metallic salts added.

Test 4.

In 19 percent sulphuric acid for 20 hours 15 minutes.

Specimen	Reagent Added	Weight	Loss
11	None, No. 11 was amalgamated........	15.88	6.36
12	$Co(NO_3)_2$	14.87	9.87
13	$Bi_2(SO_4)_3$	15.79	14.36
14	$Sb_2(SO_4)_3$	16.39	8.67
15	K_2CrO_4	16.21	12.40
16	$HgNO_3$	16.20	13.61
17	$Cr_2(SO_4)_3$	16.04	2.21
18	$CuSO_4$=0.47 g. Cu	16.06	13.96
19	$AgNO_3$=1.617 g. Ag	16.31	16.31+

Specimen No. 11 was thoroughly amalgamated. At the end of 15 hours it was found that No. 19 had completely dissolved. Only one reagent, chromium sulphate, showed any protective influence. Silver nitrate, bismuth and copper sulphates and potassium dichromate accelerated corrosion. The effect of antimony sulphate, cobalt nitrate and of amalgamation is in doubt. A few hours from the start much spongy silver had collected in the solution and on the iron of No. 19, metallic copper was evident as a powder in No. 18, and bismuth powder in No. 13. In No. 14 antimony was deposited on the iron in loosely adherent flakes, which peeled off from time to time. No silver nitrate remained in solution 19 at the end of the test. The insoluble residues left after removing the specimens were washed, dried and weighed. In 13, 14, 18 and 19 the residue was equal, within a few milligrams, to the weight of bismuth, antimony, etc., originally contained in solution, plus the amount of insoluble matter calculated for the iron dissolved in each case. Chromates and dichromates have often been recommended[9] for the prevention of the rusting of iron and steels when exposed to the air, or in sea water. The great increase in corrosion caused by the addition of potassium chromate was therefore rather surprising. A comparison of No. 15 and No. 17 suggests that the protective action heretofore ascribed to chromates may really be due solely to the chromium which they contain, and not to the chromate as such. The marked increase of corrosion by mercurous nitrate is noteworthy.

It is stated by Burgess[10] that the protective effect of arsenic in hydrochloric acid is much less than in sulphuric acid, and Test 5 was arranged to learn the effect of several substances upon corrosion by hydrochloric acid.

Test 5.

In 19 percent hydrochloric acid for 24 hours.

Specimen	Acid	Reagent	Weight	Loss
20	19% H_2SO_4	None	15.92	13.92
21	19% HCl	None	16.46	1.89
22	“ “	$CrCl_3$, about 3 g.	15.99	2.42
23	“ “	K_2CrO_4	16.55	1.91
24	“ “	$Na_3AsO_4 = 0.25$ g. As.	15.82	0.13
25	“ “	$SnCl_2 = 0.59$ g. Sn.	16.15	2.14

Hydrochloric acid dissolved about one-seventh as much iron as sulphuric acid. Potassium chromate has no effect on the rate of corrosion by hydrochloric acid, while stannous chloride and chromium chloride act as accelerators instead of retarders of corrosion.

Test 6.

For 24 hours.

Specimen	Acid	Reagent	Weight	Loss
26	19% H_2SO_4	None	16.03	7.84
27	19% HCl	None	16.43	1.83
28	19% H_2SO_4	N/25 $Bi_2(SO_4)_3$	15.93	12.13
29	“ “	N/25 $Na_2SnO_2 = 0.51$ g. Sn.	15.98	0.68
30	“ “	N/25 $Ni(NH_4)_2(SO_4)_2$	16.08	7.29
31	“ “	N/25 $Sb_2(SO_4)_3$	15.97	4.86
32	“ “	N/25 $KMnO_4$	16.45	15.14
33	“ “	N/25 $NaCl = 0.286$ g. Cl.	16.45	4.01
34	“ “	2 g. CrO_3	16.25	15.15
35	“ “	2 g. chrome alum	16.00	8.81
36	“ “	N/25 KNO_3	16.13	10.25
37	“ “	5 g. CrO_3	15.47	15.47+

Specimen No. 37 was entirely dissolved at some unknown time during the test. Chromic acid, potassium permanganate, potassium nitrate and bismuth sulphate are accelerators, sodium stannate, antimony sulphate and sodium chloride are retarders of corrosion, while nickel ammonium sulphate and chrome alum have little effect. The oxidizing agents in 32, 34 and 37 were reduced before the end of the test.

Since the previous tests had demonstrated that chromic acid and chromates do not render iron passive in sulphuric acid, the action of these and other oxidizing agents was tried in solutions of a neutral salt.

Test 7.

For 12 days, 16 hours.

Specimen	Reagent	Weight	Loss
38	29 g. NaCl + 10 g. CrO_3	15.96	1.99
39	26 g. NH_4Cl + 10 g. CrO_3	15.54	1.99
40	29 g. NaCl + 10 g. $KClO_3$	15.68	5.22
42	29 g. NaCl + 10 g. $KMnO_4$	16.21	3.71
43	29 g. NaCl + 10 g. $K_2Cr_2O_7$	15.97	0.065
51	Water + 10 g. CrO_3	15.91	0.005
52	29 g. NaCl	15.77	0.043

The addition of the oxidizing agents strongly stimulated corrosion, except in No. 43. This result needs confirmation by further experiments.

Test 8.

For 29 hours.

Specimen	Acid	Reagent	Weight	Loss
44	19% H_2SO_4	10cc HCl = 1.99 g. Cl	15.88	0.70
45	19% HCl	None	15.86	1.65
46	19% HCl	About 10 g. $CrCl_3$	16.01	1.92
47	19% HCl	10 g. K_2CrO_4	16.02	7.82
48	19% H_2SO_4	10 g. NaCl = 6.1 g. Cl	15.72	0.32

Previous tests had shown that salt and other chlorides diminished the corrosion by sulphuric acid, and the writer expected that the increased amount of salt in No. 48 would still further diminish corrosion, but was not prepared for the astonishing result obtained in No. 44. Previous tests had shown that in 24 hours the sulphuric acid dissolved from five to seven times as much iron as the hydrochloric. Now the substitution of 10 c.c. of the hydrochloric acid for an equal volume of water in the sulphuric acid reduces the corrosion to less than half that of hydrochloric acid.

Up to this time all experiments had been carried out upon the laboratory table, subject to whatever variations there might be in room temperature during the twenty-four hours. A study of the results showed that different tests were not comparable. All the tests which follow were carried out in a water bath maintained at 30° C.

Test 9.

In a water-bath at 30° C.

Specimen	Acid	Reagent	Weight	Loss	Time Hours
53	19% H_2SO_4	None	15.35	15.35+	20
54	19% H_2SO_4	22 cc. HCl = 3.98 g. Cl	15.78	0.93	24
55	19% H_2SO_4	5 g. NaCl = 3.06 g. Cl	15.70	1.24	24
56	19% H_2SO_4	None	15.65	14.92	22
57	10% H_2SO_4	None	15.75	6.62	24
58	19% HCl	None	15.74	5.06	24
59	19% H_2SO_4	None	15.14	14.84	22
60	19% H_2SO_4	5 g. KNO_3	15.63	15.63+	20
61	19% H_2SO_4	5 g. resorcin	15.84	10.36	24
62	19% H_2SO_4	5 g. hydrochinone	15.74	7.48	24

Specimens No. 53 and No. 60 were found to be entirely dissolved at the end of 20 hours, but how much earlier complete solution occurred is not known. A comparison of No. 53 and No. 54 shows that the restraining effect of chlorine is about the same, whether it is added in an acid or in a chloride. The reducing agents in No. 61 and No. 62 retard corrosion somewhat, but since an alkaline solution is needed to make them energetic reducers, it is hardly to be expected that they would have much effect in a strongly acid solution.

The lack of temperature control in previous tests tended to exaggerate differences in the rate of action of the various solutions, for the more rapid action of any solution at the outset gave it a higher temperature, which still further increased its rate of action. This is plainly seen in comparing the rates of corrosion by sulphuric and hydrochloric acids. Without the water bath, sulphuric acid dissolved six to seven times as much iron as hydrochloric acid, but with temperature control it dissolved only three times as much.

Test 10.

In water-bath at 30° C. in 19 percent H_2SO_4.

Specimen	Reagent	Weight	Loss	Time
63	3 g. K_2SO_4	15.78	15.78	24 hours
64	5 g. $(NH_4)_2SO_4$	15.81	15.81	24 "
65	5 g. $NH_4Cl = 3.27$ g. Cl	15.67	2.06	24 "
66	1 g. $NH_4Cl = 0.67$ g. Cl	15.77	10.28	24 "
67	5 g. KBr $= 3.36$ g. Br	15.62	0.24	24 "
69	1 g. $PbCO_3$	15.54	15.54+	22 "
70	None	15.22	15.22+	22 "
71	2 g. H_3BO_3	15.37	15.37	24 "
72	2 g. citric acid	15.34	15.15	24 "

Before twenty-two hours had elapsed No. 69 and No. 70 were dissolved. Potassium and ammonium sulphates, boric and citric acids, and the small amount of lead sulphate contained in its saturated solution, were without marked effect. Potassium bromide is a strong restrainer of corrosion, and ammonium chloride acts similarly, but far less effectively.

Test 11.

19 percent H_2SO_4 in water-bath at 30° C. for 20 hours.

Specimen	Reagent	Weight	Loss
73	0.94 g. $Na_3AsO_4 12H_2O = 0.25$ g. As....	15.44	0.53
74	0.47 g. $Na_3AsO_4 12H_2O = 0.125$ g. As....	15.32	0.77
75	0.094 g. $Na_3AsO_4 12H_2O = 0.025$ g. As....	15.80	13.62
76	0.016 g. $Na_3AsO_4 12H_2O = 0.004$ g. As....	15.81	14.56
77	1 g. $Na_2SnO_3 3H_2O = 0.44$ g. Sn....	15.80	1.29
78	0.5 $Na_2SnO_3 3H_2O = 0.22$ g. Sn....	15.74	2.44
79	0.1 $Na_2SnO_3 3H_2O = 0.044$ g. Sn....	15.63	4.43
80	0.05 $Na_2SnO_3 3H_2O = 0.022$ g. Sn....	15.84	7.18
80	2 g. $Na_2SnO_3 3H_2O = 0.89$ g. Sn....	15.73	0.68
82	None	15.74	15.13

The amount of sodium arsenate required for effective restraint of corrosion by 19 percent sulphuric acid lies between 0.47 and 0.09 g., or 0.125 and 0.025 g. arsenic, per 200 c.c. E. Heyn and O. Baur[11] find that 0.0069 g. As_2O_3 in 250 c.c. of 1 percent sulphuric acid diminishes the corrosion by one-third. Two grams of sodium stannate are required to produce equal protection.

In Test 12 the accelerating effects of copper, silver and platinum were compared, and also the relative corrosion by hydrochloric and nitric acids of about equal molecular strengths.

Test 12.

In water-bath at 30° C. for 24 hours.

Specimen	Acid	Reagent	Weight	Loss
83	10.5% H_2SO_4	Ag_2SO_4 = 0.2 g. Ag ...	15.73	8.15
84	10.5% H_2SO_4	Ag_2SO_4 = 0.1 g. Ag ...	15.49	7.50
85	10.5% H_2SO_4	Ag_2SO_4 = 0.02 g. Ag ..	15.61	5.06
86	10.5% H_2SO_4	$CuSO_4$ = 0.15 g. Cu ...	15.40	7.23
87	30% HNO_3	None	15.83	15.83+
88	19% HCl	None	15.88	7.78
89	10.5% H_2SO_4	$PtCl_4$ = 0.025 g. Pt	15.81	12.52
90	10.5% H_2SO_4	$PtCl_4$ = 0.075 g. Pt.	15.29	12.77
91	10.5% H_2SO_4	$HgSO_4$	15.33	4.43
92	10.5% H_2SO_4	None	15.80	5.89

Specimen No. 87 was attacked violently, and was entirely dissolved in a few minutes. The excessive activity of nitric, as compared with sulphuric or hydrochloric acid, can only be due to its strong depolarizing action in removing hydrogen from the iron. Silver and copper both accelerate corrosion, as was expected from the low overvoltage of hydrogen on these metals. Equal weights of metal show about the same effect, but in chemically equivalent quantities the effect of silver is much the greater. The small amount of silver in No. 85 seemed to diminish corrosion. Platinum had a tremendous effect at the start, and even at the end of the test was a more powerful stimulator than the other metals.

Test 13.

In 10.5 percent H_2SO_4 at 30° C. for 24 hours 15 minutes.

Specimen	Reagent	Weight	Loss
93	3 g. KI = 2.3 g. I	15.07	0.04
95	5 g. $K_2Cr_2O_7$	15.81	8.62
96	4 g. $MnCl_24H_2O$ = 1.43 g. Cl..........	15.17	1.34
97	2 g. KF = 0.65 g. F..................	15.84	3.46
98	20 cc. of 51% HF = 6.5 g. F..........	15.69	0.44
99	1 g. $Cr(OH)_3$ = 0.52 g. Cr.............	15.61	0.56
100	5 g. K_2CrO_4	15.45	8.17
101	None	15.76	5.55
102	4 g. chrome alum = 0.42 g. Cr.	15.81	3.88

The protective action of hydrofluoric acid and of potassium fluoride are nearly proportional to their fluorine content. The stimulative action of potassium chromate and dichromate is in striking contrast to the protection afforded by chromium sulphate. Chrome-alum is a much less efficient protective agent per unit of chromium than chromium sulphate. These experiments indicate the possibility of a revision in our ideas of the manner in which chromates protect iron from rusting, and may lead to the substitution of chromium salts for the chromates heretofore used to render iron "passive."

Test 14.

In water-bath at 30° C. for 20 hours 45 minutes.

Specimen	Acid	Reagent	Weight	Loss
103	19% H_2SO_4	5 g. KI = 3.83 g. I...........	15.56	0.03
104	19% H_2SO_4	1 g. KI = 0.76 g. I...........	15.57	0.06
105	19% H_2SO_4	None	15.60	13.10
106	10.5% H_2SO_4	2 g. KNO_3	15.54	5.17
107	10.5% H_2SO_4	2 g. $KClO_3$	15.64	9.97
108	10.5% H_2SO_4	None	15.31	4.40
109	19% H_2SO_4	25 cc. of 18% HBr = 5.1 g. Br	15.29	0.31

Potassium iodide proves an excellent protective agent, and hydrobromic acid acts similarly. Of the two oxidizing agents, potassium chlorate stimulated corrosion much more than did potassium nitrate, as was to be expected from its larger amount of available oxygen.

Test 15 was made to compare the effects of very small additions of several metals. At the end of a few hours the specimens were removed, brushed, dried, weighed and returned to the acid.

Test 15.

In 19 percent H_2SO_4 at 30° C.

Specimen	Reagent	Weight	Loss at end of time in hours		
			2.25	5.72	8.3
110	5 g. $K_2Cr_2O_7$	15.27	3.06	5.71	15.27+
111	$PtCl_4$ = 0.016 g. Pt.........	14.88	6.76	8.85	14.88+
112	$AuCl_3$ = 0.016 g. Au	15.78	0.19	0.85	11.33
113	$Bi_2(SO_4)_3$ = 0.020 g. Bi	15.83	0.17	0.92	12.12
114	$Sb_2(SO_4)_3$ = 0.020 g. Sb ...	15.60	0.20	1.04	11.82
115	$CuSO_4$ = 0.020 g. Cu	15.86	0.27	1.42	12.76
116	Ag_2SO_4 = 0.020 g. Ag	15.33	0.18	1.00	12.22
117	None	15.41	0.28	1.38	13.40
118	2 g. $Cr.(OH)_3$ = 1 g. Cr....	15.60	0.06	0.12	0.73
119	None	15.40	0.25	1.08	13.12

Only platinum chloride and potassium dichromate produced marked acceleration. Specimens No. 110 and No. 111 had entirely disappeared. Most of the salts, at this very low concentration, exhibited a slight protective action, as was noticed for silver sulphate in Test 12.

To test the permanence of the protection afforded by coatings of arsenic and tin, specimens Nos. 7, 8 and 9, of Test 3, after having stood in the air 41 days, were immersed in 10 percent sulphuric acid.

Test 16.

At 30° C. for 3 hours 35 minutes.

Specimen	Metal Coated by	Weight	Loss
7	Arsenic	16.44	0.29
8	Arsenic	16.59	0.20
9	Tin	15.90	0.20

For continued protection it is apparently necessary that some salt of the protecting metal be present in the acid.

In view of the conflicting statements in regard to the effect of the presence of copper sulphate in acid used for pickling iron, a direct comparison was made between sulphuric acid, copper sulphate and a combination of the two.

Test 17.

At 30° C. for 3 hours 35 minutes.

Specimen		Weight	Loss
120	19% H_2SO_4	15.81	2.84
121	19% H_2SO_4 + 20 g. $CuSO_4$	15.68	14.89
122	20 g. $CuSO_4$	15.55	4.22

For these particular concentrations the rate of corrosion by the mixture was twice as great as that by the two substances separately. Although the molecular concentration of the sulphuric acid in No. 120 was greater than that of the copper sulphate in No. 122, the latter proved the more active corrosive agent. In this connection it should be noted that the electromotive force of the primary cell, consisting of iron and copper in sulphuric acid, is 0.61 volts, computed from the data of Table I, while that of the iron-hydrogen cell is only 0.37 volts, minus the unknown overvoltage of hydrogen on iron in sulphuric acid. Platinum salts ought to be still more vigorous corrosive agents.

From the experiments given above, certain definite conclusions can be drawn and other generalizations now appear probable, but may require revision or rejection in the light of future experiments.

The writer's hypothesis, that the protective action of arsenic is due to its high overvoltage, has been in a general way confirmed. Other metals of high overvoltage have had a protective influence, while all metals of low overvoltage which deposit on iron are accelerators of its corrosion. So far as overvoltages are known, bismuth alone fails to conform to the hypothesis. Theoretically it should retard corrosion; actually it is an accelerator. Unless redeterminations of the overvoltage of bismuth and the single potential of iron shall reconcile theory with fact, the writer's hypothesis fails. The overvoltage of bismuth was presumably measured on a solid electrode. Bismuth deposited as a powder. If there is the same difference in overvoltage for bismuth as between smooth and spongy platinum, this correction would put bismuth in the list of accelerators.

The statements which follow are intended to apply only to the corrosion of iron by sulphuric acid.

Tin, chromium and mercury retard corrosion; of these, tin alone is as effective as arsenic. The protective action of mercury is very slight.

In studying the effect of different reagents on corrosion it is necessary to consider both the metal and the non-metal or acid radical, since each may have an effect of its own.

The binary salts and acids of the halogens are very good protective agents when used in considerable amounts. To combine most effectively the protective effects of a metal and a halogen, *e. g.*, tin and chlorine, much stannous chloride should not be added, for a large amount of the salt of any metal which precipitates on iron in an acid solution is likely to act as a corrosive agent; only a small amount of stannous chloride should be added, and the extra chlorine added as sodium chloride.

Oxidizing agents are in themselves accelerators of corrosion by acids, although in dilute solution this may be masked by a protective action which supervenes when the oxygen has been used up, as might happen with chromates.

Reducing agents should show more or less protective action, but this fact remains to be confirmed by further experiment.

In general, the whole subject as here presented is but a preliminary study which opens many possibilities for future investigation. It is hoped that the data appended may prove of service to those wishing to pursue the subject, and that the writer's conclusions may meet with confirmation from independent sources.

For convenience in comparing the effects of different reagents, an index is appended.

RETARDERS OF CORROSION

	No. of Specimen
Acid, hydrobromic	109
“ hydrochloric	44, 54
“ hydrofluoric	98
Arsenate of sodium	7, 24, 73, 74, 75, 76
Arsenic sulphate	8
Bromide of potassium	67
Chloride of ammonium	65, 66
“ “ manganese	96
“ “ mercury	10
“ “ sodium	33, 48, 55
“ “ tin	9, 25
Chrome alum	35, 102
Chromium sulphate	17, 99, 118
Fluoride of potassium	97
Hydroquinone	62
Iodide of potassium	93, 103, 104
Mercury chloride	10
Mercury sulphate	91
Resorcine	61
Stannate of sodium	77, 78, 79, 80, 81

ACCELERATORS OF CORROSION

Acid, chromic	34, 37, 38, 39, 51
Bismuth sulphate	13, 28, 113
Chromium chloride	22, 46
Copper sulphate	3, 18, 86, 115
Gold chloride	112
Mercurous nitrate	16
Platinum chloride	89, 90, 111
Potassium chlorate	40, 107
“ chromate	15, 47, 100
“ dichromate	95, 110
“ nitrate	36, 60, 106
“ permanganate	32, 42
Silver nitrate	4, 19
“ sulphate	83, 84, 85, 116

OF NO EFFECT OR DOUBTFUL

Ammonium sulphate	64
Antimony sulphate	5, 14, 31, 114
Boric acid	71
Citric acid	72
Potassium sulphate	63

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[3] Rustless Coatings, p. 344.
[4] Zeit. f. phys. Chem., 30, 1889 (1899).
[5] Z. f. Elektrochem., 10, 715 (1904).
[6] J. Amer. Chem. S., 32, 527 (1910).
[7] Tr. Faraday S., 3, Part I, 50.
[8] Corrosion and Preservation of Iron and Steel, p. 122.
[9] The Corrosion and Preservation of Iron and Steel, Cushman, p. 111, 113, 163. The Corrosion of Iron, Friend, p. 165.
[10] Trans. Amer. Electrochem. S., 8, 169 (1905).
[11] J. Iron and Steel Inst. 1909, I, 187.

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DISCUSSION.

PROF. C. F. BURGESS: Thousands of tons of acid are used annually for pickling purposes, and it is surprising that, in view of the tremendous application of these pickling processes, there has been comparatively little published on the action and the constitution of sulphuric acid itself. Dr. Watts points out that certain substances like arsenic retard the rate of corrosion. It is of especial interest to note that adding a little hydrochloric acid would not increase the rate of corrosion, but, on the contrary, it retards it very greatly. Other chlorides do the same thing. Adding salt to sulphuric acid will retard the action. There are certain other substances which will increase the activity of the acid, one of them being the bichromates, which are frequently called "inhibitors."

PRESIDENT W. R. WHITNEY: A great deal has been done in attempting to produce iron which will have less tendency to corrode. I would like to see this paper discussed at length.

DR. CARL HERING: Dr. Watts' suggested explanation, based on over-voltage, is very interesting, and seems to me plausible.

It recalls the question I asked before this Society some years ago: What is the physical meaning of this over-voltage? If, for instance, two cells for decomposing water are made exactly alike except that the cathodes are of different metals, then in sending a current through them in series exactly the same quantity of water will be decomposed in both, yet one will consume more energy than the other. The question therefore arises: What is the physical explanation of the consumption of this extra energy and what becomes of it? I presume it is safe to guess that it will appear somewhere as heat.

Another remark of interest was that the over-voltage is probably considerably less when the electrode is rough than when it is smooth. It seems, in other experiments also, that gases liberate themselves much more freely from small particles than from flat surfaces. There is an illustration of this in the typical champagne glass, with its deep tube in the stem of the glass. This tube always has some particles of dirt at the bottom because it can not be cleaned like other portions of the glass, and it is at the bottom of this that the gas always prefers to be liberated. In a really clean glass the champagne would probable appear flat, although as a fact it would really be retaining more of its gas, because that property which seems to correspond with "over-voltage" is greater.

DR. ALLERTON S. CUSHMAN (*Communicated*): Mr. Watts' paper opens up an interesting field of inquiry, although it should be pointed out that it is one in which the controlling factors are exceedingly complex and, up to the present time, but little understood.

The phenomenon of over-voltage is unquestionably but one of the factors which controls the rapidity of corrosion (or solution) of a metallic surface immersed in a more or less dilute mineral acid. But even the phenomenon of over-voltage is profoundly influenced by a number of variables. Caspari used the designation "over-voltage" to express the excess voltage required to begin the disengagement of hydrogen from a metallic surface, as compared with a platinized-platinum electrode. It has been shown that the fact as to whether or not hydrogen is absorbed by the metal to a great extent governs the over-voltage. All metals which, like iron (steel), absorb hydrogen in large amounts have low over-voltages, and *vice versa.*[1] In addition to this, the smoothness or condition of the metallic surface is an important factor.

A piece of cold-rolled sheet steel will have a lower solubility and higher over-voltage than the same sample which is annealed without subsequent cold-rolling. Moreover, a very slight change in the chemical constitution of the steel, in respect to the number and quantity of impurities which may be present, brings in a number of additional variable factors.

We have still to find an entirely satisfactory explanation of the following anomalies, over which I have pondered from time to time for a number of years. If a specimen of sheet iron or steel is immersed in dilute sulphuric acid containing a very small quantity of arsenic, the solution of the metal is retarded. If, on the other hand, we alloy a small quantity of arsenic with iron and roll the material into sheet form, the solubility is accelerated. In the case of copper we find just the reverse to be true; a little copper dissolved in the acid will increase the solvent action of the acid on iron, but a little copper alloyed with steel will reduce the solubility in acid to a remarkable degree.

I have attempted to explain the action of alloyed copper, at least to my own satisfaction, by supposing that its presence called for a higher over-voltage, and that the immersed metal was protected by a film of un-disengaged or ionized hydrogen. If, however, we are dealing with a steel free from copper, and put copper into solution in the acid, we get the usual depolarizing effect produced by copper unequally plated out on the iron, and thus a stimulated solvent action.

The arsenic problem presents new difficulties, and while I do not take issue with Mr. Watts' conclusion that the protective effect due to arsenic in solution is occasioned by over-voltage phenomena, I am free to confess that I am considerably at sea in respect to the explanation, and am glad to take refuge with the author in the perhaps vague assertion that "arsenic is unique among metals which precipitate themselves upon iron from solution."

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[1] See Mott: Over-voltage as a Factor in the Corrosion of Metals. Trans. Am. Electrochemical Society, **15**, 569 (1909).

I have sometimes surmised the possibility of catalytic phenomena being an important factor in the solution of metals in acids, and whether or not the presence of arsenic acted as an anti-catalytic or "poison," as Bredig found it to be in his classical researches on the catalytic reactions produced by colloidal solutions of metallic platinum and gold.

Mr. Watts has pointed out another curious anomaly which requires explanation, *viz.*, that whereas it is well known that solutions of chromic acid and its salts will protect samples of iron and steel from corrosion when immersed in liquids containing them, on the other hand, when we are dealing with a fairly strong acid-immersion test, the addition of chromic acid increases the corrosion effect. I have worked on problems similar to this, as have also Friend in England and Heyn and Bauer in Germany, and it has frequently been pointed out that when mixtures of inhibitors and stimulators are present at the same time in a solution, the effect produced will depend upon the special conditions of equilibrium present in the system. I first pointed this out in a paper on the "Inhibitive Value of Certain Pigments," presented before the American Society for Testing Materials, at its annual meeting in 1908. Heyn and Bauer and Friend have shown that there is a critical concentration for each substance dissolved in water, as far as corrosion phenomena are concerned. If, however, we have mixtures of materials in the solution, it is hard to predicate the results which will be obtained. The fact that Mr. Watts has found that chromic acid stimulates corrosion under the conditions of his experiments in nowise interferes with the value of the observations that chromic acid and its salts act as strong inhibitors of corrosion under neutral as well as under very slightly acid and alkaline conditions, provided the concentration of the chromic acid ions is sufficiently great.

I have found Mr. Watts' paper an extremely interesting one, suggestive in many ways, and it is, in my opinion, a valuable contribution to studies of corrosion.

MR. E. B. SPEAR: In regard to the rusting of iron in the presence of potassium dichromate, we have devised an experiment in our laboratory to show that the rate of corrosion is a function of the concentrations of the oxidizing agent and of the hydrogen ion. Iron becomes passive in concentrated solutions of dichromate containing little free acid, while it corrodes much faster in very dilute solutions of the oxidizing agent than it does in water containing the same amount of acid. As the acid is increased, however, the concentrated solutions of the dichromate attack the iron very rapidly.

MR. WALTER A. PATRICK: In order to study the effect of the concentration of the sulphuric acid, the following experiment was carried out. Two pieces of steel were secured, one of which had a high oxygen content (*i. e.*, was a poor steel), while the other was normal steel, but contained about 0.2 percent copper. Both were mild steels. Carefully cleaned pieces of these two steels were then placed in solutions of sulphuric acid, the concentration of which varied from about 25 percent down to 1 percent. In the strong acid the poor steel dissolved about 50 times as fast as the steel containing the small amount of copper, but in the more dilute acid solutions the difference between the two steels became less and less until in a 1 percent acid the poor steel was dissolving only 3 times as fast as the other steel. If the acid corrosion test were carried out upon the above samples with 20 percent acid, it would show that the copper steel was 50 times as good as the other steel; but with 1 percent acid the relation between the two steels would be only 3 instead of 50, which is probably much nearer the true value for practical purposes.

MR. WATTS (*Communicated*): Experiments in the corrosion of alloys of iron and arsenic, carried out in the chemical engineering laboratories of the University of Wisconsin, gave results opposite to those cited by Dr. Cushman. The samples containing arsenic were somewhat more resistant both to atmospheric oxidation and to corrosion by dilute sulphuric acid than the original iron. The maximum amount of arsenic in any of the alloys tested at the University of Wisconsin was 4 percent. The different results obtained by Dr. Cushman may have been due to the use of higher percentages of arsenic. But little information has been published concerning the constitution of the arsenic-iron alloys, so that it is impossible at present to predict their behavior throughout the whole series toward a corrosive agent such as sulphuric acid. Definite compounds of iron and arsenic appear to be present in some of the alloys.

Stead[1] says: "Arsenic and iron most readily combine to form arsenide of iron. * * * We find that on solution of arsenical steel in dilute hydrochloric or sulphuric acid practically the whole of the arsenic remains as a black, insoluble arsenide of iron."

This indicates that iron is the anode in the voltaic cell formed by the contact of iron with its arsenide in sulphuric acid, and the considerable electromotive force of this cell may be responsible for an increase in the rate of corrosion of the iron when such compounds are present.

Since this alloyed arsenic is not dissolved by the acid, it fails to exert the well-known protective action produced when a little arsenic has been previously dissolved in the acid.

The iron-copper alloys, up to a content of 8 percent copper, consist of solid solutions of copper in iron.[2] They are homogeneous, and any differences in the rates of attack of such alloys by sulphuric acid, as compared with the rate at which the acid attacks pure iron, must depend upon the inherent nature of the two materials. In binary alloys which are solid solutions we would naturally expect a mean between the properties of the elements of which the alloy is composed. Copper is attacked only slowly by sulphuric acid. It is therefore to be expected that alloys which consist of solid solutions of copper in iron will resist corrosion by sulphuric acid better than iron. This proves to be the case.

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[1] J. Iron and Steel Inst. 1888, I, 180.

[2] J. E. Stead. J. Iron and Steel Inst. 1901, II, 112.

A paper presented at the Thirty-second General Meeting of the American Electrochemical Society, in Pittsburgh, October 5, 1917, President Fink in the Chair.

THE CORROSION OF METALS BY ACIDS.

By Oliver P. Watts and Newton D. Whipple.

[Abstract.]

The authors study the rate of solution of zinc, amalgamated zinc, iron, copper, silver, and gold, in various solutions, at normal atmospheric pressures and under a vacuum, and draw many theoretical deductions therefrom regarding the discharge potential of hydrogen on various metals and the electrochemical mechanism of the corrosion.

On account of the great economic interests involved, the corrosion of metals is one of the most important of the many technical problems which today engage the attention of electrochemists. The importance of galvanic couples in the corrosion and protection of metals received early recognition, but it is only in recent years that the whole problem of corrosion has been recognized as being electrochemical in its nature. It was formerly supposed that zinc dissolved in sulphuric acid because the affinity of this metal for the SO_4 radical exceeded that of hydrogen for the same; and that for the action to go on until either the zinc or the acid was exhausted it was only necessary that the product, zinc sulphate, should be soluble.

Among the many natural phenomena to whose explanation the theory of electrolytic dissociation has been applied, is the corrosion of iron[1]; according to this, the formation of a soluble compound is not a prerequisite to the dissolving of a metal by an acid, the metal going directly into solution as ions, and any compounds which may be formed being the result of combinations which occur after solution has taken place. From either the chemical

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[1] W. R. Whitney, J. Amer. Chem. S. (1903), 1, 394.

or the ionic point of view, an electrolyte is like a room so crowded that no newcomers can enter unless some of those already present pass out to make place for them.

On account of the enormous scale on which it occurs, the rusting of iron has received more attention than any other case of the corrosion of metals, and it is admitted by all that oxygen is necessary for the continuation of this process. Since the passage of ions into solution does not demand oxygen, it appears at first sight as if the proved need for oxygen were fatal to the ionic theory of the corrosion of metals.

In the extraction of gold and silver by the cyanide process, the presence of oxygen was also found to be necessary in order that solution of the metals may take place with sufficient rapidity to make the process practical. In this case the products formed by the dissolving of the metals do not contain oxygen, and from either the chemical or the ionic view of the dissolving of metals, the function of oxygen was obscure. The extensive use of the cyanide process led to a detailed study of the chemical changes involved, and in 1903 the rôle of oxygen in the dissolving of gold by cyanide solutions was made clear for the first time by that pioneer mining engineer (who perished in the Titanic disaster) Henry F. Julian,[2] who showed by experiment that the accelerative effect of oxygen on the solution of gold by cyanide is due to its removing from the surface of the ore the hydrogen which is displaced by the gold when it dissolves. If the hydrogen is allowed to accumulate its presence greatly retards solution of the gold.

Several years later, W. H. Walker[3] gave a similar explanation of the function of oxygen in the corrosion of iron. "We have shown that the primary function of oxygen in the corrosion of iron is in depolarizing those cathodic portions of the iron upon which hydrogen tends to precipitate, and that a secondary function is the oxidation of the ferrous iron ion to the ferric form, with its subsequent precipitation as ferric hydroxide."

When iron is put in electrical contact with metals of higher potential, such as zinc or cadmium, the iron is cathode in the voltaic cell that is formed whenever the combination of metals is

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[2] Cyaniding Gold and Silver Ores. Julian and Smart, p. 65.
[3] J. Amer. Chem. S. (1907), 1264.

moistened, and therefore the iron corrodes less rapidly than if it were not in contact with the other metal. But when iron makes contact with copper, silver, or platinum, metals of lower potential, the iron is anode in the voltaic cell, and its corrosion is greater than it would be in the absence of the other metals. Landis[4] says, "Do not plate with a nobler metal a material that is likely to be subjected to wear on one spot, and which spot is to be moistened with liquids." But in order that galvanic action shall take place it is usually unnecessary for electroplated objects to be subjected to sufficient use to wear off the plating at some point, since electro-deposits of ordinary thickness are sufficiently porous to permit galvanic action as soon as the object is exposed to moisture.[5]

The excessive corrosion of iron by sulphuric acid caused by adding salts of copper, silver, or platinum, is just what would be predicted from the theory of galvanic action. Cases are known, however, in which the addition to sulphuric acid of salts of other metals, also more noble than iron, instead of stimulating corrosion of the iron, greatly retards it.[6] Compounds of arsenic have this effect, and have been used with good results in commercial work to prevent corrosion of iron pipes by acid waters.[7] The reason for this unusual protective action is the high "discharge potential"[*] of hydrogen on arsenic. The action is as follows: Since iron is electro-positive to arsenic, it displaces this element from solution, and a porous coating of arsenic is formed on the iron. In the voltaic cell thus formed arsenic is the cathode, and consequently it is on this that the hydrogen expelled by the dissolving of iron is deposited. The discharge potential of hydrogen on

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[4] Trans. Am. Electrochemical Soc. (1911), **19**, 62.

[5] Trans. Am. Electrochemical Soc. (1916), **30**, 145.

[6] Trans. Am. Electrochemical Soc. (1912), **21**, 337.

[7] Corrosion and Preservation of Iron and Steel. Cushman and Gardner, p. 297.

[*] The term "discharge potential" has been used so little in recent electrochemical literature that an explanation of this useful term may be desirable at this time. If copper be used as cathode in a solution of ferrous sulphate until completely covered with iron, a change in potential takes place from −0.51, the potential of copper, to +0.09, that of iron. If sulphuric acid is used as the electrolyte instead of copper sulphate, hydrogen is deposited in place of copper, and the potential rises only to −0.01 volt, when hydrogen is visibly evolved; the potential of the cathode when this occurs is the discharge potential of hydrogen on copper. The potential of the cathode required for the evolution of hydrogen depends on the material of which it is made, so that the discharge potential of hydrogen is different for each metal. It is earnestly recommended that "discharge potential" be used instead of overvoltage in cases where the latter term has heretofore been employed to designate the potential of an electrode required for the evolution of some particular gas.

arsenic exceeds the potential of iron in dilute sulphuric or hydrochloric acid, and hence as iron dissolves, thereby causing an accumulation of hydrogen on the arsenic, the deposition of this gas becomes more difficult, and before enough hydrogen has been displaced to escape as visible bubbles, the potential required for its further deposition equals the driving force, the potential of iron, and action therefore ceases.

Various explanations have been given for the protection afforded by amalgamation. Grove in 1837[8] suggested that the protection is due to polarization, the hydrogen that is evolved combining with the mercury to render it electro-positive. Faraday considered that the mercury produced a uniform condition on the surface, and thus afforded protection. Carhart[9] considers the protective effect to be two-fold: 1st, the elimination of local currents by the production of a film of pure zinc on the surface, and 2d, the adhesion of a film of hydrogen to the amalgamated surface.

In the references already given, the function of oxygen in the dissolving of gold and iron have been explained and the importance of hydrogen in this process has been brought out. It is only reasonable to expect that the principles which have been found to apply to the solution of gold and iron will hold for the dissolving of other metals, and it was with the hope of extending the application of these principles to the corrosion of metals generally that the experiments which follow were undertaken.

Unless otherwise specified, the tests were carried on in tumblers containing 180 or 190 c.c. of the acid or other corroding agent. The tumblers were covered by watch glasses to lessen evaporation, and were set in a constant temperature water bath. The square sheets of metal, with the exception of gold and platinum, were of such dimensions that they were held upright by the sides of the tumblers, so that both sides of the specimen were exposed to the corroding agent.

One of the authors[10] has already presented to this Society an account of experiments which show that the protection of iron by arsenic against corrosion by sulphuric acid is probably due to

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[8] Phil. Mag., 15, 81.

[9] Primary Batteries, p. 34.

[10] Trans. Am. Electrochemical Soc. (1912), 21, 337.

the discharge potential of hydrogen on arsenic being higher than the potential of iron in this acid. It has been stated[11] that the protective action of arsenic on iron is much less in hydrochloric than in sulphuric acid.

If, as is believed by the authors, the protective action of arsenic is due to the polarizing action of a film of hydrogen on the arsenic, the addition to the acid of oxidizing agents capable of removing hydrogen should wholly or partially, according to the amount of oxidizing agent used, nullify the protective effect of arsenic.

TABLE I.

Temperature of bath..............37.5° C.
Time ....45 hours
Area of specimens...............60 sq. cm.

Specimen	Reagents used	Loss in Grams
1. Fe	N. HCl 190 c.c.	4.9812
2. Fe	N. HCl 190 c.c., 5 c.c. 30% H_2O_2	5.3355
3. Fe	N. HCl 190 c.c., 0.25 g. Na_3AsO_4	0.2631
4. Fe	N. HCl 190 c.c., 0.25 g. Na_3AsO_4, 5 c.c. H_2O_2	2.9706
5. Fe	N. H_2SO_4 190 c.c.,	4.5245
6. Fe	N. H_2SO_4 190 c.c., 5 c.c. 30% H_2O_2	5.2119
7. Fe	N. H_2SO_4 190 c.c., 0.25 g. Na_3AsO_4	0.1050
8. Fe	N. H_2SO_4 190 c.c., 0.25 g. Na_3AsO_4, 5 c.c. H_2O_2	2.8118

From the experiments of Table I it is seen that corrosion in hydrochloric acid was slightly greater than in sulphuric acid, agreeing with the reaction velocities of these acids in other cases. The oxidizing agent induced extensive corrosion in No. 4 and 8, in spite of the presence of arsenic.

If the authors' hypothesis is correct, in solutions which corrode iron without evolution of hydrogen, arsenic should have no protective action. The results of corrosion by ferric chloride and ferric sulphate are given in Tables II and III.

TABLE II.

Temperature of bath..............37.5° C.
Time ....45 hours
Area of specimens..............58 sq. cm.

Specimen	Reagents used	Loss in Grams
9. Fe	N. HCl 190 c.c.	3.0315
10. Fe	N. HCl 190 c.c., 15 g. $Fe_2(SO_4)_3$	5.8159
11. Fe	N. HCl 190 c.c., 15 g. $Fe_2(SO_4)_3$, 0.25 g. Na_3AsO_4	1.6088
12. Fe	H_2O 190 c.c., 15 g. $Fe_2(SO_4)_3$	1.9326
13. Fe	H_2O 190 c.c., 15 g. $Fe_2(SO_4)_3$, 0.25 g. Na_3AsO_4	1.6276

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[11] Trans. Am. Electrochemical Soc. (1905), 8, 169.

TABLE III.

Temperature of bath................38° C.
Time ....46 hours
Area of specimens..............58 sq. cm.

Specimen	Reagents used	Loss in Grams
14. Fe	N. HCl 190 c.c., 10 g. $FeCl_3$	5.4359
15. Fe	N. HCl 190 c.c., 10 g. $FeCl_3$, 0.25 g. Na_3AsO_4	1.7528
16. Fe	H_2O 190 c.c., 15 g. $FeCl_3$	1.6552
17. Fe	H_2O 190 c.c., 15 g. $FeCl_3$, 0.25 g. Na_3AsO_4	1.4576

TABLE IV.

Specimen	Reagents used	Loss in Grams
18. Fe	H_2O 190 c.c., 10 g. $FeCl_3$	0.9501
19. Fe	H_2O 190 c.c., 10 g. $FeCl_3$, 0.25 g. Na_3AsO_4	1.0058
20. Fe	H_2O 190 c.c., 10 g. $FeCl_3$, 0.25 g. Na_3AsO_4, 5 c.c. H_2O_2	1.1608

A comparison of 12 with 13, and 16 with 17, shows such a slight protection against corrosion by ferric salts as might be expected from the lessened surface of iron exposed, due to some iron being covered by arsenic, but 18-19 shows a contrary effect; this discrepancy can not at present be explained. The corrosion produced by the combination of hydrochloric acid and ferric sulphate considerably exceeds the sum of the losses in those reagents separately. This is in agreement with results previously obtained[12] in which iron lost 2.84 grams in sulphuric acid, 4.22 grams in copper sulphate, and 14.89 grams in a combination of the two solutions. Table II shows the arsenic to have a selective action; it stops corrosion by acid, but does not interfere with corrosion by ferric sulphate, except to the small extent previously noted as probably due to a reduction in the surface of iron exposed. Nos. 19 and 20 show that the great acceleration in the corrosion of iron protected by arsenic, which was observed when hydrogen peroxide was added to acids, does not occur in ferric chloride; no hydrogen liberated in the process of corrosion, no acceleration produced by the oxidizing agent.

For more than a half-century battery zincs which are to be used in acid electrolytes have been amalgamated, to prevent useless loss of zinc when no current is being drawn from the cell. Several explanations of the protection afforded by amalgamation have already been quoted, from which it appears that hydrogen is in some way generally held responsible for the protective effect. A

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[12] Trans. Am. Electrochem. Soc. (1912), 21, 350.

comparison of the discharge potentials of hydrogen on zinc and on mercury with the potential of zinc makes clear the nature of protection by amalgamation. The discharge potential of hydrogen on zinc as computed from Caspari's values for overvoltage in sulphuric acid[18] is 0.462, slightly lower than the potential of zinc, so that pure zinc should dissolve slowly in sulphuric acid; but the discharge potential of hydrogen on mercury is 0.542, slightly higher than the potential of zinc.

When amalgamated zinc is put into dilute sulphuric acid, zinc begins to dissolve, and displaces hydrogen just as if the metal were unamalgamated; but before the deposited hydrogen has become sufficient in amount to be visible or to escape as gas, the polarization produced by it, and therefore the electrical pressure necessary to deposit more hydrogen, has risen to equal the potential of zinc, when this metal is no longer capable of displacing hydrogen, and its solution ceases. If this view is correct, addition to the acid of an oxidizing agent that is capable of removing hydrogen ought to cause amalgamated zinc to corrode, as should also the use of a corroding agent that evolves no hydrogen by its action. The results of such tests on commercial sheet zinc are given in Table V.

TABLE V.

Temperature of bath..............37.5° C.
Time..............................45 hours
Area of specimens...............60 sq. cm.

Specimen	Reagents used	Loss in Grams
21. Zn	N. HCl 190 c.c.	6.3462
22. Zn	N. CH_3COOH 190 c.c.	1.3928
23. ZnHg	N. HCl 190 c.c.	0.6718
24. ZnHg	N. HCl 190 c.c., 10 g. $K_2Cr_2O_7$	3.0527
25. ZnHg	N. HCl 190 c.c., 10 g. $NaClO_3$	1.9926
26. Zn	N. HCl 190 c.c., 2 g. $HgCl_2$	—0.3038
27. Zn	N. HCl 190 c.c.	6.1117
28. Zn	N. HCl 190 c.c., 2 g. $HgCl_2$, 5 c.c. H_2O_2	2.2844
29. Zn	H_2O 190 c.c., 10 g. $FeCl_3$	1.3895
30. ZnHg	H_2O 190 c.c., 10 g. $FeCl_3$	1.5840

It is seen from Table V that oxidizing agents stimulated the corrosion of amalgamated zinc, just as was expected, and that amalgamation does not protect zinc against corrosion by ferric chloride. No significance should be attached to the fact that the

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[18] Zeit. f. phys. Chem., 30, 89.

corrosion of amalgamated zinc by hydrochloric acid was about ten percent of that dissolved from the unamalgamated metal, for in the latter case the acid was all used up, so that had double the amount of acid been employed, the corrosion would have been only five percent of that of the unprotected zinc. In 26 there was a gain in weight, due to the replacement of some of the zinc by mercury.

As a further confirmation of the failure of amalgamation to protect zinc from corrosion by reagents which do not liberate hydrogen, the experiments of Table VI were tried, using ammonium and potassium persulphates as corroding agents. The results came as a surprise after so many experiments had shown that neither arsenic nor mercury protects from corrosion unless hydrogen is evolved to cause polarization. Samples 31, 32 and 33 show that corrosion in ammonium persulphate is cut in half by amalgamation, and that the addition of hydrogen peroxide stimulates corrosion. Nos. 34, 35 and 36 show a similar result except that protection by amalgamation was much greater in potassium persulphate. There was an evolution of gas in every case.

TABLE VI.

Temperature of bath..............37.5° C.
Time ....107 or 45 hours
Area of specimens...............60 sq. cm.

Specimen	Reagents used	Loss in Grams
31. Zn*	H_2O 190 c.c., 10 g. $(NH_4)_2(SO_4)_2$	2.5160
32. ZnHg*	H_2O 190 c.c., 10 g. $(NH_4)_2(SO_4)_2$	1.0186
33. ZnHg*	H_2O 190 c.c., 10 g. $(NH_4)_2(SO_4)_2$, 5 c.c. H_2O_2	2.8530
34. Zn	H_2O 190 c.c., 10 g. $K_2(SO_4)_2$	2.2894
35. ZnHg	H_2O 190 c.c., 10 g. $K_2(SO_4)_2$	0.1589
36. ZnHg	H_2O 190 c.c., 10 g. $K_2(SO_4)_2$, 5 c.c. H_2O_2	2.1700

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*Time 107 hours

In the experiments with ferric chloride and ferric sulphate no gas had been evolved; it was therefore thought that the discordant results obtained in the experiments of Table VI were in some way due to the gas evolved, which was naturally supposed to be oxygen. The gas set free in the reaction between zinc and ammonium persulphate was collected, and found to be hydrogen, free from oxygen, so that the protection by amalgamation and the stimulation of corrosion by hydrogen peroxide is in harmony with previous experiments. The large loss of weight of amalgamated zinc in ammonium persulphate indicates either a less evolution of hydrogen or a much more active oxidation of this than occurred in the potassium persulphate.

As a result of these experiments it is believed that the protection of zinc by amalgamation is due to the elevation of the discharge potential of hydrogen brought about by the presence of mercury. In the absence of oxidizing agents any metal will be protected by amalgamation when its potential in the solution used exceeds the discharge potential of hydrogen on itself, but is less than the discharge potential of hydrogen on mercury.

Whether viewed from the standpoint of Nernst's theory of solution pressure or from a consideration of their potentials, the metals copper, mercury, silver, platinum and gold fall into a different class as regards corrosion by acids (except for such as are oxidizing agents) than do the metals so far considered. Their solution tensions are less, and their potentials are lower than the values published, and usually accepted for hydrogen. This means that none of these metals should be able to displace hydrogen ions from electrolytes, and hence that they should not be attacked by acids.

The violent attack of copper and vigorous solution of silver by strong nitric acid seemed to the authors to mean that the displacement of hydrogen from acids by these metals must begin, just as with zinc or iron; but before the hydrogen has reached a sufficient concentration to be evolved as visible gas the potential required for its further discharge exceeds that of the metal, so that action ceases unless this incipient film of hydrogen is removed. When its removal is brought about by any means, enough metal immediately dissolves to cause the replacement of the films by expulsion of hydrogen from the acid. If the film of hydrogen be continuously and rapidly removed the solution of metal will take place at the same rate. No other view seems capable of reconciling the vigorous attack of these metals by nitric acid, and their comparative immunity to attack by sulphuric acid. If this theory is correct it ought to be possible to dissolve silver and copper rapidly by adding an oxidizing agent to any strong acid that forms a soluble salt with these metals.

In Table VII are given the potentials of several metals according to measurements by Neumann[14], the discharge potential of hydrogen calculated from values of overvoltage by several experimenters, and the heats of formation of chlorides.[15]

TABLE VII.

Potentials in normal	SO_4	Cl	Disch. Potential of Hydrogen		Potential minus Dis. Potential of Hydrogen		Heats of formation of chlorides	Anhydr.	In water
Zn	0.524	0.503	Hg	0.548	Fe	0.183	K_2,Cl_2	211220	202340
Cd	0.162	0.174	Zn	0.468	Zn	0.06256	Zn,Cl_2	97210	112840
Fe	0.093	0.087	Pb	0.408	Ni	0.006	Cd,Cl_2	93240	96250
Sn	....	—0.085	Sn	0.298	Cd	—0.0806	Fe,Cl_2	82050	99950
Pb	....	—0.095	Cd	0.248	Sn	—0.3573	Sn,Cl_2	80790	81140
H	—0.238	—0.249	As	0.158	Pb	—0.427593	H_2,Cl_2	......	78630
Cu	—0.515	....	Cu	—0.002	Cu	—0.50713	Pb,Cl_2	82770	75970
As	....	—0.550	Ni	—0.022	As	—0.708	Cu,Cl_2	51630	63710
Hg	—0.980	....	Ag	—0.082	Ag	—0.5592	Hg,Cl_2	54490	51190
Ag	—0.974	....	Pt	—0.112	Pt	—1.028	Ag_2,Cl_2	58760	......
Pt	....	—1.140	Au	—0.212	Au	—1.13844	H_2,Cl_2	44000	......
Au	....	—1.356	PtPt	—0.232	Hg	—1.528	⅔ (As,Cl_3)	40927	48840
							⅔ (Au,Cl_3)	15213	18113

The displacement of one metal from solution by another can be predicted from the values of their potentials; a metal precipitates from solution all metals of lower potential than itself. Neumann has succeeded in precipitating on a sheet of platinum by hydrogen all metals whose potentials are below hydrogen in this table. It might therefore be expected that all metals above hydrogen would displace this gas, and therefore dissolve readily in all acids whose salts of the metal are soluble, and that the metals below hydrogen would not be attacked by acids. But the value —0.238, wrongly called the potential of hydrogen, is really the discharge potential of hydrogen on platinized platinum; the change which has been brought about in the potential of platinum by causing hydrogen to be deposited on it measures the polarization of platinum by hydrogen. Since the amount of polarization by hydrogen varies with different metals, in order to determine from theoretical considerations whether or not a metal should displace hydrogen from acids it is necessary to compare the potential of the metal with the discharge potential of hydrogen on that particular metal.

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[14] Z. f. phys. Chem. (1894), 14, 203.

[15] Thermo-Chemistry, Thomsen, tr. by K. A. Burke (1908).

If the potential of a metal exceeds the discharge potential of hydrogen on it, this metal should dissolve readily in acids whose salts of the metal are soluble, but if its potential is less than the discharge potential of hydrogen, acids should dissolve it only at the rate at which the displaced hydrogen dissolves in the acid, is removed by oxidizing agents, or is otherwise disposed of. To test the correctness of these generalizations several metals of the latter class, *viz.*, lead, tin, copper, silver, gold and platinum, were treated with acids, with and without the addition of oxidizing agents.

TABLE VIII.

Temperature of bath..............37.5° C.
Time ....45 hours
Area of specimens...............60 sq. cm.

Specimen	Reagents used	Loss in Grams
37. Pb	N. CH_3COOH 190 c.c.	0.2143
38. Pb	N. CH_3COOH 190 c.c., 0.25 g. Na_3ASO_4	0.0490
39. Pb	N. CH_3COOH 190 c.c., 2 g. $HgCl_2$	0.8529
40. Pb	N. CH_3COOH 190 c.c., 2 g. $HgCl_2$, 5 c.c. H_2O_2	6.5596
41. Pb	N. CH_3COOH 190 c.c.	0.2019
42. Pb	N. CH_3COOH 190 c.c., 5 c.c. H_2O_2	6.4026
43. PbHg	N. CH_3COOH 190 c.c.	0.1515
44. PbHg	N. CH_3COOH 190 c.c., 5 c.c. 30% H_2O_2	5.5071

Table VIII shows a slow rate of solution of lead in acetic acid, which is a measure of the rate of removal of hydrogen from the surface of the metal—probably by the air dissolved in the acid. The effect of amalgamation in diminishing corrosion is trifling, as would be expected, since it only raises slightly the discharge potential of hydrogen, which already exceeded the potential of lead. The oxidizing agent had its usual effect and enormously increased corrosion, this time in every case in which it was used, since pure lead, unlike zinc and iron, can corrode only so fast as the hydrogen is removed from it.

Similar experiments with copper and tin (Table IX) show these metals to be even less attacked by sulphuric acid than was lead by acetic in the last experiments; allowing for the shorter time, attack by hydrochloric acid is about the same as the dissolving of lead by acetic acid. These metals are readily dissolved in the presence of oxidizing agents, except for 54, in which a fine, white precipitate indicated the formation of an insoluble compound. It has been shown that when iron or copper is hammered or cold-worked the potential is raised, and the tendency to corrode is increased. A comparison of 47 with 49 indicates that this is probably true of tin also.

TABLE IX.

Temperature of bath................38° C.
Time ....19 or 22 hours
Area of specimens.........64 or 60 sq. cm.

Specimen	Reagents used	Loss in Grams
45. Cu	N. HCl 180 c.c.	0.1171
46. Cu	N. HCl 180 c.c., 10 g. $KMnO_4$	4.6084
47. Sn† cast	N. HCl 180 c.c.	0.0947
48. Sn† cast	N. HCl 180 c.c., 10 g. $KMnO_4$	3.6160
49. Sn† hammered	N. HCl 180 c.c.	0.1155
50. Cu*	N. H_2SO_4 180 c.c.	0.0226
51. Cu*	N. H_2SO_4 180 c.c., 10 g. $K_2Cr_2O_7$	2.8637
52. Cu*	N. H_2SO_4 180 c.c., 10 g. $NaClO_3$	4.3084
53. Sn*†	N. H_2SO_4 180 c.c.	0.0373
54. Sn*†	N. H_2SO_4 180 c.c., 10 g. $K_2Cr_2O_7$	0.0171
55. Sn*†	N. H_2SO_4 180 c.c., 10 g. $NaClO_3$	8.3576

* Time 19 hours.
† Area of specimens 64 sq. cm.

The noble metals, silver, gold and platinum, are similar to copper and tin in that their potentials are less than the discharge potential of hydrogen upon them. These metals should therefore be but slightly attacked by acids unless an oxidizing agent is present. Tests with these metals are given in Tables X and XI.

TABLE X.

Temperature of bath..............37.5° C.
Time ....45 hours
Area of specimens...............60 sq. cm.

Specimen	Reagents used	Loss in Grams
56. Ag	N. H_2SO_4 190 c.c.	0.0015
57. Ag	N. H_2SO_4 190 c.c., 5 c.c. 30% H_2O_2	1.6953
58. Ag	N. CH_3COOH 190 c.c.	0.0016
59. Ag	N. CH_3COOH 190 c.c., 5 c.c. 30% H_2O_2	1.7997

Although some silver dissolved in the pure acids, the rate of corrosion is less than for any metal previously tested; the stimulating effect of the hydrogen peroxide was also less than heretofore. These facts indicate that much less hydrogen is displaced by silver before equilibrium is reached than in case of the metals previously tested.

TABLE XI.

Temperature of bath..............37.5° C.
Time ....45 hours
Area of specimens.......4, 12 or 24 sq. cm.

Specimen	Reagents used	Loss in Grams
60. Au	N. H_2SO_4 190 c.c.	0.0017
61. Au	N. H_2SO_4 190 c.c., 5 c.c. H_2O_2	0.0018
62. Au	N. H_2SO_4 190 c.c., 5 g. $NaClO_3$	0.0004
63. Au	N. H_2SO_4 190 c.c., 5 g. $KMnO_4$	0.0000?
64. Au*	N. HCl 190 c.c.	0.0008
65. Au*	N. HCl 190 c.c., 5 c.c. H_2O_2	0.0070
66. Au*	N. CH_3COOH 190 c.c.	0.0005
67. Au*	N. CH_3COOH 190 c.c., 5 c.c. H_2O_2	0.0005
68. Pt†	N. HCl 190 c.c.	0.0000
69. Pt†	N. HCl 190 c.c., 5 c.c. H_2O_2	0.0006
70. Pt†	N. HCl 190 c.c., 5 g. KNO_3	0.0002

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* Area of specimens 12 sq. cm.
† Area of specimens 4 sq. cm.

The gold in 63 had a purplish coating, which because of the thinness of the metal, could not be removed before weighing, hence it is probable that there was a trace of gold dissolved in this case. With the exception of 65, which is a special case and will be referred to later, there was no appreciable solution of gold or platinum, and oxidizing agents were without their usual stimulating effect on corrosion. Thinking that the velocity of reaction might be sufficiently stimulated by more concentrated acid and increase of temperature to make corrosion visible, the experiments of Table XII were conducted with gold leaf in an evaporating dish which was heated over a Bunsen burner.

The addition of a chloride or a bromide to a mixture of oxidizing agent and acid caused prompt and complete solution of the gold. Aside from 73, in which there is a possibility of the liberation of chlorine by decomposition of the acid, there was only one case, 72, in which the gold dissolved without the presence of a chloride, bromide or iodide, and in this the action was so slow that many hours were required to dissolve the bit of gold leaf. No tests were made for traces of dissolved gold, since the purpose of these experiments was to determine if in the presence of oxidizing agents other acids would dissolve gold at a rate comparable to that at which it is attacked by aqua regia, and at which all other metals used in these tests (except platinum) have been corroded when oxidizing agents were present.

TABLE XII.

The Solution of Gold in Acid Plus Oxidizing Agents.

Acid	Temp.	Time	Oxidizer	Result
71. H_2SO_4 30%	90	15 m.	CrO_3	Gold leaf remains
H_2SO_4 30%	70	10 m.	$KMnO_4$	Gold leaf remains
H_2SO_4 30%	90	....	HNO_3	Gold leaf remains
H_2SO_4 30%	..	....	$NaNO_2$	Gold leaf remains
H_2SO_4 30%	..	....	KBr	Gold dissolved
72. H_2SO_4 80%	150	20 m.	CrO_3	Gold remains
H_2SO_4 80%	Cold	24 h.	CrO_3	Gold dissolved
73. $HClO_4$	80	....	HNO_3	Gold remains
$HClO_4$	95	....	$NaNO_2$	Gold remains
$HClO_4$	95	....	CrO_3	Gold dissolved
74. HBF_4	Hot	....	HNO_3	Gold remains
HBF_4	Hot	....	KBr	Gold dissolved
75. H_3PO_4	98	5 m.	CrO_3	Gold remains
H_3PO_4	98	....	$NaNO_3$	Gold remains
H_3PO_4	..	....	HNO_3	Gold remains
H_3PO_4	..	....	KI	Gold slowly dissolved
H_3PO_4	..	....	KBr	Gold quickly dissolved
76. H_3PO_4	90	....	$KMnO_4$	Gold remains
77. H_3PO_4 H_2SO_4 50%	115	....	CrO_3	Gold remains
H_3PO_4 H_2SO_4 50%	142	....	CrO_3	Gold remains
78. H_3PO_4	130	30 m.	CrO_3	Gold remains
H_3PO_4	Boiling	80 m.	CrO_3	Gold remains
H_3PO_4	..	....	NaCl	Gold dissolved
79. HCl 15%	60	....	CrO_3	Gold quickly dissolved

The dissolving of gold by other reagents than aqua regia has been recorded by many experimenters. Comey[16] states that gold is dissolved by concentrated sulphuric acid to which either potassium permanganate or iodic acid has been added; and that selenic acid is the only single acid that dissolves the metal. Lenher[17] found that gold dissolves in sufficient amount to respond to chemical tests in either hot concentrated sulphuric or phosphoric acid containing potassium permanganate, lead peroxide, manganese dioxide, or nitric acid, and that in some of these solutions gold dissolves even at zero degrees centigrade.

The great difference in the rate of solution of gold by aqua regia or any combination of a halogen acid with an oxidizing agent, in comparison with its rate of dissolving in other acids and

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[16] Dictionary of Solubilities, p. 172.

[17] J. Amer. Chem. S. (1904), 26, I, 550.

an oxidizing agent, seems to indicate some fundamental difference in the nature of the dissolving of gold by aqua regia and by the other acids. The effect of oxidizing agents in stimulating the dissolving of lead, tin, copper and silver in acids indicates that these metals displace an appreciable amount of hydrogen, the rate of removal of which by the oxidizing agent fixes the speed of dissolving of the metal. Granting the solution of gold by sulphuric or phosphoric acid and oxidizing agents, the very slow rate of action indicated by these experiments in comparison with the action of similar solutions on the metals just mentioned means a correspondingly slow oxidation of the displaced hydrogen. Since the oxidizing agents were as powerful, and in several cases the same as used with the other metals, the slow rate of oxidation of hydrogen must be due either to the presence at any instant of only an extremely small quantity of hydrogen on the gold, or to the replacement of the oxidized hydrogen at this very slow rate. There is no reason for thinking that gold can displace hydrogen from hydrochloric acid more rapidly or to a much greater extent than from other strong acids; therefore the rapid solution of gold by aqua regia shows that this is not a case of the displacement of hydrogen by the metal, but, like the dissolving of iron by ferric chloride, a reaction in which hydrogen is not evolved. The starting point of the reaction must be the oxidation of the hydrogen of the acid; after which solution of the gold may be conceived to occur either chemically, by combination with nascent chlorine, or ionically, by electrostatic attraction between chlorine and gold ions.

Gold and platinum, being readily dissolved only by aqua regia or a solution of a halogen acid and an oxidizing agent, are thus distinguished from lead, copper, tin, and silver, with which they were at first classed by the authors.

A study of Table VII shows an interesting relation between heats of formation and the results of these experiments. In aqueous solution the heat of formation of hydrochloric acid exceeds that of the chlorides of copper, lead, mercury, gold, and of course of silver and platinum, and hence none of these metals should be capable of displacing hydrogen from water solution of hydrochloric acid; but in the anhydrous condition the heat of formation of hydrochloric acid is less than that of all of the above chlorides, except those of arsenic, gold and platinum, so that, when water is left out of consideration, all of these metals except the three last mentioned should displace hydrogen from hydrochloric acid. The facts are in accordance with this. When water is allowed to play its part, copper, lead, mercury, silver, gold and platinum are not readily dissolved by non-oxidizing acid solutions; but when the hydrogen of water is taken care of by an oxidizing agent all of the above, except gold and platinum, dissolve in acids, provided their salts are not insoluble. A classification of the metals according to whether or not their potentials exceed the discharge potential of hydrogen on them leads to the same grouping as does a consideration of the heats of formation in aqueous solution; and experiments with acids containing oxidizing agents draw the dividing line between the two classes at the same point as does a consideration of the heats of formation of the anhydrous chlorides, *viz.*, just below silver.

The third set of data in Table VII, obtained by subtracting the discharge potential of hydrogen from the potential of the metal, furnishes a rough index of the rate at which pure metals may be expected to dissolve in acids; when this index is negative the rate of solution is limited to the speed with which the displaced hydrogen is removed from the surface of the metal, and for rapid solution an oxidizing agent is necessary.

The necessity for supplying oxygen in the treatment of gold ores by cyanide has already been referred to. S. B. Christy[18] found the potential of gold to have the following values: in N.KCN + 0.37, in N/10 KCN + 0.23, in N/100 KCN + 0.09, and in N/1000 KCN —0.38 volt. The need for oxygen in dissolving gold signifies that the potential of gold in the solutions used in cyaniding gold ores is less than the unknown discharge potential of hydrogen on gold. To verify this, measurements were made in tenth normal potassium cyanide. No gas could be observed on immersing gold in this solution, but at a cathode potential of +0.42 volt (N.calomel electrode = —0.56) bubbles of hydrogen clung to the gold, and with the aid of a lens the escape of a tiny bubble was occasionally observed. On raising the impressed E. M. F. until the current density of 0.05 ampere per square decimeter was obtained, the potential of the cathode had increased to +0.57 volt, and the escape of gas was readily seen.

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[18] Amer. Chem. J. (1902), 27, 354.

The potential of gold in potassium cyanide is less than the discharge potential of hydrogen upon it; hence the necessity for oxygen in order to dissolve this metal in cyanide solutions.

The nature of protection by amalgamation has already been discussed in the light of these experiments. In a paper on "The Function of Oxygen in the Corrosion of Metals"[19] the prevention of the continued corrosion of iron by the film of hydrogen which is supposed to deposit on it is attributed to the high electrical resistance of hydrogen gas, and in discussing the accelerative effect of certain voltaic couples and of impurities on the rusting of iron, the same author attributes this to a catalytic oxidation of hydrogen by the cathode material or impurity. Speaking of the slight corrosion of zinc relative to that of iron in salt water, he says,[20] "The explanation consistent with the electrolytic theory is that the zinc does not dissolve and corrode, not because there was formed an adherent and protective layer of zinc hydroxide, but because the zinc does not catalyse the reaction $H_2 + O = H_2O$ with sufficient rapidity to continually remove the hydrogen from the surface of the zinc. Although the catalysing action of the iron surface is not so rapid as is the platinum surface, it has sufficient rapidity to depolarise the iron strip and to render continuous the solution, and therefore the corrosion of the iron. * * * The author has already shown that 'mill scale' or magnetic oxide of iron is strongly electro-negative to iron. Since mill scale is insoluble in water and cannot of itself enter into the reaction, its only function must be analogous to that of platinum or other insoluble conductor of this kind, *viz.*, to furnish a surface on which the hydrogen liberated by the dissolving of iron can separate and be catalytically oxidized to water again."

It is the opinion of the authors that the observed protection of iron by hydrogen is due, not to the *resistance* of the gas, but to the rise in potential produced by its presence on the iron. The protection of iron and zinc against corrosion, by contact with arsenic and zinc respectively, has been shown to be due to the high discharge potential of hydrogen on these metals; and the excessive corrosion of iron and zinc induced by contact with mill scale, silver, platinum, etc., is believed by the writers to be due

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[19] W. H. Walker, Trans. Am. Electrochemical Society (1908), 14, 178.

[20] Jour. Iron & Steel Inst. (1909), I, 75.

to a low value for the discharge potential of hydrogen on these materials, and not to any particular power of catalysing the oxidation of hydrogen. The real office of platinum as a stimulant to the corrosion of another metal is to furnish a cathode that is polarized to only a slight degree by the collecting of hydrogen on it, and which, together with the metal that is corroding, constitutes a cell of high working E. M. F.

The superiority of nitric acid over other mineral acids as the general solvent for metals has long been recognized. These experiments show that the special value of nitric acid, aside from nitrates being more generally soluble than other salts, lies in its being at the same time an acid and an oxidizing agent.

The foregoing experiments indicate that the inherent nature of the reaction between acids and metals is always the same. On immersion in an acid, metal begins to go into solution and hydrogen is displaced. But the law of mass action applies here. As hydrogen accumulates, the driving force required to deposit more of this gas increases, and if the potential, solution pressure, or whatever other term may be chosen to designate the relative displacing power of metals in electrolytes, be very low, like that of copper or silver, equilibrium is quickly reached and the action comes to a standstill. If the potential of the metal is high, as for zinc and iron, the reaction goes on, the density of the hydrogen film increases to such a point that gas begins to escape, and as equilibrium has not yet been reached, the reaction continues, as is usual in chemical changes when one of the products escapes from the field of action. The effect of oxidizing agents is to remove one product, hydrogen, and so prevent attainment of the equilibrium which is otherwise quickly reached with the metals of low potential, copper, mercury, silver, etc. If the oxidizing agent is a vigorous one it may remove hydrogen more rapidly than it normally escapes from the more positive metals, zinc and iron, and the rate of solution of these metals is accelerated. If hydrogen is removed from the metal very slowly, attack by the acid must also be slow, like the dissolving of silver in sulphuric and acetic acids. If some means be provided for removing hydrogen from the surface of the metal more rapidly than usual, the speed of dissolving is thereby increased. In every case the rate of solution of metal by an acid is governed by the rapidity with which hydrogen is removed from the field of chemical action.

To supplement this study of the corrosion of metals by acids a few experiments were tried with alkalies. Because most of the metallic hydroxides are insoluble, only a few metals are available, from which zinc, tin and lead were chosen as representative.

Since hydrogen is the material displaced by the metal which dissolves, it was expected that the effect of amalgamation and of oxidizing agents on the rate of corrosion would be the same as in acids, except as modified by the changed potentials of the metals in this new electrolyte.

TABLE XIII.

Temperature of bath..............37.5° C.
Time ....45 hours
Area of specimens..............60 sq. cm.

Specimen	Reagents used	Loss in Grams
80. Sn	N. NaOH 190 c.c.	0.0302
81. Sn	N. NaOH 190 c.c., 0.25 g. Na_3AsO_4	0.0292
82. Sn	N. NaOH 190 c.c., 10 g. $KMnO_4$	0.6771
83. Sn	N. NaOH 190 c.c., 10 g. KNO_3	0.0300
84. Pb	N. NaOH 190 c.c.	0.1101
85. Pb	N. NaOH 190 c.c., 0.25 g. $NaAsO_4$	0.1026
86. PbHg	N. NaOH 190 c.c.	0.0850
87. Pb	N. NaOH 190 c.c., 5 g. $KMnO_4$	0.0978
88. Pb	N. NaOH 190 c.c., 5 g. KNO_3	0.0938
89. Pb	N. NaOH 190 c.c., 5 g. $NaClO_3$	0.0942
90. Zn	N. NaOH 190 c.c.	0.0363
91. Zn	N. NaOH 190 c.c., 0.25 g. $NaAsO_4$	0.1016
92. ZnHg	N. NaOH 190 c.c.	0.0326
93. Zn	N. NaOH 190 c.c., 5 g. $KMnO_4$	0.3318
94. Zn	N. NaOH 190 c.c., 5 g. KNO_3	0.7052
95. Zn	N. NaOH 190 c.c., 5 g. $NaClO_3$	0.0856

The first experiments, Table XIII, gave some unexpected results. The accelerative effect of oxidizing agents was much less than in acids, and varied greatly; not only did corrosion vary with different oxidizing agents, but also for the same agent with different metals. Potassium permanganate caused the greatest corrosion of tin, but with zinc this reagent proved less effective than potassium nitrate, which did not corrode tin at all. None of the oxidizing agents increased the corrosion of lead. Amalgamation decreased the corrosion of lead and zinc very slightly.

Arsenic stimulates the corrosion of zinc (90, 91) because the discharge potential of hydrogen on arsenic (see Table VII) is much below that on zinc; it is a case of substituting a cathode which polarizes to a much less degree by hydrogen. Arsenic fails to stimulate the corrosion of lead and tin similarly (80, 81, 84, 85), because the potential of these metals in sodium hydrate is less than the discharge potential of hydrogen on arsenic; the voltaic cell formed by either of these metals with arsenic is completely polarized by hydrogen, and its E. M. F. becomes zero.

TABLE XIV.

Temperature of bath	46° C.
Time	45 hours
Area of specimens	60 sq. cm.

Specimen	Reagents used	Loss in Grams
96. Sn	180 c.c. NaOH (200 g/L), 5 g. picric acid	3.7324
97. SnHg	180 c.c. NaOH (200 g/L)	0.0055
98. SnHg	180 c.c. NaOH (200 g/L), 5 g. picric acid	3.1014
99. Zn	180 c.c. NaOH (200 g/L)	0.0168
100. ZnHg	180 c.c. NaOH (200 g/L)	0.0130
101. Zn	180 c.c. NaOH (200 g/L), 5 g. picric acid	5.8750
102. ZnHg	180 c.c. NaOH (200 g/L), 5 g. picric acid	4.3198
103. Pb	180 c.c. NaOH (200 g/L)	0.0770
104. Pb	180 c.c. NaOH (200 g/L), 5 g. picric acid	1.3030
105. PbHg	180 c.c. NaOH (200 g/L)	0.0185
106. PbHg	180 c.c. NaOH (200 g/L), 5 g. picric acid	1.4685

In Table XIV the strength of the caustic solution was increased, the temperature raised, and picric acid was used as the oxidizing agent. The results are comparable to corrosion by acids. Amalgamation diminished corrosion slightly, and the oxidizing agent greatly stimulated corrosion of both amalgamated and pure metals. As in Table XIII, the stimulation of corrosion by the oxidizing agent is much less for lead than for zinc and tin.

TABLE XV.

Potentials of zinc, lead, and tin in normal NaOH and discharge potential of hydrogen on these metals.

	Poten.		Disch. P.	P. at 0.05 amp./$dm.^2$
Zn	+0.83 ?	<	+0.83	+0.96
Sn	+0.54	>	+0.65	+0.74
Pb	+0.21	>	+0.32	+0.40

Since gas was evolved from both commercial and C. P. zinc on immersing it in normal sodium hydrate, it is evident that the potential of this metal exceeds the discharge potential of hydrogen.

The values given for the discharge potential on tin and lead are probably slightly too low, for although bubbles of gas could be seen clinging to the cathodes, none was observed to escape. In every case an increase of current density caused a rise in potential of the cathode, and the limit was not reached at 0.05 amp./sq. dm.

What should be the effect of a vacuum on the rate of solution of amalgamated zinc by acids?

Carhart,[21] to show that the protection of zinc by amalgamation is due to the adhesion of a film of hydrogen, says "When amalgamated zinc is plunged in water, acidified with one-twentieth of its volume of sulphuric acid, it is not attacked at ordinary atmospheric pressure. But if a vacuum is produced above the liquid, bubbles of hydrogen are again freely evolved from the zinc surface. Upon readmission of the air, bubbles again adhere to the plate, and the chemical action is arrested."

If a vacuum stimulates corrosion of amalgamated zinc, it should also accelerate the dissolving of other metals in acids which corrode them but slowly at atmospheric pressure, because of the polarizing effect of hydrogen. To test this the experiments of Table XVI were tried, one set at atmospheric pressure, the other in such a vacuum as could be obtained by the laboratory filter pump.

TABLE XVI.

Temperature ....21 to 22° C.
Time ....45 hours
Area ....60 sq. cm.

Specimen	Reagents used	Loss in Grams
	(In Vacuum—2.4 to 3.5 cm. of mercury)	
107. Fe	N. H_2SO_4 190 c.c.	0.7332
108. Fe	N. H_2SO_4 190 c.c., 0.25 g. Na_3AsO_4	0.0083
109. Pb	N. CH_3COOH 190 c.c.	0.0374
110. Cu	N. H_2SO_4 190 c.c.	0.0044
111. Zn	N. NaOH 190 c.c.	0.0101
	(At Atmospheric Pressure)	
112. Fe	N. H_2SO_4 190 c.c.	1.6266
113. Fe	N. H_2SO_4 190 c.c., 0.25 g. Na_3AsO_4	0.0287
114. Pb	N. CH_3COOH 190 c.c.	0.0841
115. Cu	N. H_2SO_4 190 c.c.	0.0208
116. Zn	N. NaOH 190 c.c.	0.0772

At the start, the above test showed a much greater evolution of gas from the samples in the vacuum than from those under

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[21] Primary Batteries, p. 34 (1891).

atmospheric pressure. Apparently Carhart's statement was true, and corrosion would be stimulated by the vacuum. Towards the end of the test, however, it was noticed that action was more rapid on several of the samples at ordinary pressure, but it was not then suspected that reducing the pressure had diminished, rather than increased, corrosion; it was only when the specimens were weighed that the truth was learned, *viz.*, that in every case reduction of pressure had diminished corrosion.

In order to ascertain that a possible difference in temperature between the two sets of specimens was not the cause of the different rates of corrosion, temperature measurements were made of solutions under similar conditions, except that no metals were present. Numerous bubbles of gas collected on the interior surfaces of the tumblers in the vacuum, which could only be air. The average of many readings showed a difference of less than four degrees in temperature, too slight to account for the lessened corrosion. The reason for the lessened corrosion in the vacuum is that the reduction of pressure removes from the liquids the dissolved air, which at atmospheric pressure acts as a depolarizer for hydrogen. Proof of the depolarizing action of the air present in ordinary solutions of the laboratory is seen by comparing the curves of cathode polarization in plates I and II of a paper presented before this Society in 1914 by C. N. Hitchcock.[22] The effect of removing the dissolved air either by boiling or by the use of a vacuum, was to cause a greater polarization of the cathode by hydrogen.

The experiment given by Carhart has been quoted in the same language by P. Benjamin,[23] and Tommasi,[24] and is attributed to De la Rive in 1843. The result of repeating it points to the desirability of testing with modern apparatus many of the alleged "facts" of our natural sciences that have been passed down to us through a long period of years.

This study of the corrosion of representative metals and of the electrochemical principles involved, has led to certain conclusions, some general, others specific.

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[22] Trans. Am. Electrochemical Soc., 15, 418 and 420.

[23] The Voltaic Cell, p. 347 (1893).

[24] Traité des Piles Electrique, p. 45 (1889).

1. The hypothesis of one of the authors, presented to this Society in a previous paper,[25] that the protective effect of arsenic on the corrosion of iron by sulphuric acid is due to polarization by hydrogen, is confirmed by the following facts:

(a) The corrosion by acids of iron protected by arsenic was invariably greatly stimulated by oxidizing agents.

(b) Arsenic does not protect iron from attack by corrosive agents which evolve no hydrogen by their action.

2. Amalgamation protects zinc from corrosion by acids because the discharge potential of hydrogen on mercury exceeds the potential of zinc. Protection by arsenic and by amalgamation are alike in their nature.

3. Tin and lead are only very slowly dissolved by non-oxidizing acids, although their potentials are such as would cause their ready solution in acids, if it were not for the unusually high discharge potential of hydrogen on them. Removal of hydrogen by an oxidizing agent causes these metals to dissolve readily in acids that otherwise corrode them very slightly.

4. Corrosion by acids, of metals below hydrogen in solution pressure or position in the usual electrochemical series, *viz.*, copper and silver, has been caused by the presence of oxidizing agents, and the reason for this action has been set forth in detail.

5. The oft-quoted statement that the corrosion of amalgamated zinc in dilute sulphuric acid is accelerated by a vacuum, has been shown to be incorrect. By removing the depolarizing oxygen of the air, reduction of pressure retards corrosion, not only of amalgamated zinc, but of other metals whose solution is hindered by a polarizing film of hydrogen.

6. As regards corrosion by acids the metals experimented with, and probably all others, may be classified as follows:

(a) Metals whose potentials exceed the discharge potential of hydrogen on them; these dissolve readily in acids, except such as form insoluble salts.

(b) Metals whose potentials are less than the discharge potential of hydrogen on them; these dissolve readily in acids only in the presence of oxidizing agents. Gold and platinum are not

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[25] Trans. Am. Electrochemical Soc. (1912), 21, 340.

readily attacked by the acids in general, even when these contain oxidizing agents.

7. The superiority of nitric over other acids as a general solvent for the metals—long recognized—is due to its being at the same time an acid and an oxidizing agent, which enables it to dissolve metals of the second class, which non-oxidizing acids cannot do.

8. Oxygen is necessary to success in cyaniding gold ores because in dilute cyanide solutions gold is a metal of the second class.

9. Measurements of the discharge potential of hydrogen in solutions of potassium cyanide and sodium hydrate, and experiments on the corrosion of metals in the latter, lead the authors to think that the above classification of metals, the action of oxidizing agents, and protection by other metals, will apply to the *dissolving of any metal in any electrolyte* from which it displaces hydrogen when passing into solution.

10. The above classification of metals according to the relative magnitude of their potentials in comparison with the discharge potential of hydrogen on them, applies not only to the solution of metals, but to their electrolytic deposition. Plating baths for depositing metals of the first class cannot be strongly acidified without causing the deposition of much hydrogen in place of an equivalent amount of metal; but a large proportion of acid may be added to solutions for the deposition of metals of the second class without greatly lowering the current efficiency through the deposition of hydrogen.

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DISCUSSION.

F. N. SPELLER[1]: I wrote out these notes relating to the practical application of the principles so well laid out in Watts' and Whipple's paper, for the reason that the subject of this discussion has already been partially covered in two or three rather extensive papers. It consists of the research on methods for conserving the life of galvanized-iron water pipe for hot water.

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The rapid destruction of hot-water supply pipes under modern conditions presents a problem involving the principles discussed in this paper, the practical solution of which promises to be of far-reaching importance.

Water for domestic use is usually heated under 60 to 80 pounds pressure to about 160° F., and in large buildings is usually circulated in a closed circuit from the heater through the risers and returns. The large amount of water used in these days of convenient bathing facilities and the high temperatures carried has undoubtedly shortened the life of the pipe considerably.

Several years ago the writer started some experiments on the removal of the free oxygen from water by contact with a large surface of iron, and in December, 1915, a small plant, designed on this principle, was installed in this city, in the Irene Kaufmann Settlement. This is still in successful operation. (The method will be seen by looking at the section of the storage tank, filter, and heater shown on the following pages.)

By circulation of the heated water between steel sheets the latter become corroded, the free oxygen is used up primarily in keeping the surface of these plates active; the excess of hydrogen goes into solution.

The soluble gas collected from this water showed the following composition:

	Raw Water	Treated Water
Oxygen	15.6 percent	*1.59 percent
Hydrogen	0.3 percent	22.17 percent
Carbon Dioxide	0.3 percent	0.12 percent
Nitrogen (by Diff.)	81.8 percent	76.12 percent
Temperature	160° F.	162° F.

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* The oxygen collected from the hot water is low, due to corrosion of the iron storage tank and connections.

The amount of free oxygen in domestic water usually ranges from 5 to 9 cc. per liter.

The system at the time this plant was installed consisted of old galvanized iron pipe, which was leaking every week and was ready to be replaced. No leaks have occurred with the "passive" water, and new pipe installed at the same time for test purposes shows practically no corrosion.

Brass or copper pipe naturally does not fail so quickly under these conditions; however, it is to be expected from what we know of the electrochemical principles involved that these pipes may also be protected in the same way. In new installations of such a size as to warrant the extra equipment required to render the water passive to metal, galvanized steel pipe would seem to be the most economical material.

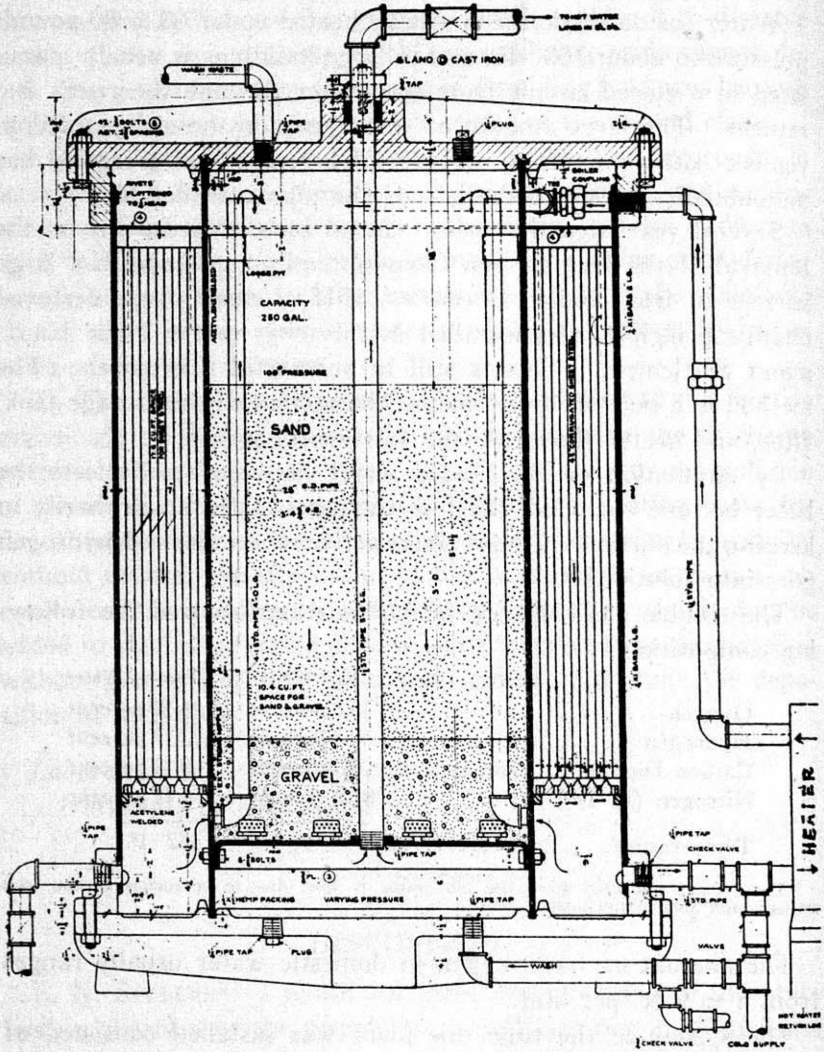

FIG. 1. System for Removing Dissolved Oxygen from Hot Water.

The unbroken film of hydrogen on the inside of a piping system of this kind is probably a more perfect protective coating than any other so far devised.

O. P. WATTS (*Communicated*): Further confirmation of the writer's views on the nature of the protection afforded by amalgamation has just been obtained with amalgamated iron. Since the discharge potential of hydrogen on mercury exceeds the potential of iron the theory leads to the conclusion that amalgamation should protect iron from corrosion in acids. By the use of sodium amalgam it has been possible to amalgamate iron. This was immersed in 15 percent sulphuric acid, and for two days there was no visible action, but on the third morning the iron had entirely disappeared and only mercury remained. The only explanation that the writer can offer for this sudden attack, where there had

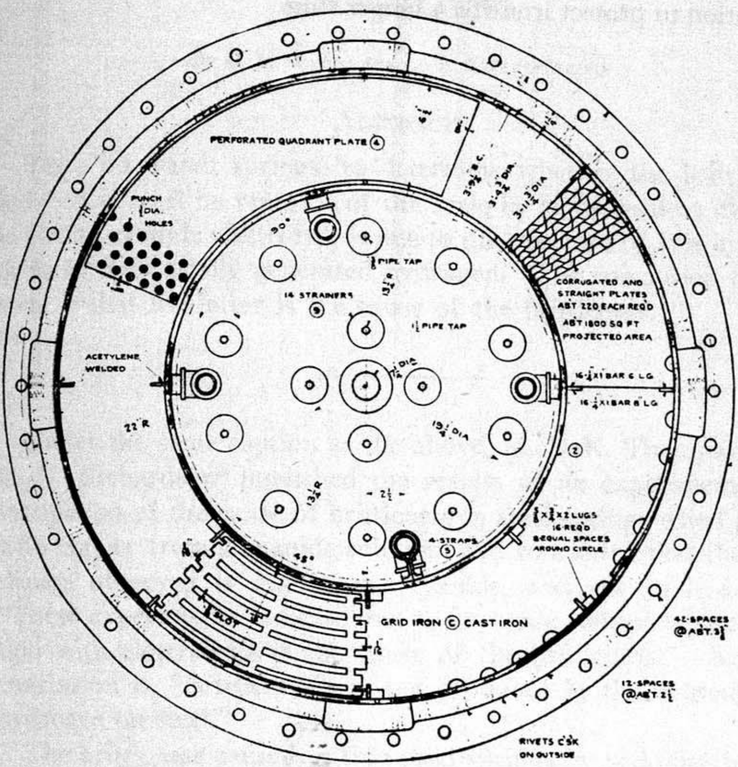

FIG. 2. Cross-Section of Fig. 1.

previously been protection, is that the superiority of the force of cohesion between the particles of mercury over the adhesion between mercury and iron finally resulted in the gathering of the mercury into globules, thus leaving considerable areas of the iron exposed. Amalgamation protects iron from rusting in water for about the same length of time. It is hoped that further experiments will lead to a better understanding of this failure of amalgamation to protect iron for a longer time.

A paper to be presented at the Thirty-third General Meeting of the American Electrochemical Society, to be held in the Appalachian South, April 28-May 5, 1918.

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BRITTLENESS PRODUCED IN STEEL SPRINGS BY ELECTROPLATING.

By O. P. WATTS[1] AND C. T. FLECKENSTEIN.[2]

ABSTRACT.

Tests on watch springs, to determine whether the brittleness induced in steel by removal of the scale by acids used as cathode in strong cyanide electrolyte is due to the presence of free cyanide or to electrolytically generated hydrogen. The conclusion of the tests is that the latter is the cause of the brittleness.

Under the same caption as the above, M. DeK. Thompson and C. N. Richardson[3] published the results of an experimental investigation of the cause of brittleness in steel springs when plated with copper from a cyanide solution, and concluded that the brittleness observed is due to the cyanide, and not to hydrogen. "These experiments indicate that the cyanide radical in combination with electrolysis is the cause of the brittleness." Another conclusion is, "Brittleness was not produced by the liberation of hydrogen on steel."

The brittleness caused in thin steel springs by pickling in acids for the purpose of removing scale has long been recognized, and has very generally been ascribed to absorption of hydrogen by the steel. That the matter is of interest to technical men is indicated by the fact that two of the papers presented at the last meeting of this society dealt with methods of preventing such embrittling of steel. Coulson[4] removes scale from steel without exposing it to the action of hydrogen by using it as anode, and

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[2] University of Wisconsin.
[3] Met. & Chem. Eng., 1917, 16, 83.
[4] Tr. Amer. Electrochem. S., 1917, 32, —.

reports entire freedom from brittleness; Fuller[5] secures the same result when copper-plating steel from a cyanide solution by first coating the steel with tin. Although the experiments of Coulson and Fuller indicate that hydrogen is probably responsible for brittleness, they do not absolutely prove this. To secure more definite evidence in the case "Cyanide *vs.* Hydrogen," the authors have carried out a number of experiments, which are here presented.

Watch springs were selected as the material for the tests, since, on account of their thinness and temper, they are particularly susceptible to brittleness. The test for brittleness consisted in bending the spring around a steel rod, ¼ inch (6 mm.) in diameter. The untreated springs withstood this test, whether bent with or opposite to their natural curvature. Springs recorded as brittle broke when bent in the same direction as their curvature, by no means a severe test. The springs varied from 0.16 to 0.23 m.m. in thickness.

TESTS.

A spring was immersed in 30 percent sulphuric acid for two minutes, and was very brittle after this treatment.

Springs were then used as cathode in several electrolytes from which hydrogen is deposited on the cathode on electrolysis, with the results shown in Table I.

TABLE I.

Exp.	Electrolyte	Time	Amp.	Amp./sq. dm.	Result
1.	30% H_2SO_4............	5 min.	0.05	2.5	Spring very brittle.
2.	n.K_2SO_4	5 min.	0.05	2.5	Brittle.
3.	n.HCl	3 min.	0.06	3	Very brittle.
4.	n.KCl	3 min.	0.06	3	Brittle, but less so than No. 3.
5.	NaOH (15.5 g./100 c.c.)	5 min.	0.04	0.26	Not brittle.
6.	NaOH (ditto)........	15 min.	0.04	0.26	Brittle, bluing removed.

When used as cathode in the hot "electric cleaner" at 9 volts and thus exposed to a storm of hydrogen, a spring is rendered quite brittle in 15 seconds, and in 30 seconds is ruined.

In order that electro-plating may adhere to the springs it is

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[4] Tr. Amer. Electrochem. S., 1917, 32, —.

TABLE II.

No.	Metal Deposited	Bath	Hydrogen Evolution	Deposit	Brittleness	Time, Min.	Amp.	Amp./sq.dm.
7.	Cu	Cyanide, free Cy.	Yes	Fair	Brittle	20	0.002	0.21
8.	Cu	Alk. tartrate	No	Poor	Not brittle	60	0.002	0.16
9.	Cd	Cyanide	No	Good	Not brittle	39	0.05	2.6
10.	Cd	Cyanide and free Cy.	Yes	Fair	Brittle	40	0.02	0.18
11.	Cd	Fluoborate, acid	Yes	Good	Brittle	30	0.05	0.31
12.	Cd	Fluoborate, faintly acid	No	Good	Brittle	10	0.10	4.2
13.	Au	Cyanide, free Cy.	No	Good	Not brittle	12	0.12	1.1
14.	Zn	Sulphate + Cl	No	Poor	Not brittle	40	0.004	0.46
15.	Zn	Sulphate + Cl, slight acid	No	Poor	Not brittle	40	0.004	0.74
From Hot Baths, temperatures 82 to 85°C.								
16.	Ag	Cyanide, free Cy.	No	Good	Not brittle	5	0.082	2.0
17.	Cu	Cyanide	No	Poor	Not brittle	7	0.11	0.54
18.	Cu	Cyanide, free Cy.	No	Bright	Not brittle	4	0.11	1.0
19.	Cu	Cyanide, much free Cy.	Yes	Bright	Brittle	5	0.11	0.5

necessary that the bluing be removed and that they be freed from every trace of grease. Since the usual means employed for these purposes cause the liberation of hydrogen and render the springs brittle, resort was had to a hot alkaline solution for the removal of grease, while the bluing was removed in several different ways: (1) a solution of $FeCl_3$, (2) a boiling solution of 10 grams ammonium citrate in 100 c.c. of water, (3) concentrated hydrochloric acid containing about 3 percent by volume of formalin. The second of these solutions proved most satisfactory, usually removing the bluing in a few seconds without even diminishing the luster of the spring. The third solution acts almost instantaneously, and if the spring is not exposed to its action for more than one second it is not injured, but is rendered brittle by immersion for a minute.

After being freed from grease and bluing, the springs were plated as indicated in Table II. Unless free cyanide is specified, the excess of this usually present in plating baths was removed by adding a salt of the metal to be deposited, until a permanent precipitate resulted. Electrolysis was at room temperature, about 23° C., unless otherwise stated. Since Thompson and Richardson used their cyanide copper bath hot, it was thought desirable to test the effect of heat with a few of these solutions, although it was expected, from the lessened brittleness of iron and nickel when deposited from hot solutions that the only effect of heating the electrolyte would be to lessen somewhat the brittleness of the springs.

In every case in which the evolution of hydrogen could be detected, and in one case where none was observed, the spring was rendered brittle. By removing the free cyanide from the copper solution and using it hot it was possible to deposit copper on the spring without making it brittle, but the plating was too poor to be of value commercially. No. 18, however, was an excellent deposit. Hydrogen is not evolved from silver or gold baths at reasonable current densities even in the presence of free cyanide, and in no case did the plating of springs from these solutions render them brittle.

It seems certain that any brittleness of steel springs acquired

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[6] Tr. Amer. Electrochem. Soc., 1917, 31, 303.

during plating cannot be due to cyanide, and it seems highly probable that brittleness caused either in pickling or plating is due to hydrogen.

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[*Written discussion of this paper is invited, and may be sent to the Secretary, Jos. W. Richards, South Bethlehem, Pa., or read at the meeting.*]

A paper presented at the Thirty-third General Meeting of the American Electrochemical Society, at Birmingham, Ala., May 3, 1918, President Fink in the Chair.

WHY BUSY RAILS DO NOT RUST.[1]

By OLIVER P. WATTS.[2]

ABSTRACT.

The author reviews at length the observations made since 1843 on the fact that idle rails appear to rust faster than busy ones. He criticizes some of the attempted explanations, and shows by experiment that they are not valid. Believing galvanic action to be chiefly responsible for the protection of the busy rails, measurements were made which showed the used head of a busy rail to be electrically positive to the rest of the rail. Confirmatory tests were made by straining (cold working) iron rods, showing the worked part to be electro-positive to the unworked. The author concludes that his observations, experiments and explanations have fully exposed the reasons for the phenomenon in question.—[J. W. R.]

It is a common observation that rails in the main line of a railroad never rust seriously, although those made of the same material but laid in a siding where there is little or no traffic, are soon badly rusted.

The observation of this phenomenon dates back to the infancy of the railroad. Robert Mallet[3] quotes a report of George Stephenson as follows: "One phenomenon in the difference of the tendency to rust between wrought iron laid down as rails, and subjected to continual motion by the passage of the carriages over them, and bars of the same material either standing upright, or laid down without being used at all, is very extraordinary. A railway bar of wrought iron laid carelessly upon the ground

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[1] Manuscript received March 4, 1918.

[2] Associate Professor of Chemical Engineering, University of Wisconsin.

[3] Report of Brit. Assoc. for the Advancement of Science, 1843, p. 28.

alongside of one in the railway in use, shows the effect of rusting in a very distinct manner; the former will be continually throwing off scales of oxidated iron, while the latter is scarcely at all affected."

In commenting on this observation of Stephenson, Mallet says, "When rails lying parallel on the same line of way, but one set in and the other out of use, are examined, appearances do undoubtedly seem to support the opinion. The unused rails are found covered with red rust, often coming off in scales parallel to the surface, while those in use present a light brown or buffish coat of rust, without any loose scales. I am much disposed however to believe that there is no real difference in the amount of corrosion in the two cases, and that the difference in appearance arises partly from a *deceptio visus,* by the effect of the bright and polished upper face of the used rail (kept so by constant traffic) contrasted with the rusty face of the unused rail, and partly from the fact, that as fast as rust is formed upon the rail in use, it is shaken off by the vibration of passing trains and blown away by the draft of wind which accompanies their motion, and that the rail is soiled and partially blackened by coke and other dust, etc."

From 1842 to 1849 Mallet[4] conducted three series of experiments with full-sized rails, each series comprising rails laid in the track, others laid beside those in use but not traveled over, and still others laid in the track but protected from atmospheric oxidation by a coating of tar. After making allowance for losses by abrasion, he reported the loss by corrosion in grains avoirdupois per square foot per year to be as follows:

Time in Days.	1st Exp. 303	2d Exp. 730	3d Exp. 1460
Rail idle	213.38	76.00	96.18
Rail in use	103.04	32.87	83.53
Difference	110.34	33.13	12.65

Mallet assumed that the top of traveled rails did not corrode, and hence omitted the area of the top in reckoning the surface of used rails. A recalculation of his results on the basis of the total surface of used rails gives 87.30, 27.85, and 70.77 for the losses of rails in use instead of the values published by Mallet; the corresponding differences in corrosion of idle and busy rails

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[4] Report Brit. Assoc. for Advancement of Science, 1849, 88.

are 126.08, 48.15, and 25.41 grains per square foot per year. It is noteworthy that the longer the period of exposure, the less the difference between the corrosion of busy and idle rails. This will be referred to again later. In explanation of the different rates of corrosion Mallet calls attention to the fact that "every metal is electropositive to its own oxide," and says, "Now the rust formed upon a railway bar in use is perpetually shaken off by the vibration of traffic, and thus this source of increased chemical action is removed."

W. H. Barlow[5] in 1868 comments on the phenomenon as follows: "The great difference between the effects upon rails laid in a siding and rails laid in the main line was, that the one by the wear of traffic had a polished surface, and the other had not; and he thought it quite possible that a galvanic action arose between the polished and the unpolished surfaces, which tended to preserve the general body of the rail."

Cushman, Friend, and Sang, in their books on the corrosion of iron[6] call attention to this comparative freedom from rust of busy rails, and suggest various explanations for it. Sang says, "Galvanic action between the smooth head of the rail and the rest of it has been suggested to explain this immunity from rust, but it is not at all likely that the foot would owe its protection to the thin stratum of denser metal so far removed from it. If that dense skin on the top of the rail were not crushed beyond its elastic limit, it would, on the contrary, tend to accelerate the corrosion of the steel in contact with it. The real reason for this difference of behavior seems to lie in the observed fact that oxidation is apparently arrested, or at least greatly retarded, by vibration. Explanations seem to stop at this point, but a simple theory can be built on the assumption that the vibration causes a shedding of the rust as soon as it is formed on the spots that are not protected by mill scale, and there is, therefore, no acceleration of the action due to the accumulation of spongy and electro-negative rust."

Commenting on the above explanation, Friend says, "No doubt this is a partial explanation, but the freedom from rapid rusting

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[5] Proc. Inst. Civil Eng., 27, 570.

[6] Cushman: Corrosion and Preservation of Iron and Steel, 1910, p. 108.
Friend: Corrosion of Iron and Steel, 1911, pp. 99, 118, 247.
Sang: Corrosion of Iron and Steel, 1910, p. 71.

may be due in part to the rise in temperature caused by the rush of trains over the metals, whereby the rails are maintained at a temperature slightly above that of their surroundings. The result is that liquid water has no good opportunity of condensing upon them, or, if once condensed, it is rapidly vaporized and corrosion retarded."

Cushman ascribes protection to "the fact that frequent and recurring vibration was sufficient to break up points of specific potential differences on the surface."

The idea that rails in constant use owe their immunity to rust to galvanic action between the strained and unstrained metal does not at present seem to be accepted. This is perhaps not strange, for until comparatively recently[7] it had not been surely demonstrated by experiment that cold-working renders iron electropositive, and it was also generally held that the E.M.F. between strained and unstrained iron or steel, granting that a difference of potential exists, is too small to exert a protective effect on the rest of the rail, especially on those parts which are several inches distant from the head of the rail.

Believing galvanic action to be chiefly responsible for the observed difference between the rusting of used and idle rails, the writer endeavored to ascertain if the head of a used rail is really positive to the remainder of the rail, a point which seems to have been left undetermined so far in the discussion of this question. Through the kindness of Mr. G. N. Prentiss, chemist for the Chicago, Milwaukee & St. Paul R. R., a section of used rail was secured. Pieces were cut from the top and the bottom, and covered with paraffine except for one side, so that the exposed surfaces should be approximately equal and that on the piece from the top only the worn surface of the rail should make contact with the electrolyte. The E.M.F. between these pieces was measured in normal potassium chloride by means of a potentiometer. The initial voltage was 0.078 volt, rising in five minutes to a maximum of 0.084, from which value it slowly fell to 0.029 at the end of an hour, during which time the electrodes were not moved. On shaking both electrodes the E.M.F. rose to 0.056, but dropped in 3 minutes to 0.037. The potential measured by a millivoltmeter of 16 ohms resistance immediately after the last reading

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[7] Burgess and Thickens: Tr. Amer. Electrochem. Soc., 1908, 13, 31.

by the potentiometer was only 0.015, which fell in 2 seconds to 0.005 volt. A millivoltmeter is unsuited for reading the E.M.F. between electrodes of such small surface as these, *viz.*, 6 sq. cm.

Instead of removing any slight differences of potential that naturally exist on the surface of the rail, as was contended by one of the authorities on corrosion previously referred to, the passage of trains develops a difference of potential exceeding 80 millivolts, between the upper surface and the rest of the rail. The question now is: To what extent is this E.M.F. responsible for the lessened corrosion of busy rails?

The prevention of the corrosion of iron by connecting the metal as cathode and sending current to it from a source of E.M.F. outside of the corroding solution has been the subject of several investigations, and this principle is the basis of a number of patented processes for preventing the deterioration of metals and alloys when exposed to severe corrosive conditions. Gee[8] found 0.088 ampere per square foot (1 per sq. meter) to be more than sufficient to protect iron from corrosion in 1 percent sodium chloride solution. Harker and McNamara[9] found 0.004 ampere per square foot (0.044 per sq. m.) to be sufficient to prevent the corrosion of iron in sea water, and Clement and Walker[10] obtained the same result by using a current density of 0.11 ampere per square foot in N/100 sulphuric acid. In the Cumberland process for preventing the corrosion of boilers 0.001 ampere per square foot (0.011 per sq. m.) has proved sufficient for the purpose.[8]

That the E.M.F. between strained and unstrained iron is great enough to cause selective corrosion in dilute acids was conclusively proved by the experiments of Burgess and Thickens previously referred to. In view of the small current density that was found to prevent corrosion of iron under the severe conditions of immersion in sea water, it is to be expected that the strained condition of the upper surface of used rails will exert a considerable protective action on the rest of the rail when the electrolyte is so slightly corrosive as is the dew or rain water which wets the rails. It might seem, therefore, that the whole matter has been cleared up; but while the formation of a local couple by contact of two dissimilar metals in an electrolyte lessens the corrosion of the

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[8] Trans. Faraday Soc., 1913, 9, 120.

[9] J. Soc. Chem. Ind., 1910, 29, 1286.

[10] Trans. Amer. Electrochem. Soc., 1912, 22, 193.

cathode, the rate of corrosion of the anode is thereby increased, and the question arises whether or not the total loss in weight of both materials is increased or diminished by putting them in contact.

To determine this a bar of mild steel (about 0.4 percent C) ¾ in. (1.9 cm.) square and 4 inches (10 cm.) long, was machined in a lathe to a diameter of ⅝ in. (1.6 cm.) for a distance of an inch (2.5 cm.) in the middle of the bar, leaving the ends unchanged. The bar was then twisted through 180° in a testing machine, by which a local couple having an E.M.F. of 80 millivolts was formed between the cold-worked middle and the unstrained ends. The bar was then machined to a diameter of 0.563 in. (1.4 cm.) throughout its entire length. A similar cylinder was prepared from unstrained metal, and the two were immersed to a depth of 3¼ inches (8.2 cm.) in N/5 hydrochloric acid for 72 hours. After cleaning, drying, and weighing, it was found that the bar in which the local couple had been formed by cold-working had lost 6.768 grams, while the other had lost only 5.436 grams. This means that the efficiency of cathodic protection by the current generated by the local couple was much less than 100 percent; at an efficiency of 100 percent the excessive corrosion of the anodic portion of the bar caused by the voltaic action would have been exactly counterbalanced by the protective effect on the cathodic portions, and the loss in weight of this specimen would have been the same as that of the unstrained metal.

In acid of the same strength as that used in this experiment, and also in sea water, Harker and McNamara found that the corrosion of zinc or iron which naturally occurred in these solutions could be overcome by inserting an anode of the same metal and making the corroding metal cathode, while passing a current exactly equivalent to the amount of metal previously lost. Clement and Walker reported the same condition to hold with regard to the protection of iron in N/100 sulphuric acid even when an insoluble anode was employed, *i. e.*, the efficiency of cathodic protection is 100 percent when the source of E.M.F. which produces the current is situated outside of the corroding solution. The low efficiency of protection found by the writer in the case of strained *versus* unstrained iron, corresponds to the wasting of an unamalgamated zinc in a voltaic cell with an acid electrolyte. In neutral electrolytes, as when rails are laid in a track, a high efficiency of protection is to be expected, just as there is a high efficiency of utilization of an unamalgamated zinc anode in neutral electrolytes.

Mallet's experiments on the rusting of used and idle rails showed an apparent efficiency for the protective action greatly in excess of 100 percent. It is of course impossible that this can be directly due to the protective effect of current flowing from the head of the rail, but it is a simple matter to find a logical explanation for it. As has already been indicated, it is generally recognized that the presence of rust is a stimulator to further rusting, and that the thickness, age, and porosity of the rust are factors of importance in determining the rate at which rusting proceeds. Traffic keeps bright the upper surface of the rail, where the coat of rust would otherwise be heaviest, and the current flowing from this lessens the thickness, and probably modifies the quality of the coat of rust on other parts of the rail; the result must be a slower accumulation of rust on used than on idle rails (meaning those which have never been used), and therefore less vigorous action by that stimulator of rusting, rust itself. This view is supported by Mallet's observation that the rates of rusting of used and of idle rails become more nearly equal as the time of exposure is increased.

Among explanations offered by previous writers for the lessened corrosion of rails in use are:

1. That vibration causes shedding of rust and so, in the presence of less of this stimulator of corrosion, rusting will be diminished.

2. That vibration breaks up areas of different potential that are naturally present on the surface of iron or steel.

3. That there is a voltaic action between bright or polished and dull or rough iron which, in some manner not explained, lessens the total corrosion of the rail.

4. That the rise in temperature produced by the passing of trains causes a more rapid evaporation of moisture from the used rails, and for this reason lessens corrosion.

This paper proves that an E.M.F. exists between the top and other portions of used rails acting in such a direction as to protect the rest of the rail; but it is manifestly impossible that a current generated by corrosion of one part of a bar of metal in a single solution shall, by its protective action on the other part, directly lessen the total corrosion.

The writer presents the view that the lessened corrosion of rails in use is due to a combination of two of the causes mentioned by previous writers, *viz.*, voltaic action between strained and unstrained metal in the rail, which results in a slower formation of rust on the cathodic portions, and that thereby the normal accelerative action of rust is greatly diminished; and the complete removal of rust from the top of the rail, where it would otherwise form most rapidly and exert the greatest accelerative effect on rusting.

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DISCUSSION.

C. G. Fink[1]: This subject of corrosion is probably the most important subject of electrochemistry from our Government's point of view, and the Bureau of Standards and other large laboratories have carried out a very large amount of work along this line.

Jos. W. Richards[2]: The phenomenon of the strained part being electro-positive toward the unstrained is due to the fact that work has been done upon it and has changed its shape, and therefore it has a little more energy to give out when it dissolves than if it were unstrained. It is the old question of taking a spring and coiling it; when it is coiled you have stored up in it some mechanical energy. If now that coiled spring is dissolved in acid, it must give out and will give out, in the form of heat, the heat of solution of the unstrained steel plus the equivalent of the mechanical energy which was put into it in cooling it. In the same way, the strained portion has some mechanical energy to give out which the unstrained portion has not, and therefore if you put in a solution a piece of strained iron and a piece of unstrained iron, the strained iron will act as the anode, because in going into solution it gives out more energy than the unstrained.

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[1] Head of Laboratories, Chile Exploration Co., New York City.

[2] Prof. of Metallurgy, Lehigh University, Bethlehem, Pa.

The strained part of the rail will therefore act as an anode and the unstrained part, which is the rest of the rail, as cathode, and therefore protected by any current which may flow through the film of moisture on the rail.

Carl Hering[3]: Is it an experimental fact that the strained portion is always the anode?

Jos. W. Richards: According to this paper, yes.

Carl Hering: Is there no other evidence?

Jos. W. Richards: I believe that has been rather elaborately tested and proved, and this paper confirms that view.

Carl Hering: I did not question it, and theoretically it seems that it should be so; I was merely interested in knowing whether the fact was established.

H. D. Hibbard[4]: To the explanation given in the paper should, I think, be added the one that busy rails are being continually spattered with oil. The explanations given in the books of the last century seemed to me inadequate, and for the past forty years I have considered the protecting influence of oil to be the reason why busy rails rusted less rapidly than those in an idle track alongside. I have thought that idle rails between busy rails such as guard rails at bridges and at frogs rusted no more rapidly than the rails which bore the traffic, but know of no determinations bearing on that point, though it may be worthy of quantitative study.

A drop of oil on a warm rail, as in summer time, spreads to many times its original area and its protective power is quite lasting.

O. P. Watts (*Communicated*): Mr. Hering will find further experimental evidence, corroborated by photographs, of the fact that strained iron is anodic to the unstrained metal, in reference 7 of this paper, the presidential address delivered by C. F. Burgess before this Society in 1908.

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[3] Consulting Electrical Engineer, Philadelphia, Pa.

[4] Consulting Metallurgist and Engineer, Plainfield, N. J.

A paper presented as part of a Symposium on Corrosion at the Thirty-ninth General Meeting of the American Electrochemical Society, at Atlantic City, N. J., April 21, 1921, Colin G. Fink in the Chair.

THE EFFECT OF COPPER AND SILVER SALTS ON THE CORROSION OF IRON BY ACIDS.[1]

By Oliver P. Watts[2] and Harold C. Knapp.[3]

Abstract.

A record of tests on the corrosion of iron by sulphuric acid in the absence or presence of various salts of copper and silver. The conclusion drawn is that in general corrosion is stimulated by the presence of these salts. The theory of this action is discussed. A remarkable example of electrochemical corrosion in sea-water is given. [J. W. R.]

There is a time-honored belief, quite generally held by those who have studied corrosion, that the addition of a copper or a silver salt accelerates the corrosion of iron by sulphuric acid. This acceleration is supposed to take place in two ways: First, the metal of the dissolved salt is replaced by iron, thus causing direct corrosion of the latter; second, the copper or silver precipitated on the surface of the iron sets up a voltaic couple with the iron as anode and the other metal as cathode, and if the discharge potential of hydrogen on the new cathode is less than on iron, as is the case with copper and silver, corrosion is stimulated.

In a detailed paper on the solution of metals by acids presented at the 38th meeting of this Society in October last, W. D. Richardson reported the results of experiments on the corrosion of iron by normal sulphuric and hydrochloric acids, with and without the addition of salts of copper and silver. Speaking of this voltaic or "catalytic action," as he calls it, of silver salts, he says, "No noticeable effect was produced on any of the metals tried in

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[1] Manuscript received February 26, 1921.

[2] Assoc. Prof. Chem Eng., University of Wisconsin.

[3] University of Wisconsin.

hydrochloric or sulphuric acids." Regarding the action of copper salts he says, "The copper was added in the form of chloride, sulphate and nitrate to the respective acids, 10 grams of metallic copper being present per 100 liters of acid. In hydrochloric and sulphuric acid none of the iron plates showed any change of rate." Further he says, "According to the older view of the electrolytic theory, copper in contact with pure iron ought to catalyze positively in non-oxidizing acids, but this is not the case. Its effect on the purer metals is negligible, nor does it affect the cast metals appreciably in non-oxidizing acids." Unfortunately the implied newer view of the electrolytic theory, according to which copper and silver salts should exert no accelerative effect on the corrosion of iron by acids does not appear in the paper, and the reader is left to wonder what this can be.

TEST I.

In $N.H_2SO_4$ *with Addition of* $CuSO_4$.

No.	Material	Grams Cu/Liter	Loss in Grams by Corrosion		Ratio Cat./Acid Corrosion
			Total	By Catalysis	
1.	Copper steel	0	0.0635	.....	.....
2.	" "	2.5	0.7517	0.2486	3.92
3.	" "	0.1	0.1348	0.0538	0.85
4.	Ordinary steel.....	0	5.5074	.....	.....
5.	" "	2.5	5.9947	0.0477	0.008
6.	" "	0.1	5.5886	0.0637	0 011

Having previously conducted a few experiments on the effect of copper sulphate on the corrosion of iron by sulphuric acid, the authors could not accept the above statements as representing the facts, and therefore the experiments reported below were carried out.

The materials used for corrosion were ordinary sheet iron (probably a mild steel) purchased at a local hardware store, copper steel supposed to contain about 0.25 percent of copper, and Armco iron. The test pieces, 5 cm. square, were pickled in pure sulphuric acid to remove scale, dried, weighed, and immersed in an upright position in 200 c.c. of acid at 30° C. for 24 hours. A sufficient quantity of copper sulphate or silver carbonate was in some cases added to give either 2.5 or 0.1 grams of metal per liter. The latter amount was that used by Mr. Richardson. The loss by voltaic or catalytic action is calculated by deducting from the total loss in weight the amount of iron that should be dissolved by the metallic salt added, and also the loss caused by the acid alone in the same test.

It is seen that with the larger amount of copper voltaic action is nearly four times the direct corrosion by the acid, but with the smaller quantity of copper voltaic action is somewhat less than corrosion of the copper steel by the acid. With ordinary steel voltaic action is about the same for either amount of copper, and although this is about the same in amount as for the copper steel, it plays an utterly insignificant part in the total corrosion, because of the tremendous corrosion by the acid.

TEST II.

In $N.H_2SO_4$ *with Addition of* Ag_2CO_3.

No.	Material	Grams Ag./Liter	Loss in Grams by Corrosion		Ratio Cat./Acid Corrosion
			Total	By Catalysis	
7.	Copper steel	0	0.1001	.....	.....
8.	" "	2.5	0.3696	0.0111	0.11
9.	" "	0.1	0.4311	0.3207	3.2
10.	" "	0.01	0.2751	0.1733	1.73
11.	Ordinary steel....	0	5.6545	.....	.....
12.	" "	0.1	5.5677	—0.1043	—0.018
13.	" "	0..01	5.5764	—0.0798	—0.014

The figures of Test II apparently indicate less action by the large amount of silver salt than by either of the lesser quantities. This anomaly is explained by the observation that specimen No. 8 was surrounded by a spongy deposit of silver an eighth of an inch thick. This served as a diaphragm and retarded the diffusion of acid to the steel. With ordinary steel the presence of a silver salt diminished corrosion—probably by lessening the surface of steel directly exposed to the acid.

With the lessened rate of corrosion due to more dilute acid, although the loss by voltaic action is but slightly changed, it is relatively more important.

TEST III.

In N/50.H_2SO_4 with Addition of $CuSO_4$.

No.	Material	Grams Cu/Liter	Loss in Grams by Corrosion		Ratio Cat./Acid Corrosion
			Total	By Catalysis	
16.	Copper steel	...	0.0296	.....	....
17.	" "	2.5	0.5802	0.1110	3.75
18.	" "	0.1	0.1307	0.0936	3.16
19.	" "	0.01	0.0576	0.0263	0.89
20.	Ordinary steel....	0	0.0669	.....	....
21.	" "	2.5	0.5904	0.0839	1.25
22.	" "	0.1	0.1234	0.0390	0.58
23.	" "	0.01	0.1030	0..0344	0.51

TEST IV.

In N/50.H_2SO_4 with Addition of Ag_2CO_3.

No.	Material	Grams Ag./Liter	Loss in Grams by Corrosion		Corrosion Ratio Cat./Acid
			Total	By Catalysis	
26.	Copper steel	0.	0.0429	.....	....
27.	" "	0.1	0.1119	0.0515	1.20
28.	" "	0.01	0.1025	0.0579	1.35
29.	Armco iron	0	0.0234	.....	....
30	" "	0.1	0.1072	0.0663	2.83
31.	" "	0.01	0.0622	0.0371	1.59
32.	Ordinary steel....	0	0.0828	.....	....
33.	" "	0.1	0.1180	0.0177	0.21
34.	" "	0.01	0.1130	0.0285	0.34

TEST V.

In N/50.H_2SO_4 with Addition of $CuSO_4$.

No.	Material	Grams Cu/Liter	Loss in Grams by Corrosion		Ratio Cat./Acid Corrosion
			Total	By Catalysis	
35.	Copper steel	0	0.0876	.....	....
36.	" "	0	0.0903	.....	....
37.	" "	0.1	0.2932	0.1867	2.10
38.	" "	0.1	0.2732	0.1667	1.87
39.	Armco iron	0	0.0603	.....	....
40.	" "	0	0.0680	.....	....
41.	" "	0.1	0.2461	0.1645	2.57
42.	" "	0.1	0.2869	0.2053	3.20
43.	Ordinary steel....	0	1.7340	.....	....
44.	Stove-pipe iron..	0	1.7948	.....	....

Tests IV and V show voltaic action on the more resistant metals to be from 1 to 3 times the amount of corrosion by the acid. The corrosion of duplicate specimens in test V varies by 3 percent for copper steel in acid alone and by 11 percent in the presence of copper sulphate; similar variations for Armco iron are 7 and 16 percent. These wide variations indicate that great caution must be exercised in ascribing observed differences in corrosion to the presence or absence of some metal in the alloy or to the presence of some particular chemical in the electrolyte. As a whole these experiments indicate that voltaic action by copper and silver does stimulate the corrosion of iron and mild steel by acids, particularly in the case of the more resistant materials.

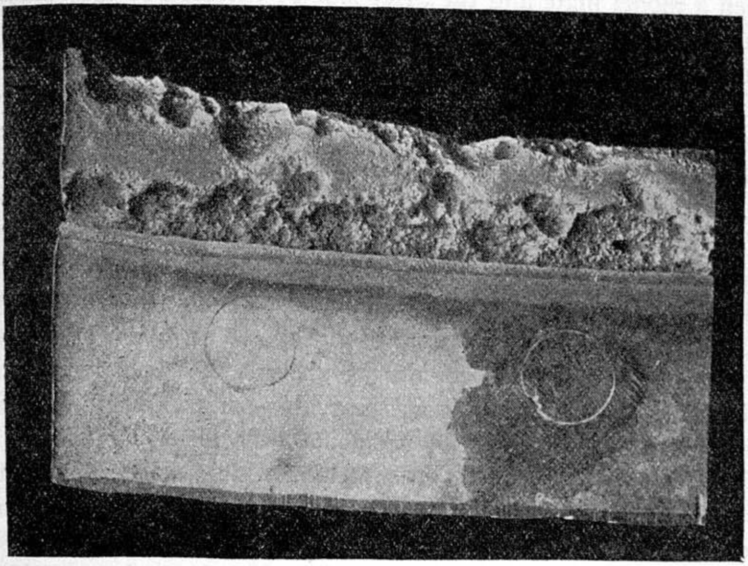

FIG. 1.

Electrochemists recognize that the relative position of two metals in the electrochemical series does not entirely determine the magnitude of voltaic corrosion, but that this is affected by the extent of surface of the cathode, by the discharge potential of hydrogen on the cathode, by the presence or absence of oxygen to act as a depolarizer, by the resistivity of the electrolyte, by the formation of protective films on the anode, etc. Yet the difference of potential between the metals is the fundamental cause of corrosion, and the other conditions are merely modifiers of its action. That ignorance of the serious effects of voltaic action and incorrect conclusions drawn from faulty experiments may have disastrous results is shown by the sad fate of the "monel metal yacht," *Sea Call*. The outside of this big schooner was made of monel, a nickel-copper alloy, with the exception of the stem, keel, sternpost and rudder frame, which were steel. Fig. 1 shows what happened. This is a photograph of the contact between a monel plate and the after side of the steel rudder frame. In three months afloat holes were eaten entirely through the steel, three-quarters of an inch thick, and it was apparent that this would soon have been entirely destroyed. Other exposed steel parts were similarly affected; the vessel was condemned as unseaworthy and was broken up without having made a single voyage. An important factor in this remarkable case of corrosion was the enormous size of the cathode (monel) in comparison with the anode (steel). The hydrogen, plated out on the monel by the dissolving of the steel, was distributed over such a great surface, and so much dissolved air was present that polarization by hydrogen must have been almost entirely prevented. As a result, the initial E. M. F. of the couple was available for producing current, which is rarely the case with accidentally-occurring couples.

This $500,000 experiment in corrosion should serve as a warning of the seriousness of long-continued voltaic action in a good electrolyte, and it should be recognized that electrochemical theory affords a better basis for predicting what will occur when a voltaic couple of two particular metals is exposed to sea water for months, than do laboratory experiments of a few hours, or even days, duration.

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DISCUSSION.

W. D. Richardson[1]: This paper has for consideration some work that I did and reported to this Society at its last meeting.

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Certain experiments that I made showed that copper, when present to the extent of one-tenth of a gram of metal per liter of acid, did not accelerate the solution of certain samples of iron and steel in hydrochloric and sulphuric acid. The authors of this paper have reported experiments which show that in some cases copper and also silver does accelerate the action, but I should like to call attention to the point that in some of their experiments they show no accelerated action, particularly those shown on pages 156 and 157, the last two figures in the last column in each case. In one of these instances, the amount of copper used was the same as the amount I use, and in another case the amount was two and one-half times as great, and yet they report no essential change of rate to action of the copper, which is exactly what I reported.

In other instances they do find increased action. Naturally, I do not want to go on record as believing that in no case can copper accelerate corrosion, but I think we should consider the fact that copper does behave with a most peculiar manner in connection with corrosion, and this is shown by the effect of copper in copper steel, for instance. Again I conducted experiments in which I added the same amount of copper to normal nitric acid, and in this acid not only did copper not increase the rate of corrosion, but it decreased it very materially, almost one-third. It acted in a negative manner when present in a normal oxidizing acid, whereas, in my experiments, it did not change the rate in a non-oxidizing acid, and I suggested that possibly there was some connection between the behavior of copper in connection with an oxidizing acid and its behavior in copper steel under oxidizing conditions, that is, atmospheric conditions. The authors of this paper apparently take exception to the fact that it speaks of catalytic action in these cases, and they suggest, by inference, at least, that I should say voltaic action. I have no objection to that at all, except that in the paper which they are considering, I also considered the effect of formaldehyde in connection with these acids; and sometimes formaldehyde acts as a negative catalyst, and sometimes it does not change the rate. Now I wanted to call all these things by one name, and since catalytic action is the phrase which cloaks our ignorance, under these conditions I called it catalysis. The authors also apparently took exception to the statement as follows: (I am quoting my own words) "According to the older view of the electrolytic theory, copper in contact with pure iron ought to catalyze positively in non-oxidizing acids." These authors then remark, "Unfortunately the implied newer view of the electrolytic theory, according to which copper and silver salts should exert no accelerating effect on the corrosion of iron by acids does not appear in the paper, and the reader is left to wonder what this can be."

I did not mean to imply any new view according to which copper and silver salts should exert no accelerative effect. I wish, and I have often wished, in the course of my experiments, that these things would behave according to theory, it would simplify our work. Matters do not occur according to the simple idea or the simple conception of the electrolytic theory of corrosion as advanced in the early days, and that is what I meant when I spoke of the older view of it. The recent view, and it is coming more and more into prominence, is that while this older view of a simple electrolytic theory is at the basis of all corrosion phenomena, there are so many modifying, upsetting and antagonizing influences that it does not take a straight course as we might expect if we had no further knowledge of it. Let me call your attention to one upsetting influence, rust, which I have emphasized over and over again, may accelerate, in a general way, the corrosion of iron. If it forms a closely adherent layer of the physical nature of a paint film over the entire surface, it may stop corrosion by preventing the access of water or oxygen, and if it is tightly adherent in patches, it may cause deep pitting. Now here we have the same general influence acting in different ways, in all instances upsetting the ordinary action of the corrosive substances and elements.

I believe we have another influence to contend with which may act in different and perhaps antagonistic ways, namely, oxygen. We know that oxygen is the chief disturbing influence in ordinary corrosion; it is the principal substance which causes corrosion to go in some other way than we might expect from the simple theory. We know that the corrosion of iron goes on at practically the zero rate in the absence of oxygen and in the presence of water, and we know it may go on very rapidly in the presence of pure oxygen and less rapidly in air. We know, too, that the influence of oxygen or an oxidizing agent on the surface of iron may be such as to produce the passive condition, and when this condition supervenes, the iron behaves as monel metal and there is no corrosion at all. I have been led to suspect by some phenomenon, that I have mentioned in an earlier paper in connection with some work on cast iron, that a modified passivity may supervene in instances where we have not suspected it. I do not know that this theory explains it, but in the case of cast iron we have some very peculiar rust-resisting properties, and it may be that under certain conditions the iron coupled with graphitic carbon and under oxidizing conditions may assume, temporarily at least, or from time to time, or intermittently, a passive condition which may stop the corrosion. In discussion with Dr. Burgess last evening on the subject of copper steel, I spoke with him about the experiments which I had made, adding copper to normal nitric acid, with the result that the corrosion rate was lower, and he suggested that possibly in that case passivity was induced. I then spoke to him about the effect of graphitic carbon on cast iron, and it may be that in the case of the copper steel, we have an induced passivity, or partial passivity, or intermittent passivity, which may account for the action of the copper in that instance. I think none of us can afford to be at all dogmatic in our discussions of corrosion, and particularly when we are dealing with a metal like copper of proved peculiar behavior.

COLIN G. FINK[2]: The general condition of our corrosion research today is not very inviting. Reports cannot readily be compared, as methods of investigation are so different. The investigator usually has to start out to prove a definite thing, and he must carry out his experiments along a certain line. He must prove that his company's product is good. Now if the tests do not fit into this formula, they are either not carried out or not published.

W. D. RICHARDSON: I want to say a word in regard to the differences between hydrochloric acid and sulphuric acid. We regard them both as non-oxidizing acids. If any one will refer to my paper, "The Gap Between Theory and Practice in the

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[2] Consulting Electrometallurgist, So. Yonkers, N. Y.

Production of Corrosion-Resisting Iron and Steel," and later papers, he will find that in some experiments I made I used sulphuric acid in connection with aluminum plates; with Duriron plates, it was shown that sulphuric acid behaves very similar to nitric acid. In other words, sulphuric acid seems to be able to act as though there were no oxygen influences present. We cannot set up passivity in the presence of an alkali; we can set it up in the presence of an acid.

J. A. AUPPERLE[3]: I would like to call attention to the fact that very often conclusions are drawn from insufficient data, and in this paper "the materials used for corrosion tests were ordinary sheet iron, probably a mild steel, purchased at a local hardware store, copper steel supposed to contain about 0.25 percent of copper and Armco iron." No analyses are given; therefore I do not believe the conclusions are justified from the information at hand.

Our researches seem to check Mr. Richardson's that the contact of copper has considerable influence on the rate of corrosion, retarding it in one instance and increasing it in another. The photograph on page 159 is very interesting. The authors have called attention to the great difference in the size of the electrode, the electro negative metal, steel, being extremely small, while the electro positive monel metal was extremely large. This is a very important point and undoubtedly has considerable influence on the rate of corrosion.

G. W. COGGESHALL[4] (*Communicated*): The authors show by their tabulated results that what they called voltaic action by copper and silver salts does stimulate the corrosion of iron and mild steel by acids. Their tables also show more definitely, however, another point. In the $N/50$ solution of H_2SO_4, as shown in tests IV and V, the plain acid without addition gave a corrosion loss on commercially pure iron of 0.02 and 0.06 grams. The corrosion loss for copper steel in the same acid shows respectively 0.04 and 0.088 grams loss, which is respectively 40 and 100 percent greater for the copper steel. Furthermore, the total corrosion loss with the addition of silver and copper salts in no case

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[4] Chemical Engineer, The Institute of Industrial Research, Washington, D. C.

is as great with the commercially pure iron as with the copper steel. These results were obtained with dilute sulphuric acid about 0.10 percent strength.

O. P. WATTS (*Communicated*): Mr. Richardson says, "In some of their experiments they show no accelerated action," referring particularly to specimens 5, 6, 12 and 13.

In discussing 5 and 6 the authors had already pointed out in the paragraph immediately preceding Test II, that, where corrosion by the acid alone is very great, the accelerative action of the copper salt is but an insignificant part of the total corrosion, although the amount of corrosion by voltaic action is approximately the same as with the more dilute acid, but in all cases where corrosion by the acid was slow, either because of its dilution, or because of the resistant nature of the metal, the accelerative effect of the copper or silver salt is unmistakably apparent.

Taken at their face value, Nos. 12 and 13 would seem to indicate that in normal sulphuric acid silver exerts a protective effect on ordinary low-carbon sheet steel; but this is contrary to its effect in all other cases. Where corrosion of iron by the acid is very rapid, the time during which voltaic action by the silver can take place must be limited, for the silver deposited must soon be undermined by solution of the iron, and, once detached, cannot again be deposited, for it is not appreciably attacked by the acid. The conditions for securing a reliable conclusion regarding voltaic action in the case of specimens 5, 6, 12 and 13 are then very unfavorable, and when specimens 12 and 13 run counter to experience with the 27 other specimens, it is probably best to register a verdict of "not proven" for these two.

Mr. Aupperle says that he does not believe the authors' conclusions are justified because no analyses are given. The conclusion stated in the sentence which ends immediately below Fig. 1, could perhaps be improved by inserting the adjective "commercial" before iron, so that it would read, "Voltaic action by copper and silver does stimulate corrosion of commercial iron and mild steel by sulphuric acid." While insertion of analyses of the three different materials tested would have added to the completeness of the paper, a knowledge of the exact composition of the particular sheets of Armco iron or of Keystone copper steel can in no way alter the facts regarding the effect of a copper salt on their corrosion in sulphuric acid.

A comparison of the losses of specimens 38 and 42 shows that Mr. Coggeshall's sweeping statement that "the total corrosion loss with the addition of silver and copper salts in no case is as great with the commercially pure iron as with the copper steel," is not warranted.

A paper presented at the Forty-second General Meeting of the American Electrochemical Society held in Montreal, September 21, 1922, President Schluederberg in the Chair.

THE DEZINCIFICATION OF BRASS.[1]

By Ralph B. Abrams[2]

Abstract.

Experiments are recorded, the results of which indicate that the mechanism of dezincification appears to be as follows: The first step is the dissolving of the brass as a whole. The copper in solution then redeposits replacing brass as a unit. This redeposition will not take place unless there is some means of holding the dissolved copper in contact with the brass. This can be accomplished in two ways, one by the presence of a membrane, the other by having a large excess of dissolved copper present. Obviously this latter possibility is a remote one, especially so far as natural conditions are concerned. The membrane may be anything whatsoever, so long as it performs the function of keeping the dissolved copper in contact with the brass. Whether or not dezincification shall take place can be controlled by merely supplying or taking away the membrane. Briefly then, the dezincification of brass is the dissolving of the brass as a whole, the holding of the dissolved copper in contact with the brass by a membrane, and the subsequent redeposition of the copper.

The subject of the dezincification of brass has been one of current interest for many years to students of the corrosion of nonferrous alloys. This corrosion has been studied from almost every conceivable point of view, in an effort to throw light on its actual mechanism. Dezincified brass is commonly understood to mean brass which, after undergoing service for a period of years, has so disintegrated under the influence of sea water that only a

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[1] Manuscript received July 7, 1922.

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porous mass of seemingly metallic copper with a brass colored coating on the surface remains. It is really brass minus the zinc, and minus those physical qualities which make brass valuable. This product of corrosion is weak, brittle, and fails under the slightest stress.

In using the word "dezincification" in this paper, it is to be understood to mean brass which has undergone the corrosion above described, regardless of what the actual process of this corrosion has been. The question of dezincification has been one of vital import to users of brass condenser tubes and other brass parts which are subject to the action of sea water. It was perhaps the distress of the maritime users of brass that spurred the efforts of men of science to find the real cause of this action. As has been said, the question has been attacked from all sides. It may prove interesting to review a few of the more prominent ideas advanced. Mr. Arnold Philip, admiralty chemist, Portsmouth,[3] believes in the existence of "minute zinc-copper couples, functioning as small electrical cells, all over the surface of the brass." He called attention not only to molecular couples of copper and zinc, but also to molecular couples of compounds of copper and zinc. The action of such couples results, he believes, in the dissolving out of zinc and leaving copper behind.

Mr. Samuel Whyte and Dr. Desch concur in the idea of a couple action between the *alpha* and *beta* constituents of brass. Their idea agrees well with the statement by Mr. Rawdon.[4]

"The preferential attack of the *beta* phase is to be attributed to its higher zinc content, which renders it more electro-positive than the copper-rich *alpha* constituent. When an electrolyte is present, electrolysis occurs either by means of the application of an external e. m. f., by contact with some metal that is less electro-positive than the alloy, or by reason of the electrochemical difference in potential between the *alpha* and *beta* phases. The *beta* is always attacked first; its zinc largely passes into solution leaving behind the porous copper masses occupying the spaces initially filled with the *beta* matrix. This type of corrosion may be regarded as electrolytic leaching out of zinc."

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[3] Journal of the Faraday Society, 1915, p. 244.

[4] Tech. Paper No. 103. Bureau of Standards.

A different opinion is presented by Dr. Bengough and Dr. Hudson in the fourth report of the British Corrosion Committee of the Institute of Metals.

"The provisional view of the present authors as regards 70:30 brass is that the normal action in ordinary types of neutral or nearly neutral water is predominantly one of oxidation, and that the action of couples if such exist is too seriously hampered to be effective.. . . . . .It does not appear to the authors absolutely certain, however, that any copper is left *in situ* when zinc passes into solution; what appears to be left may really be redeposited."

An extract[5] of the fifth report by the same committee was published a few months ago. In this, from a study of the corrosion of copper, it is concluded as follows:

"Also that the first action of the corrosion is upon a thin oxidized coating rather than upon the underlying metal. Now if a piece of smooth copper be immersed in chloride solutions, the oxidized surface gradually changes into an almost insoluble cuprous chloride (CuCl), which is ordinarily swept away by gravity or by water currents, but which may adhere to the surface. In the latter case cuprous chloride becomes oxidized according to the reaction

$$4CuCl + O = Cu_2O + 2CuCl_2$$

into cuprite crystals and the very corrosive soluble cupric chloride. It is easily proved that cupric chloride is very corrosive to copper

$$CuCl_2 + Cu = 2CuCl$$

and the end product is where we started from. Therefore the reactions occur in cycles at spots underneath the gelatinous salts permeable to oxygen in solution.

"Brass in chloride solution acts similarly. As noted before, the first attack gives a layer of copper oxide, plus a little zinc oxide, the zinc mainly going into solution as $ZnCl_2$. The reactions on the copper then proceed as outlined just above. If the insoluble chlorides adhere to the surface, cupric chloride is formed. Cupric chloride attacks zinc as well as copper,

$$CuCl_2 + Zn = ZnCl_2 + Cu$$

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[5] Chem. and Met. Eng. Feb. 15, 1922. p. 305.

with the formation of a soluble zinc chloride and the deposition of crystalline or powdery copper."

It was in view of this diversity of opinion and because of the widespread interest in the problem that the present investigation was undertaken.

The great difficulty in attempting to study the actual mechanism of the so-called dezincification of brass is that under natural conditions the process requires several years. In the short time available for these experiments, it was therefore impossible to reproduce this corrosion by the mere immersion of brass in artificial sea water. Hence the problem was to hasten the action without distorting the results. Dilute hydrochloric acid presented itself as a probable agent to accomplish this. Corrosion by hydrochloric acid ought to be the same as corrosion by sodium chloride except that the discharge potential of hydrogen on brass from a hydrochloric acid solution is far below what it is from a sodium chloride solution. Therefore the action with hydrochloric acid should proceed with greater velocity than with sodium chloride. If this be the only difference in the performance of the two solutions, then the substitution of hydrochloric acid for sodium chloride should not affect the process of dezincification no matter what its mechanism is. This was tested by experiment. It will be well to mention here that the brass strips used in all the following experiments were about one millimeter in thickness, weighed 0.35 gram per square centimeter of area, and had a total weight of about 10 grams.

Experiment 1

Five brass strips were submerged in separate tumblers of normal hydrochloric acid and covered with glass plates to prevent evaporation. After four weeks the specimens were examined.

Result: In every case when the sample was removed from the hydrochloric acid, the acid not only showed no trace of the characteristic blue color of a copper salt in solution, but it was perfectly clear and colorless. The brass itself showed no sign of corrosion on the surface, except for the appearance of a few small particles of crystalline copper. The specimens were brittle and could be broken by the fingers with ease. Beneath a brass colored surface the specimens were found to consist entirely of copper. In those cases where the corrosion had not gone to completion, there was a layer of brass at the center with layers of copper on either side. In two samples where the corrosion had gone completely through the thickness of the brass, instead of finding one continuous mass of copper, there were two distinct layers of copper which could easily be pulled apart. The surface between them was smooth and flat.

From the above result, the effect of dilute hydrochloric acid in producing dezincification can not be doubted. With this agent at hand with which the problem can be attacked, a systematic study of it can now be attempted. The first question is to show whether this phenomenon is a leaching out of the zinc or whether it must be explained by another theory.

Experiment 2.

Brass strips were submerged in normal hydrochloric acid. The solution was agitated by bubbling air through it.

Result: At the end of 26 hours the samples were completely dissolved. This experiment was repeated four times with the same result.

Experiment 3.

Brass strips were again placed in normal hydrochloric acid. This time a mechanical stirrer was used to keep the acid in motion. In this case no air came in contact with the specimens.

Result: The brass again corroded uniformly, both the copper and the zinc dissolving. There was no dezincification. The action was slower in this case than in Experiment 2. In 240 hours approximately 10 grams dissolved. The hydrochloric acid in this experiment was replaced with a fresh solution every 24 hours to prevent an accumulation of dissolved copper. Upon repetition, this experiment yielded the same results.

In Experiment 1, it was seen that if the brass were undisturbed, dezincification took place. In Experiments 2 and 3, with stirring, corrosion was complete, that is, both the copper and the zinc dissolved. If this process of dezincification were one of the selective corrosion of brass, the stirring of the solution would have no more effect than to aid the action. Why then is the dezincification stopped? It must be because the brass is first corroded as a whole and then the copper redeposited. By stirring, the copper was prevented from redepositing, by being washed away as soon as it dissolved. The action in both experiments was the same. The circulation of the solution in both cases hastened the corrosion and prevented the dissolved copper from coming in contact with the brass. It was to prevent an accumulation of the copper that the solutions were renewed daily.

The increased rate of corrosion in Experiment 2 over that in Experiment 3 is accounted for by the fact that the oxygen acts as a depolarizer, removing the hydrogen and hastening the action. Another circumstance which favors the view that the copper has been redeposited is that in Experiment 1 two distinct layers of copper were formed instead of one continuous mass. If the action had been a mere leaching out of zinc, this could not be explained. But if the action is considered as one of redeposition, it can easily be seen that the deposition of copper on both sides of the strip would leave two distinct sheets of copper when all the brass between was dissolved.

The action of dezincification can thus far be described as, first, the solution of the brass as a whole, putting the copper and zinc into solution and then the redeposition of the copper replacing the brass not the zinc alone. It is significant in this connection to note the following facts which have long been known. The potential of amalgamated zinc in acid solution is practically that of zinc. When amalgamated zinc is corroded by acids only zinc dissolves—a case of true dezincification. The potential of the alloy, amalgamated zinc, is that of the substance which goes into solution, the zinc. So, the potential of brass must be that of the substance which dissolves. The potential of brass is, however, very close to that of copper.

The point to be emphasized here, therefore, is that it is not the zinc which gives the potential to the brass, as the zinc does in the amalgam, nor is it the copper, but the substance—brass itself—acts as a separate entity with a potential of its own, capable of being replaced as a unit. Now ordinarily when copper is precipitated from solution by zinc, the action is so rapid that the deposit is the usual black spongy one. The difference in potential between the copper and the brass is so small that the action is very slow, so that the copper has the chance to deposit in the bright metallic form in which it is found.

In order to secure reasonably rapid corrosion without the use of acids, brass was used as anode with a very feeble current in different neutral solutions.

Experiment 4.

A brass strip was used as an anode in a 3 percent solution of potassium sulphate with a carbon cathode. The current density was 0.25 ampere per square foot. The time allowed was ten days.

Result: The brass strip was completely corroded. The copper was deposited at the cathode while the zinc formed a precipitate of zinc hydrate in the solution. The experiment was repeated with the same results.

Experiment 5.

A brass strip was used as an anode in a 3 percent sodium chloride solution with a carbon cathode. The current density was 0.25 ampere per square foot. The time of electrolysis was 14 days.

Result: In this case, only copper was left at the anode. Again the copper left was in the form of two thin sheets which could be pulled apart as in Experiment 1. At the cathode some copper deposited and there was a precipitate of zinc hydrate in the solution. The experiment was repeated with the same results.

Experiment 6.

Experiment 5 was repeated except that the solution was circulated by bubbling air through it.

Result: There was complete corrosion of the brass this time with no deposit of copper on the anode. The result at the cathode was the same as in Experiment 5. This experiment was repeated with the same results.

The results of these experiments are very significant. It is found in Experiment 4 that brass corrodes as a whole when used as an anode in sulphate solution; also in Experiment 6 the brass corrodes completely in chloride solution. In Experiment 5 an apparent dezincification takes place. It must nevertheless be concluded from this that, when brass acts as a soluble anode, both the copper and zinc dissolve in their respective proportions. Experiment 5 is not, as it may seem at first glance, contrary to this hypothesis. It is noted that some copper was deposited on the cathode during the action, which means that, for some reason, the rest of it was prevented from getting away from the anode.

It is evident at least from this that there is a tendency for the brass to dissolve as a whole although some factor intervenes. The fact too, that two strips of copper, with a smooth surface between them, were found again indicated clearly that the copper remaining was redeposited (as in Experiment 1) and could not have been left behind as the result of selective electrolytic corrosion in Experiment 5. It is evident that the circulation in Experiment 6 prevents this. In other words the corrosion in Experiment 5 would have proceeded as in Experiment 6, had not something intervened to keep the copper formed directly in contact with the brass so as to cause re-deposition. Just what happened will be investigated presently. It is sufficient for the present to have shown that brass acts as a soluble anode in chloride and sulphate solutions.

Admitting then that brass is a soluble anode, if the copper which dissolves at the anode be kept in contact with or away from that anode at the will of the experimenter, it is possible to control whether or not dezincification shall take place. With this in mind Experiment 5 can be explained. A membrane of insoluble cuprous chloride which formed on the brass, kept most of the dissolved copper in contact with the brass thereby causing redeposition. In Experiment 6 when the air was blown through the solution, any cuprous chloride which tended to form would immediately be oxidized to cupric chloride and washed away. If it was an insoluble membrane of cuprous chloride which performed the function of keeping the solution of the copper salt in contact with the brass, then if an electrolyte is used in which the cuprous chloride is soluble, the formation of such a membrane should be prevented and complete corrosion should result. Two such solutions were employed—concentrated hydrochloric acid and a saturated solution of sodium chloride.

Experiment 7.

A brass strip was used as anode in a solution of concentrated hydrochloric acid. Melted paraffin was poured on the surface of the electrolyte to prevent evaporation and water-line corrosion. The cathode was carbon. The current density was 0.25 ampere per square foot. The time of action was 10 days.

Result: The brass was completely corroded.

Experiment 8.

Experiment 7 was repeated except that a saturated solution of sodium chloride was used instead of hydrochloric acid. The time was 15 days.

Result: Again there was complete corrosion of the brass.

It is obvious from the results that the assumption made was correct. Since the vessels were sealed with paraffin, there was no chance for the air to have any effect. The result was apparently due to the fact that cuprous chloride is soluble in strong chloride solutions, so that there was no membrane present to keep the dissolved copper in contact with the brass. If the dezincification is due to the presence of a membrane, when another membrane instead of cuprous chloride is supplied, then redeposition of copper should again take place.

Experiment 9.

Brass screws were used as anode. They were screwed into white pine saturated with concentrated hydrochloric acid. The wood was used to act as a membrane; the concentrated hydrochloric acid was used as electrolyte to dissolve any cuprous chloride which may have been formed. A carbon cathode was used. The current density was 0.25 ampere per square foot. The surface exposed to air was paraffined to prevent evaporation. The time allowed was 25 days.

Results: The screws were found to be copper with a core of brass in the center, which had not yet been attacked. There was no copper at the cathode.

Experiment 10.

A brass strip was wrapped tightly with several layers of filter paper and cheese cloth and bound with string. This was done to have a membrane with which to keep the copper in contact with the brass. This strip was used as anode, and a carbon rod for cathode in a concentrated solution of sodium chloride. The current density was 0.25 ampere per square foot. The time was 21 days.

Result: When the strip was examined, the lower half was found to consist entirely of copper, while the remainder had not yet been attacked. Much of the copper from the brass was not held by the improvised membrane, but was deposited on the cathode. The copper left behind was again found in the form of two thin sheets.

These experiments substantiate the contention that, for dezincification to occur, a membrane of some sort, no matter what, is necessary to keep the copper in contact with the brass. In Experiment 4 it has already been seen that brass is completely soluble when used as an anode in potassium sulphate solution. Now if the results of Experiments 9 and 10 are true, then by merely enclosing the brass in a membrane, dezincification should occur.

Experiment 11.

A brass strip, wrapped as in Experiment 10, was used as anode in a 3 percent potassium sulphate solution as electrolyte with a carbon cathode. The surface of the solution was paraffined as usual. The current density was 0.25 ampere per square foot. The time was 16 days.

Result: The strip when removed had a brassy color on the outside, but it was found to be solid copper. This experiment was repeated twice with the same results.

Experiment 12.

An unwrapped brass strip was corroded as anode in a 5 percent zinc sulphate solution. The surface of the liquid was covered with paraffin. The current density was 0.25 ampere per square foot. The time of corrosion was 20 days.

Result: The brass corroded uniformly as a whole, with no signs of a copper deposit.

Experiment 13.

A brass strip was treated the same as in Experiment 12 except that it was bound with filter paper, cheese cloth and string to give a membrane effect.

Result: The metal remaining at the anode in this experiment was copper and some of the brass which had not been corroded.

Experiments 4 and 12 show that brass is completely corroded when used as an anode in potassium sulphate and zinc sulphate solutions. From Experiments 11 and 13, it appears that the membrane, by keeping the dissolved copper in contact with the brass caused redeposition of copper. Whether the membrane be cuprous chloride, or one artificially supplied, its function is the same, and it produces the same result—dezincification. In general, dezincification may be expected whenever the brass is so wrapped that the dissolved copper is kept in contact with it long enough to redeposit.

It is worth noting that if the only purpose of the membrane is to keep a supply of dissolved copper at the brass, then as long as there is a plentiful supply of copper in solution, no membrane should be necessary to produce redeposition. In previous experiments, electrolysis of unwrapped brass in sulphate solutions has never resulted in dezincification.

Experiment 14.

A strip of brass was used as anode in a 10 percent copper sulphate solution. A current density of 0.25 ampere per square foot was used for 14 days.

Result: Pure copper was left at the anode. This experiment was repeated twice with the same results.

Experiment 15.

Strips of brass were placed in separate solutions of cuprous and cupric chlorides for 14 days and allowed to corrode chemically.

Result: Only copper remained which again was in the form of two sheets that could be pulled apart. The quality of the copper in this case was as tough and ductile as any copper plate obtained from an electroplating bath.

From these last two experiments, it is seen that as long as there is a plentiful supply of dissolved copper present, redeposition of the copper is obtained in spite of the fact that a sulphate solution is used. This bears out the theory that the function of the membrane is to keep the copper in contact with the brass.

SUMMARY.

The so-called dezincification can be reproduced in a few weeks in normal hydrochloric acid just as it occurs in nature in several years.

When the acid is agitated, it is seen that the brass dissolves as a whole.

The two layers of copper found in dezincified brass, can only be explained on the basis of re-deposition.

When used as anode, brass dissolves as a whole in sulphate solutions and in agitated chloride solutions.

When an insoluble membrane of cuprous chloride was allowed to form dezincification took place.

In an electrolyte in which cuprous chloride is soluble, such as concentrated hydrochloric acid or saturated sodium chloride solution, dezincification does not take place.

If another membrane is supplied in electrolytes in which cuprous chloride is soluble, then dezincification again takes place.

An artificial membrane is sufficient to cause redeposition of copper in sulphate solutions which ordinarily give complete corrosion.

Finally it was observed that when an adequate supply of dissolved copper was maintained, by using a solution of a copper salt as electrolyte, dezincification was obtained without any membrane whatever.

This investigation was undertaken at the suggestion of Dr. O. P. Watts to whom the author is indebted for many valuable suggestions in the course of these experiments.

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DISCUSSION.

F. S. Weiser[1]: The author does not mention either the composition or the physical condition of the brass used in his experiments. It is important to know its analysis, also whether it was hard or annealed, as I believe that the results may be dependent, to some extent, upon the composition and condition of the metal.

Colin G. Fink[2]: No doubt brasses containing lead would behave differently in a sulphuric acid solution; likewise brasses containing a little tin would behave differently in nitric acid. You would get a different surface film under these conditions.

G. D. Bengough and **R. May**[3] (*Communicated*): The present writers welcome heartily this paper and find themselves in agreement with most of the conclusions reached. For some years they have held the view that certain types of brass behaved as entities in initial corrosive action; i. e., that zinc-copper units took part in the action as a whole, and that copper was redeposited from solution. In the fifth report to the Corrosion Research Committee of the Institute of Metals (Journ. Inst. of Metals, 1920, **23,** No. 1) will be found some experiments carried out with cupric chloride solutions which gave results closely similar to those described by Mr. Abrams. The writers are also in agreement with the conception of the influence of membranes outlined in the paper. An interesting example of this is that a trace of arsenic in brass (say 0.04 percent) will greatly hamper so-called dezincification in sample, by forming a closely adherent layer of (probably) metallic arsenic or copper arsenide on the brass, upon which copper will not deposit; in this case the membrane hampers deposition of copper owing to its closely adherent and other characteristics, instead of encouraging it as in the case of Mr. Abrams' membranes, which were either loosely adherent or porous, and able to prevent diffusion away from the brass. In ordinary corrosion in sea water there is no doubt that the necessary conditions for deposition of copper are produced by the presence in the brass of a certain type of zinc

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[1] Waterbury, Conn.

[2] Consulting Electrometallurgist, New York City.

[3] London, England.

oxy-salt, the mode of production and composition of which have recently been the subject of detailed investigation by the writers, whose results will be published shortly. They have little doubt that the main thesis of the authors, namely, that brass may behave as an entity when corroded, and that the resulting copper is redeposited, of which they have been long convinced, will, in course of time, come to be regarded as correct, in spite of almost universal rejection at the present time.

The writers do not regard the initial action of sodium chloride on brass as being the discharge of hydrogen on the brass. A report to the Corrosion Research Committee of the Institute of Metals (Sept. 20, 1922) fully discusses the initial corrosive action of sodium chloride and other solutions on brass and other metals.

O. P. WATTS[4] (*Communicated*): According to some investigators, dezincification is the result of a mere leaching out of zinc; others consider that a portion, at least, of the copper found in dezincified brass has been redeposited. Mr. Abrams has shown clearly and unmistakably the mechanism of dezincification, and has pointed out the conditions under which this dangerous form of corrosion will occur. It should now be possible, by laboratory tests such as he used, to learn whether any addition can be made to brass that will render it immune to this type of corrosion, or whether some zinc-free alloy must be employed for service where brass is now subject to destruction in this manner.

It is probably thought by most people that dezincification of brass concerns only the makers and users of condenser tubes and a few other articles with which the average man seldom or never comes in contact. The following recital of my personal experiences shows that this is not so, but that dezincification is of very common occurrence, and may not only be annoying, but even dangerous, to those who sail on salt water in small boats. My experience is with the corrosion of brass and "bronze" fittings on a small auxiliary yacht, which has contributed greatly to my joys, and occasionally to my sorrows, during the past ten years.

The first year no corrosion was apparent, but the second sum-

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[4] Assoc. Prof. of Chem. Eng., Univ. of Wisconsin, Madison, Wis.

mer a friend and I had been cruising less than a week on the Maine coast when a leak developed between the head and body of a bronze pump that supplies sea water to the toilet. On attempting to tighten the brass screws which hold these parts together, the screws were twisted off. Dezincification had taken place where the screws passed through a leather valve, which was, of course, always damp.

The following year another case of dezincification was encountered. To fasten the bronze terminal of a water inlet pipe against the inside of the hull below the water line, the builder had ordered four ¼-inch bronze bolts. Observing a slight leak between this plate and the hull, I attempted to tighten the bolts; they at once twisted off because of dezincification. They were replaced by bolts turned to size from ½-inch monel rod.

The next encounter with dezincification was in the bronze lag screws which held the stuffing box on the propeller shaft against the stern post. When backing slowly from a dock the propeller struck an obstruction—not hard enough to bend the blades—yet the shock broke off both lag screws and a stream of water began to run in, so that the yacht had to be hauled alongside a wharf where she would be aground at low tide, in order to prevent her from sinking during the night. This meant a day's delay in sailing. The fractured surfaces appeared to be copper throughout. The lag screws had been in place eight years; just what fraction of this time was required to convert the half-inch bronze rod into copper, it is impossible to say from this experience.

Corrosion of brass by sea water in motion is slow; but where salt water is continually in contact with brass, and circulation is prevented by paint or some other film pervious to water, or the brass is imbedded in wood, so that the copper salts produced by the initial corrosion of the brass are held in contact with the metal, the rapid and deadly dezincification sets in.

The sheet brass used as purchased, had considerable springiness, and was evidently not in the annealed state. The screws were also tested as purchased, and probably contained the 2 to 2½ percent of lead usually added to screw-machine stock. These corroded in chloride solutions in the same manner as the sheet brass, and I have found that machine-made brass screws suffer seriously from dezincification in sea water. It will be interesting to test Dr. Fink's prediction regarding the corrosion of lead-bearing brass in sulphate solution, and this will be done in a continuation of the study of dezincification which is now in progress.

A paper presented at the Forty-fourth General Meeting of the American Electrochemical Society, held in Dayton, Ohio, September 27, 1923, President Hinckley in the Chair.

A STUDY OF WATER-LINE CORROSION.[1]

By KENNETH M. WATSON[2] and O. P. WATTS[3].

ABSTRACT.

Experiments were carried out to determine the cause of water-line corrosion. Strips of zinc, copper and brass were partially submerged into various corrosive liquors. Results indicate that although the depolarizing effect of oxygen is necessary for the corrosion of many metals in certain solutions, the contact of air with the upper surface of a liquid is never directly responsible for the occurrence of water-line corrosion. This phenomenon is caused by the slow downward flow of the heavier film of corrosion products along the surface of the metal, which draws in at the upper surface of the liquid a supply of fresh solution. Since all the metal except that at the surface of the liquid is in contact with partly exhausted solution, corrosion is most rapid at the surface. Although there is an even greater circulation of solution down the face of anodes used in the plating and refining of metals, water-line corrosion does not take place. In that work the rate of corrosion is determined by the distribution of current over the anode surface, which depends on Ohm's law and is only slightly affected (at the usual current densities) by the amount of corrosion product contained in the film of solution that touches the anode.

INTRODUCTION.

The subject of water-line corrosion is one which has been of current interest to scientific investigators of corrosion problems for several years and has gained considerable attention from commercial sources, due to its destruction of valuable apparatus

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[1] Manuscript received June 11, 1923.

[2] Department of Chemical Engineering, University of Wisconsin, Madison, Wis.

[3] Associate Professor of Chemical Engineering, University of Wisconsin.

and materials in industry. Various theories have been advanced as to the causes of this phenomenon, but little actual experimental research is recorded as having been carried out in an attempt to gain definite information as to the causes and mechanism of the action. The work subsequently described in this paper was undertaken with the view in mind of testing the theories which are current among corrosion specialists and, if possible, of gathering additional information on the subject, which might be of value in understanding and combating the resulting effects.

It might be well at this point to explain what is understood by the term "water-line corrosion." As the name would indicate the expression refers in general to the severe, localized corrosion which is met with in the case of metals which are partially submerged in a slowly corrosive solution. This corrosion takes place over a narrow range at the point where the metal emerges from the liquid, that is, where air, metal, and liquid are all in contact. The corrosion may take the form either of deep pitting, giving a result that resembles the work of a drill press, or of a clean cutting of the metal along a line, almost as though a saw had been used.

One of the first cases of water-line corrosion which was called to the attention of the authors was that of the zinc electrode of an old sal ammoniac cell. The cell had been standing for some time without use, and on taking it apart it was noted that the zinc electrode, although for the most part in fairly good condition, was cut almost in two at a point corresponding to the water-line of the solution. Other cases of severe water-line corrosion have been met in the condenser tubes of sea going ships, where a serious commercial problem results. Further trouble of a more or less serious nature is constantly being encountered in laboratories and manufacturing concerns in the use of metal apparatus in corrosive solutions. A case recently brought up dealt with the failure of a common, galvanized hot water tank, such as is used in nearly every home, by deep pitting and general corrosion at the water-line. Thus it is seen that the subject is one of practical importance, which merits careful attention in the study of the subject of corrosion in general.

One of the explanations of this effect, which has long been held as plausible, is based on the accelerating action which oxygen has on any form of corrosion. It is argued that, since oxygen can be absorbed from the air only at the surface of the liquid, it would be natural to expect that the concentration of oxygen dissolved would be higher at the surface and therefore corrosion would proceed most rapidly at that point. The fact is further pointed out that in most solutions there is a "creep" of the liquid up the sides of objects partially submerged in them. This would result in a thin film of solution over the metal, which would be in constant contact with the air and therefore probably almost saturated with oxygen which, through its depolarizing action, would greatly accelerate corrosion at that point.

The effect of oxygen on the rate of corrosion is undeniable, and it is probable that the depolarizing effect of absorbed air has considerable to do with water-line corrosion as claimed in the above theory, especially in solutions where there is a marked tendency to "creep." However, careful studies of water-line effects produced in the laboratory have caused at least one author to disagree with this theory. In the fifth report to the Corrosion Committee of the Institute of Metals,[4] by Guy D. Bengough, R. M. Jones, and Ruth Pirret, the following statement is made:

"It is a familiar fact that an increased amount of corrosive action is liable to occur in the neighborhood of an air, sea-water surface in contact with certain metals and alloys as compared with that of the immersed portions of the same materials. It is usually supposed that such increased action occurs at or just below the waterline, and that it is due to the depolarizing action of the air whereby electrolytic action is greatly stimulated. A little investigation however soon shows that it is by no means as simple as would be expected on this view . . . . . It soon became clear that the greater part of the increased corrosive action did not usually occur at the water-line but above it and sometimes considerably above it, *e. g.*, as much as 2 cm. . . . . The "water-line" attack in neutral liquids may be considered as essentially a deposit type of attack and is set up because the conditions near the water line are favorable to the formation of harmful deposits from the products of corrosion; and the whole action is no doubt assisted by the oxidizing action of the air."

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[4] Journal of the Institute of Metals, 23, 125.

In a further discussion[5] on the protection of condenser tubes, Mr. Bengough states that, "As an instance of attack by corrosion products the well known effect of preferential attack at a water line is an example. This is mainly dependent on the nature and distribution of the products of corrosion and is *not,* as is usually supposed, due principally to the depolarizing action of the air. Under certain conditions the products of corrosion may give rise to "concentration cells," which may give rise to very rapid pitting."

Because of the importance of the problem and the interest shown in it the following experimental work was undertaken in an attempt to straighten out the diversified theories which prevail at present, and to gather additional information on the mechanism and effects of water-line corrosion.

RECORD OF EXPERIMENTAL WORK.

The metal specimens used in the following experiments were for the most part cut from sheets of about 0.37 mm. thickness, the usual size being about 2.5 x 15 cm. These specimens were bent at right angles at a point about 3.75 cm. from one end and set in the solution in which they were to be tested, contained in ordinary tumblers. The bent-over end of each rested against the inner wall of the tumbler just below the top and served to keep the specimen in an upright position and away from the sides. The tumblers were filled with the solutions to within about 1.2 cm. of the top and in some cases connected to a Mariotte bottle to maintain constant levels. In the majority of the cases, however, the water which was lost from the solution was replaced by daily additions. The slight variation of water-line did not appreciably affect the results as compared with those obtained when using the constant-level device.

In preliminary experiments it was found that when corrosion is accompanied by vigorous evolution of gas, as in the attack of zinc by dilute hydrochloric acid, water-line corrosion does not occur. The choice of corroding solutions was therefore limited to such as did not cause liberation of gas.

Samples of zinc were exposed in dilute hydrochloric acid and in solutions containing about 100 g. per L. of sodium chloride, po-

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[5] Journal of the Institute of Metals, 26, 442.

tassium nitrate, and ammonium nitrate, and also in a nearly saturated solution of calcium chloride. In the hydrochloric acid, as stated above, there was no evidence of water-line corrosion. There was no water-line corrosion in ammonium nitrate in 20 days, but under the layer of salt which covered the zinc for a distance of 2.5 cm. above the surface of the liquid the zinc was deeply pitted, and at the upper edge of this deposit the zinc was cut nearly in two. In the other solutions corrosion was so extremely slow that there was no noticeable effect at the end of the period of 3 months, to which the experiments were limited.

After 8 days in normal hydrochloric acid sheet copper was corroded entirely in two at a point 1 mm. below the water-line. Brass behaved similarly in a slightly longer time. In normal sulfuric acid corrosion of copper and brass was much slower than in hydrochloric acid, and, strange to relate, the maximum corrosion occurred 3 to 5 mm. *above* the water-line, beneath crystals of metallic salts which had formed there through "creeping" of the solution. In 40 days holes were eaten entirely through the metal at that point. Exclusion of air by a layer of lubricating oil entirely stopped corrosion. In dilute hydrobromic acid water-line corrosion was well-marked on copper in 10 days. In solutions of chromic, formic, acetic, phosphoric, fluoboric and fluosilicic acids corrosion was so slow that no results were obtained in the time available.

A narrow band of cheese cloth was tied tightly about the middle of sheets of brass and copper, and these were then placed in hydrochloric acid so that the cloth extended both above and below the water-line. In 9 days specimens were cut entirely in two at both edges of the cloth, and also showed deep cuts at the water-lines, as well as general corrosion over the whole surfaces. When air was excluded by pouring on a film of oil, corrosion below and at the water-line was stopped, but the sheet was severely corroded in the air at the top of the cloth. That air (or oxygen) is necessary for the corrosion of brass and copper in hydrochloric and sulfuric acids is amply confirmed by these experiments.

Sheets of copper were fastened to the bottoms of tumblers which were filled with hydrochloric acid, inverted in larger dishes of the same liquid, and supported above the bottom so that half of the tumbler was above the acid in the outer dish. Hydrogen was then passed into the tumbler until the liquid level was the same within as without the tumbler. Any air that reaches the copper must come in from below, and if water-line corrosion is due to a higher concentration of depolarizing air at the upper surface than throughout the main body of liquids, the most rapid corrosion in this case must take place at the bottom of the sheet of metal. At the end of 15 days the specimen was completely cut off at the water-line. This establishes definitely that even where oxygen is necessary in order that any corrosion may take place, water-line corrosion is not due to any particular depolarizing action at the boundary surface between air and liquid.

Several experiments were tried in which the corrosion of copper in hydrochloric acid was stimulated by addition of an oxidizing agent to the liquid, instead of waiting for oxygen to be absorbed from the atmosphere. Both bromine and potassium dichromate were used as oxidizing agents, with the vessels open to the air, and also covered with a layer of oil. There was sharp water-line corrosion in every case, and access or exclusion of air seemed to be without effect.

The true explanation of water-line corrosion was suggested by a phenomenon frequently seen during the corrosion of metallic anodes by use of the electric current, where the dissolving of the metal creates a film of denser solution next to the metal, which can be seen to flow down along the surface of the anode and stream off from its lower end. Water-line corrosion was thought to be due to a similar circulation which keeps all of the metal plate except that near the liquid surface in contact with partially exhausted solution, and causes the metal at the surface of the liquid to be bathed by the stream of fresh solution which is drawn in to take the place of that which flows downward along the metal surface.

To determine if such circulation actually takes place in cases of water-line corrosion a strip of copper was placed in a narrow stereopticon cell containing normal sulfuric acid, to which 50 g. per L. potassium dichromate had been added, and the progress of corrosion watched by transmitted light. In a few minutes the expected circulation was clearly visible, and a constant stream of corrosion products flowed down the specimen and off from its lower end. A slight flow across the surface of the solution to the copper was also detected. Similar examination of a strip of copper in dilute nitric acid showed quite different results. In this case there was a slight current flowing toward the metal at the bottom and then upward along the metal surface. This was caused by a slow evolution of gas at the surface of the metal, which acted like an air-lift pump and prevented the downward flow that would otherwise have taken place. Experiments not previously mentioned had shown that water-line corrosion of copper in dilute nitric acid does not occur, but while corrosion is fairly uniform, it is slightly greater at the bottom than elsewhere. The reason for the failure to secure water-line corrosion of zinc in hydrochloric acid, mentioned earlier, is apparent.

The above view of the nature of water-line corrosion is confirmed by the following experiments: A narrow strip of copper was suspended in a solution of hydrochloric acid containing potassium dichromate, and an open glass tube was placed around it so that the tube dipped 2.55 cm. into the solution. In 2 days the copper was cut through, not at the liquid surface, but opposite the bottom of the tube. The same result was obtained in a longer time in hydrochloric acid, without the addition of any oxidizing agent but exposed to the air.

A sheet of copper was suspended in a tumbler so that half of it was above and half below a perforated paraffin disc, which extended horizontally across the tumbler, and the tumbler was filled with normal hydrochloric acid. In 8 days the regular water-line corrosion had taken place, and the specimen was cut through at the surface of the solution. On removing the remainder of the specimen from the solution it was found that corrosion had been almost as severe immediately below the paraffin disc as at the surface of the liquid, and the metal was nearly cut off at that point.

When a strip of copper was suspended in hydrochloric acid containing potassium dichromate and circulation was caused artificially by a small, electrically-driven propeller, the specimen was cut off in 2 days, but opposite the propeller instead of at the water-line. In plain hydrochloric acid exposed to the air the same result was obtained.

DISCUSSION.*

Colin G. Fink[1]: I do not altogether agree with the authors in their general theory. It has been our experience that the air is a great factor in the corrosion of anodes. In the development of insoluble anodes for various electrolytes, we have repeatedly observed that alloys which are very resistant to the electrolyte if completely submerged in the electrolyte may, if partially exposed to the air, corrode rapidly at the solution line.

Alex Lowy[2]: Has any work been done in regard to nitrogen or other gaseous layers? I think an experiment of this type would either eliminate the oxygen theory or else be ideal for that particular explanation.

C. J. Rodman[3]: Possibly I can answer that question. With an oxygen or air atmosphere above the liquid, the terminal at the liquid gas junction corroded noticeably. We wanted to find some way of getting away from that type of corrosion, and tried inert atmospheres. This cut down corrosion substantially. By coating the metal at the liquid gas junction with inert materials, such as waxes or glass, the corrosion was obviated entirely. It has been suggested that oil be used to float over the aqueous solution to effect a non-corrosion of the metal at the liquid-gas junction. This procedure does lessen corrosion but, due to about 12 to 15 per cent by volume solubility of O_2 in oil, corrosion is still possible, yet the conditions of the experiment admit of a liquid junction of electrolyte and oil which does away with the high surface tension and concentration effects.

If the authors had been a little more comprehensive in their title

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* In the absence of the authors the above paper was presented by Colin G. Fink.

[1] Head Div. of Electrochemistry, Columbia Univ., New York City.

[2] Professor of Organic Chemistry, Univ. of Pittsburgh, Pittsburgh, Pa.

[3] Research Lab., Westinghouse Elec. and Mfg. Co., East Pittsburgh, Pa.

and discussed types of liquid line corrosion, other phenomena, such as oil-air junction corrosion could be discussed to advantage here.

Beautiful examples of this occur in oil insulated apparatus, and would possibly lend valuable data in explaining some of the interesting phenomena on water line corrosion.

COLIN G. FINK: Referring to the authors' tests in an atmosphere of hydrogen, there is one point that we forgot and that is the spray effect, which is also very important and has a lot to do with this air line corrosion. Oxygen gas at the anode takes with it a certain amount of electrolyte. There is a constant wash of electrolyte plus air over the electrode surface right above the solution line. If you can eliminate the spray, *e. g.*, by covering the electrolyte with a film of oil, in a large number of cases your "necking" disappears. That oil test is similar to the test of using an inert atmosphere. If you exclude the air, most "necking" disappears.

W. B. SCHULTE[4]: One of the troubles that arise in the discharge of dry cells is the cutting off of the zinc can at the top point of the electrolyte, whether the electrolyte is held in a blotting paper, or whether it is in what is known as a paste electrolyte. The cutting through of the zinc at the surface is something that we try to avoid.

EDWARD C. SMITH[5]: I think we have always experienced that same difficulty, but have found no particular remedy for it. When we have tried covering any area of active zinc, we have, of course, increased the current density beyond it, which resulted in the metal being eaten through to a greater extent close to the area blocked off.

LEON MCCULLOCH[6]: May I call attention to a chemical reaction that may take place at the water line surface, such as you may have in dry cells exposed to ammonium or sodium chlorides.

Suppose we have a strip of zinc partially submerged in a solution of sodium chloride and above it air or oxygen. The

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[4] C. F. Burgess Labs., Madison, Wis.

[5] National Carbon Co., Inc., Fremont, Ohio.

[6] Research Dept., Westinghouse Elec. and Mfg. Co., East Pittsburgh, Pa.

oxygen will depolarize hydrogen and give you a flow of current across the water line surface. Above you will have NaOH formed and down below you will have zinc chloride formed. That gives an alkaline area above and a neutral area below. The alkali possibly attacks the zinc, liberates hydrogen, and results in a chemical reaction right at the surface.

KENNETH M. WATSON (*Communicated*): In reply to Dr. Fink's discussion I wish to say that it was not intended in this paper to make any statement to the effect that oxygen is not necessary for corrosion in general, or that it has no influence on water line corrosion. In many cases corrosion cannot proceed at all without the presence of oxygen in some form, and action in all ordinary cases is probably accelerated by the addition of oxygen. The point made was that in certain cases in which corrosion is able to proceed independent of the oxygen of the air, as when an oxidizing agent exists in the solution, the water line effect will be obtained even though there is no contact of the liquid with the air. This fact disproves the theory that water line corrosion of that type is due to a higher concentration of oxygen dissolved from the air at the surface.

It is difficult to conceive of the application of the circulation theory of water line corrosion to the cutting off of the zinc cans of dry cells. This type of corrosion is evidently different from any of those studied, and it is possible that Mr. McCulloch's explanation is the correct one.

A paper presented at the Forty-sixth General Meeting of the American Electrochemical Society, held in Detroit, Mich., October 2, 3 and 4, 1924.

TESTS FOR GRADING CORROSION-RESISTING ALLOYS.[1]

By WM. E. ERICKSON and L. A. KIRST.[2]

ABSTRACT.

As a rapid method of selecting from a large number of iron alloys those which would possess the rust-resisting qualities of stainless steel, Kurtz and Zaumeyer[3] applied an acidified solution of copper sulfate to the cleaned metal surface. While this test probably detected all alloys having marked resistance to corrosion, it did not differentiate between those of high and those of only moderate resistance. The experiments, results of which are here reported, were undertaken in the hope of separating these alloys into several groups according to their resistance to corrosion. The alloys were tested with solutions of $CuSO_4$, $AgNO_3$, $PtCl_4$, $AuCl_3$ and $PdCl_4$. Of the common metals silicon and chromium appear to be the most resistant to corrosion. The addition of either or both of these elements to iron reduces the corrodibility very appreciably.

THEORY OF PROPOSED TEST.

The theory used as a working hypothesis in the method to be proposed, is as follows:

1. Every metal or alloy has what is termed a solution pressure, or a measurable tendency to go into solution. The magnitude of this varies for each different material. It is, therefore, possible to arrange them in a series so that those metals which have the higher solution pressures are near the top. Such a series has already been established, and is known as the electrochemical series. As an illustration of the workings of this arrangement we might take as an example zinc and gold in a chloride solution, in which the former has a higher solution pressure. A drop of

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[1] Manuscript received July 2, 1924.

[2] University of Wisconsin, Madison, Wis. Senior thesis, 1921.

[3] Kurtz and Zaumeyer. This volume. Preprint 26.

gold chloride solution is placed upon metallic zinc. The zinc, having a higher solution pressure, displaces the gold in the solution until the gold is almost all plated out. From this it is concluded that a metal of high solution pressure will precipitate a metal of low solution pressure.

2. From the foregoing it is seen that the lower a metal is in the series, the greater is its resistance to being dissolved; and, consequently, the greater is the resistance to corrosive agents, atmospheric and otherwise. This simply brings us back to the method used to formulate the original electrochemical series. In this method, solutions of salts of the various metals were made, and strips of each metal were then dipped into each solution. In some cases the metal in solution plated out and metal from the strip went into solution, while in others nothing occurred. A table was then arranged, in which any metal displaced or plated out any metal lower in the series. In other words, each metal in such a series is more resistant to corrosion than those above it in the series. We considered using a method similar to the above to grade corrosion-resisting alloys. By means of the electrochemical series, a series of solutions can be prepared, each more corrosive than the previous one. By testing any specimen with a drop or two of each of these solutions in order of their increasing corrosiveness, some solution will be found from which the metal will plate out. The same will hold true of each succeeding solution. By this means we should be able to differentiate between the resistances to corrosion of the various metals and alloys, and to separate these into groups.

The advantages claimed for this particular method are that it can be performed in a much shorter period of time, and is nearly as conclusive as an acid test. Even with the most resistant alloys, results can be obtained in less than five minutes.

According to the meager data obtainable in text books, palladium is placed between platinum and silver in the electrochemical series. However, in all of our experiments a palladium chloride solution was found to be more corrosive than the chloride solutions of either gold or platinum. Since we had regarded the solution pressure of palladium as between that of silver and platinum, we made new potential measurements to determine its

TABLE I.

Results of Tests on Pure Metals.

X indicates the deposition of the metal in solution.

	$CuSO_4$	$AgNO_3$	$PtCl_4$	$AuCl_3$	$PdCl_4$
Silicon................	0	0	0	0	0
Chromium..............	0	0	0	0	0
Tungsten..............	0	0	0	0	X
Nickel................	0	0	X	X	X
Molybdenum...........	..	X	X	X	X
Manganese............	X	X	X	X	X

TABLE II.

Results of Tests on Non-Ferrous Alloys.

X indicates the deposition of the metal in solution.

Cr Per Cent	Si Per Cent	Ni Per Cent	W Per Cent	Monel* Per Cent	Other Metals Per Cent	$CuSO_4$	$AgNO_3$	$PtCl_2$	$AuCl_3$	$PdCl_2$
20	..	40	40	..	......	0	0	0	X	X
10	2	63	15	..	10 Mo	0	0	0	X	X
..	..	50	50	..	......	0	0	0	X	X
20	2	78	..	..	......	0	0	X	X	X
10	..	..	15	75	......	0	0	X	X	X
10	2	..	..	88	......	0	0	X	X	X
10	2	..	15	..	73 Fe, 10 Mo	0	0	X	X	X
10	1	..	..	..	64 Fe	0	0	X	X	X
13	2	..	..	..	0.1 C	0	0	X	X	X
13	1.3	..	..	..	0.4 C	0	0	X	X	X
†	..	..	5	75	......	0	0	X	X	X
20	2.5	..	15	77.5	......	0	X	X	X	X
12	2	..	..	81	......	0	X	X	X	X
15	..	..	..	60	10 Mo	0	X	X	X	X
10	..	..	..	90	......	0	X	X	X	X
20	1.5	..	..	78.5	......	0	X	X	X	X

* These alloys were made by adding different elements to the indicated quantity of monel metal.

† Fe-Cr 25 per cent.

position. A potentiometer was used to measure the difference of potential between the palladium and a normal calomel electrode in a normal potassium chloride solution with the following results:

Palladium (plated)	Gold	Platinum
—0.78	—0.55	—0.53

TABLE III.

Tests of Ferrous Alloys.

No.	Cr Per Cent	Si Per Cent	Ni Per Cent	V Per Cent	Other Metals Per Cent	$CuSO_4$	$AgNO_3$	$PtCl_4$	$AuCl_3$	$PdCl_4$
126A	10	3	..	..	5 W........	0	0	X	X	X
126B	7.2	3	9	..	....	0	0	X	X	X
133N	13	1.8	..	..	....	0	0	X	X	X
133R	10	6	..	..	....	0	0	X	X	X
133V	13	5.5	..	..	....	0	0	X	X	X
133O	13	0.5	..	..	....	0	0	X	X	X
133G	13	3.6	..	..	....	0	0	X	X	X
133C	8	2.2	..	..	....	0	0	X	X	X
136L	20	1	..	..	3 Mn.......	0	0	X	X	X
136U	30	1	..	..	3 Mn.......	0	0	X	X	X
136H	17	1.5	..	..	....	0	0	X	X	X
136G	13	..	..	..	....	0	0	X	X	X
136R	8	1	20	..	....	0	0	X	X	X
137S	20	1	10	..	0.3 Mn......	0	0	X	X	X
137B	2	..	..	..	....	X	X	X	X	X
137H	16.2	..	..	..	....	0	0	X	X	X
137L	10	2	..	..	2 Ti........	0	0	X	X	X
141B	21.8	..	..	..	....	0	0	X	X	X
141G	21.4	1	..	1	3 Mn.......	0	0	X	X	X
141C	10.3	2	..	1	....	0	0	X	X	X
144U	10	..	..	..	....	0	0	X	X	X
146H	10	..	..	..	....	0	0	X	X	X
146L	10	2	20	..	....	0	0	X	X	X
148A	6	..	..	0.3	18 W; 0.4 C.	0	0	X	X	X
154G	10	..	10	..	....	0	0	X	X	X
154B	10	..	12	..	....	0	0	X	X	X
154I	10	2	10	..	....	0	0	X	X	X
154K	10	..	10	..	1 C.........	0	0	X	X	X
154A	10	..	8	..	....	0	0	X	X	X
111S	10	2	..	..	....	0	0	X	X	X
122E	10	3	..	..	....	0	0	X	X	X
133M	8	1	..	..	....	0	0	X	X	X
136A	6	1.5	14	..	....	0	X	X	X	X
154F	7	..	10	..	....	0	0	X	X	X
155L	10	..	..	0.3	0.65 C......	0	0	X	X	X
155K	10	2	..	0.3	0.6 C........	0	0	X	X	X
113N	..	3.7	..	..	....	0	0	X	X	X
155R	10	..	..	..	10 Mo......	0	0	X	X	X
155S	10	..	..	..	5 Mo......	0	0	X	X	X
155V	10	..	..	..	10 W.......	0	0	X	X	X
156G	10	..	..	0.2	2 W.......	0	0	X	X	X
156H	10	..	..	0.3	2 W.......	0	0	X	X	X
156I	10	..	..	0.3	2 W; 0.6 C.	0	0	X	X	X
156J	10	..	..	..	2 W; 0.6 C.	0	0	X	X	X
156P	10	2	..	0.3	2 W.......	0	0	X	X	X

Although these measurements may be subject to error, they bear out the results obtained in our work with palladium chloride as a corrosive agent. In every case where an alloy was used, the palladium plated out of solution, whereas in several different instances where high tungsten, chromium, and silicon alloys were tested, the platinum chloride solution was non-corrosive to the extent of deposition.

On the basis of these facts and assumptions, five solutions were made up, each more corrosive than the preceding. The solutions, in order of their corrosive power, and the position of the metal in the electrochemical series, are as follows:

Copper Sulfate
Silver Nitrate
Platinum Chloride
Gold Chloride
Palladium Chloride

The test was applied to the metals and alloys listed by grinding a spot free from scale, polishing with tripoli on standard polishing wheels, removing polishing grease in the electric cleaner, and applying a drop of the corrosive solution. According to our views, if copper sulfate deposited copper on a strip of metal, each succeeding solution ought to deposit its metal out of solution. In every case this assumption held true. Again, if gold chloride does not precipitate gold on the metal, it is expected that none of the previous solutions will deposit their metal on the specimen. This also held true without exception.

The results of these tests are shown in the following tables. The data in Table I show the results of tests on the pure metals, which we supposed were quite resistant to corrosion. Table II deals with non-ferrous alloys, and Table III concerns our findings on ferrous alloys.

CONCLUSION.

The data from the tests on alloys of chromium, silicon and tungsten show that these alloys are quite resistant to corrosion. This statement is generally considered true, as it has been known by others for some time. However, this fact is borne out more conclusively by the observed resistances to corrosion of the pure metals. Silicon and chromium resisted corrosion even by palladium chloride, while tungsten was affected only by this solution. Generally speaking, chromium and silicon seem to be the two metals most resistant to corrosion, and their presence in an alloy in a reasonable percentage would seem to be desirable to prevent the action of corrosive agencies.

When over eight per cent of chromium is present in an iron alloy, the amount is sufficient to prevent the deposition of silver. The deposition of platinum, gold and palladium is not prevented by making the chromium content even as high as 30 per cent. Hence, any additional chromium does not give an advantage commensurate with the increase in cost due to the chromium. In one specimen where the only alloying metal present is 4 per cent of silicon, the same degree of protection is afforded as is given by 8 or 10 per cent of chromium. It appears to be true that when the silicon and chromium are present in amounts sufficient to prevent corrosion to a markedly increased degree, there is formed a solid solution by the two metals.

This method of testing for corrosion appears to be promising. In no cases were the theories of the procedure reversed by the facts. The foregoing shows that the basis for our assumptions was sound.

Practically all of the ferrous alloys above 8 per cent chromium are located in the interval between silver nitrate and platinum chloride, because they allow the deposition of platinum and not that of silver. From the above there would seem to be a need for an intermediate testing reagent, which would serve to further differentiate between the corrosion-resisting properties of the different alloys. We, however, did not know of any metal whose solution pressure was intermediate between that of platinum and silver.

These experiments show that the method is rather promising. It furnishes a means of selecting from a large number of alloys those which are highly resistant to corrosion, and of separating these into groups according to their probable resistance to corrosion. The real merit of these tests can only be learned by testing a series of alloys which have been graded by these tests, under actual service conditions.

All alloys tested are much more expensive and resistant than are likely to be employed to resist atmospheric corrosion, and are such as might be used successfully in places where corrosion is very severe, as in chemical manufacture. For selecting alloys for such uses the acid test should doubtless be applied in addition to the tests here employed.

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DISCUSSION.

O. P. WATTS[4] (*Communicated*): In applying this method of testing it should be noted that the acid-radical as well as the metal of the corroding solution is a factor in the result produced. Several metals and alloys owe their resistance to corrosion to a protective film of oxide on their surfaces, a film which is not capable of displacing metals from solution in the manner of this test, and which may, in certain cases, be dissolved by only a few of the long list of known corrosive solutions. This is brought out in the following data obtained by George P. Ryan.[5]

In a solution of copper sulfate none of the following caused the deposition of copper, but on adding a few drops of hydrofluoric acid copper plated out:

	Per Cent	Per Cent
Stainless steel	12 Cr	0.3 C
137L Iron	10 "	2 Si
133R Iron	10 "	6 Si
133O Iron	13 "	0.5 Si
133N Iron	13 "	1.8 Si
133G Iron	13 "	3.6 Si
133U Iron	13 "	5.5 Si
137H Iron	16.2 "	..
Iron	20 "	1.5 Ni
Silicon	..	..
Duriron	..	..

No deposit of copper appeared on the following even on addition of hydrofluoric acid:

Chromium.
Ferrochromium, 70 per cent Cr.
Molybdenum-chromium, 50 per cent Cr.

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[4] Professor of Chemistry, Univ. of Wisconsin, Madison, Wis.
[5] University of Wisconsin.

In the use of many non-corrosive alloys this harmful effect of some particular acid-radical is often encountered. The immunity of duriron to attack by sulfuric and nitric acids, and its corrosion by hydrochloric acid is a well-known example of this. By varying the acid-radical as well as the metal in the corroding solutions, it should be possible to differentiate between corrosion-resisting alloys even more completely than has been done in these tests.

A paper presented at the Sixty-fourth General Meeting, held at Chicago, Ill., September 7, 1933, Dr. F. N. Speller presiding.

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THE ELECTROCHEMICAL THEORY OF CORROSION.[1]

By Oliver P. Watts.[2]

Abstract.

The thirtieth anniversary of the announcement of Dr. W. R. Whitney that the corrosion of metals is an electrochemical phenomenon seems an appropriate time for "taking account of stock" in the electrochemical theory of corrosion. Although the majority of students of corrosion now accept the electrochemical theory, there is apparently a wide difference of opinion regarding fundamentals of the process. It therefore seemed important that the opinions, the results of study and experimentation, should be brought together in a single paper, where the points of agreement and of difference might be apparent. Accordingly letters were written to eleven men prominent in the field of corrosion in England and the United States. The replies received, together with the editor's views, follow.

Wilder D. Bancroft.[3]

For a metal or alloy to corrode in contact with an aqueous solution, the formation of the corrosion products must involve a decrease in the free energy of the system. The potential difference between sodium and aqueous solutions is so great that a reaction will take place no matter how pure the sodium is. With pure zinc the over-voltage of hydrogen at the zinc surface may be so high that practically no reaction will take place in the absence of some metal like lead which will form a short-circuited voltaic cell.

While a sufficient potential difference is essential, it is usually not the most important factor practically though it may be theoretically. The factor which stops corrosion in most cases is the formation of a protective film. Magnesium corrodes more rapidly in a solution of a

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[1] Manuscript received July 10, 1933.

[2] Assoc. Prof. of Chemical Engineering, Univ. of Wisconsin, Madison, Wis.

[3] Prof. of Physical Chemistry, Cornell University, Ithaca, N. Y.

magnesium salt than in pure water because the magnesium salt peptizes the magnesium hydroxide enough to prevent the formation of an impermeable film. Some of the tin-rich copper alloys are much more resistant to corrosion than pure tin or pure copper, though they are of course less noble than pure copper.

The lead peroxide grid of a storage battery does not behave like a short-circuited cell because the lead peroxide film keeps the lead of the grid from coming in contact with the sulfuric acid.

WILLIAM BLUM.[4]

Abstracted by the editor from a paper in Vol. 52, Trans. of this Society, p. 405-432, and from a personal letter.

"As indicated in the title of that paper, I believe it is preferable to refer to electrolytic rather than electrochemical corrosion. The term electrochemical has such a broad meaning that in an extreme sense it may be taken to include any chemical changes in which electrical charges are involved. On the other hand, "electrolytic" implies the occurrence of two distinct processes at points separated by a finite distance. With such a distinction I think we must recognize that there are many examples of pure chemical corrosion. For instance, the burning of iron in dry oxygen or dry chlorine is an example of corrosion in which there is no evidence of any electrolytic action. When, however, we deal with aqueous solutions or with moist gases, it is probable that charged ions are present and most of the reactions that occur involve reaction with ions, in which case electrolytic action is probable.

"Natural corrosion, if electrolytic, depends upon one part of the metal becoming anodic and another cathodic. This can occur only if there is a difference in the composition or physical properties of the two parts of the metal, or of the solution adjacent to them. If two parts of the metal differ in composition, that part which has the higher "solution pressure" tends (initially) to become anodic. Such differences in composition of the metal may also become evident through their effect on the polarization required on them for hydrogen discharge or oxygen reduction respectively. A difference in physical condition of the metal always tends to cause the part with smaller crystals, or in a state of strain, to become initially anodic with respect to coarser crystals or unstrained metal.

"Differences in the composition or concentration of the solution adjacent to different parts of the metal always tend to cause that part which

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[4] Chemist, Bureau of Standards, Washington, D. C.

has the most negative potential to become anodic and vice versa. This includes such factors as acidity, dissolved oxygen concentration, or metal salts concentration of the two parts of a solution. A metal area in a portion of solution with high oxygen content tends to become cathodic because it has a relatively positive potential, at which reduction (cathodic reaction) readily occurs. As previously shown, cathodic reduction of oxygen can be considered as an electron reaction, which is more likely to occur than the frequently assumed process of hydrogen evolution and subsequent reduction of oxygen by hydrogen.

"Electrolytic theory as defined in this paper implies that the direct product of corrosion is always an ion, which then automatically comes into equilibrium with undissociated molecules in the solution. From this point of view the formation of ferrous chloride by the anodic solution of iron in hydrochloric acid is the secondary result of the combination of ferrous ions and chlorine ions and not a direct result of corrosion.

"Apparent exceptions to the electrolytic theory of corrosion of metals in aqueous solution are likely to be caused by incomplete evidence. At least it is difficult with present knowledge to state categorically that all processes are, or are not, electrolytic.

"The whole theory of electrolytic corrosion implies that corrosion is caused or accomplished by passage of electrons through the metal from the part that is corroding to some part that is not corroding. From this standpoint it is locally immaterial whether the electrons come from inside or outside of the system.

"According to the electrolytic theory, which I am not defending but simply assuming for purposes of illustration, there can be no corrosion except as there is a difference in potential between two parts of the surface, due either to an initial difference in composition, in physical condition, or in the surrounding mediums. Whether that is due to a difference in concentration of oxygen or hydrogen or to localized impurities, if corrosion is electrolytic, then there is a flow of current between one part which is acting as the anode and another part acting as cathode.

"Unfortunately it is even more difficult to define "catalytic action" than electrolytic corrosion. It is certain that the processes of corrosion such as hydrogen evolution and oxygen reduction are greatly affected by the condition of the surface. To this extent, therefore, catalytic processes are involved, although such a definition does not throw light on the process of corrosion."

ULICK R. EVANS.[5]

I hardly feel that a formal definition of the electrochemical theory is possible, but I will gladly set down my reasons for thinking that corrosion-changes often—although not always—take an electrochemical course.

Where a reagent acting on metal can produce a *freely soluble* compound of the metal as the *primary* product, there is no reason to assume the necessity for electric currents flowing from one part of the metal to another; nor is there any evidence that such currents exist. For instance, when a solution of iodine in aqueous potassium iodide acts on metallic iron, iron iodide is produced, which dissolves in the water, leaving the iron surface exposed to further attack. Doubtless, if we study the matter on an atomic scale, an electron movement may be considered to occur between iron and iodine atoms, but in this sense, probably all (or, at least, most) chemical reactions are electrical. "Simple combination" between iron and iodine is perfectly possible, and provided that iodine has equal access to all parts of the surface, I do not think that the corrosion is accompanied by any flow of electric currents over appreciable distances.

But it seems probable that such simple cases are comparatively unusual at low temperatures, because so often a direct chemical combination would tend to choke itself. Consider the case of water containing dissolved oxygen. This may act on the metal, converting the surface to oxide, but such oxides are sparingly soluble and, being comparatively impervious to oxygen *molecules* at ordinary temperatures, will tend to protect the part below from attack. In general, direct attack will here be slow, except in the presence of substances which can dissolve an oxide, or render it porous, or (indirectly) prevent the layer of liquid next the surface from becoming saturated with the oxide; numerous examples could be given of all these exceptional cases, but the fact remains that direct action of dissolved oxygen on most metals is slow, although often measurable.

Bengough's work has shown that even very pure salt-free water attacks the purest zinc perceptibly in presence of oxygen, but the action is extremely slow. At high temperatures, the oxide film is pervious to oxygen molecules and direct combination between metals and molecules and dry oxygen can occur, producing a film or scale of oxides; at medium temperatures, the film thus formed is of the order of the wave length of light and produces interference tints, while at low tempera-

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[5] Assistant Director of Metallurgy, Kings College, Cambridge, England.

tures the film produced by pure air remains too thin to be visible while in contact with the bright metal. It can, however, be detected optically and, if isolated from the metallic basis by dissolving away the metal below it (e. g., in iodine), the previously invisible film becomes quite visible. This invisible film is at ordinary temperatures impervious to oxygen molecules, and protects the metal from visible change, when exposed to dry air at room temperature. It is not impervious to ions, and consequently does *not* prevent attack by liquid water except in special cases such as aluminum or chromium alloys; these materials yield films which are only very slightly pervious to ions and which tend to become less pervious as time goes on, so that good protection is often afforded; such films, however, are better described as self-healing than impervious.

These principles, which rest on a good experimental basis, explain why at ordinary temperature direct chemical attack is usually slow. But it often happens that electrochemical mechanism will give freely *soluble* primary corrosion products, where direct attack would give a sparingly soluble primary product, and thus electrochemical corrosion can proceed apace where direct attack would choke itself. Consider the case of zinc, in sodium chloride solution containing oxygen. If, *for any reason at all,* an electric current flows between one part of the metallic surface to another, zinc chloride will be formed at the anodic part, and sodium hydroxide at the cathodic part; oxygen is needed—as a depolarizer—for the cathodic reaction, if the attack is to proceed smoothly.

Now where the zinc chloride and sodium hydroxide meet, they will form hydrated zinc oxide (or under some conditions basic zinc chloride may appear, but for simplicity this may be neglected). Here the sparingly soluble body will be precipitated *at an appreciable distance from the metal,* and will not in general interfere with further attack. Thus although the direct (chemical) mechanism and the indirect (electrochemical) mechanism, *both* lead to the production of oxide (in one case, hydrated), they produce it at different places; the first change is self-stifling, while the second can usually proceed without hindrance. In cases where the electrochemical mechanism would lead to a sparingly soluble compound as the *primary* product, (e. g., lead in a sodium sulfate solution) the attack is negligibly slow.

Now almost any lack of uniformity in the conditions is capable of setting up the necessary flow of electric current. Assuming that the liquid is absolutely uniform at all points, chemical or physical differences in the metal, or the state of repair of the invisible oxide-skin upon it, are capable of providing the e.m.f.; but differences in the liquid are equally capable of providing an e.m.f., an example being provided by the differential aeration currents generated simply by local difference in the rate of replenishment of oxygen. There is no evidence that impurities in the metal are needed for electrochemical corrosion in the presence of oxygen.

Many metals are capable of eliminating hydrogen readily from acids in the absence of oxygen, and on a much smaller scale from neutral salt solutions. Thus oxygen is not needed for corrosion. But the hydrogen-evolution type of attack is much more dependent on the presence of impurities than the oxygen-absorption type. Indeed Palmaer's recent work makes it difficult to avoid the conclusion that absolutely pure metal would be quite unattacked by oxygen-free acids. But it should be noted that not all impurities, when added to "ordinary pure" metal, stimulate attack by acid. Vondracek's work on zinc shows clearly that although certain additions stimulate corrosion, others retard it; some additions retard attack while in solid solution, but stimulate it when they come to be reprecipitated as a separate phase.

The electrochemical view of corrosion is something more than a theory, since in certain cases the currents flowing between different parts of the metal have been measured and found to account for the corrosion which is actually observed. But the experimental facts give no warrant for the supposition that simple combination is impossible. There are still cases which are insufficiently understood, but in general the facts strongly suggest that in general the electrochemical mechanism is only important in cases where there is some topochemical hindrance preventing or retarding the direct and simple type of attack. It happens, however, that these cases comprise a large proportion of the practically important types of corrosion.

COLIN G. FINK.[6]

We have been very strong adherents of the electrochemical theory of corrosion. Our researches covering many years have fully supported us in the belief that all corrosion in aqueous solution is electrochemical in nature. We have never found a case which we could describe distinctly as chemical corrosion. Thus, for example, when

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[6] Head, Division of Electrochemistry, Columbia University, New York City.

we try to dissolve a very pure base metal in acid, we find the procedure to be extremely slow. Immediately upon the addition of 1 drop of platinum chloride the dissolution of the pure base metal proceeds very rapidly.

The experiments of Cushman and Walker which resulted in the very pretty ferroxyl test, showed differences in *macro* areas of iron and steel samples, the samples being imbedded in a jelly, and after a short time the difference in polarity was indicated by blue and pink zones. This test to our mind is an important one; on the other hand it does not take care of the fundamental electrochemical phenomena. Accordingly, with the assistance of Dr. Claude M. DeCroly[7] and Dr. F. J. Kenny,[8] tests were carried out, the outcome of which showed that the surface of any metal or alloy is composed of numerous point-to-point couples. The work was carried out in an atmosphere of pure nitrogen under the microscope and we believe the results are reliable. Many check tests have been made and we have found no digression from our original findings. We find, furthermore, that the local point-to-point couples can be eliminated by various treatments. Thus, for example, by differential dissolution, also by heat-treatment and by plating the surface with another metal. The main point to bear in mind is that a surface which has been equi-potentialized and maintained in this equi-potentialized condition will resist corrosion indefinitely. This, we believe, is one of the strongest proofs in support of the electrochemical theory.

The question naturally arises, "To what are these local couples due?" We have found that local couples may be brought about by a dozen different causes: Thus, for example, (1) difference in composition; (2) difference in heat-treatment or difference in strain; (3) difference in exposure to light; (4) difference in orientation of individual crystals in the surface (the potential at the side of a crystal is different from the potential at the end of a crystal); (5) presence of dust particles and other foreign matter on the surface of the metal; (6) difference in the degree of dryness of the surface, etc. In general, we have observed in determining the point-to-point couples under the microscope that the strain area is anodic; likewise the area covered by a dust particle is usually anodic. The interesting fact is that areas made anodic through strain can be equi-potentialized by chemical treatment.[9]

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[7] Trans. Am. Electrochem. Soc., 56, 239-73 (1929).

[8] Trans. Electrochem. Soc., 60, 235-65 (1931).

[9] Fink and Kenny, Trans. Electrochem. Soc., 60, 235-65 (1931).

The assertion is often made that a pure metal is more corrosion-resistant than an impure metal. This statement does not hold true in general. We have found, for example, that metals that were only 99 per cent pure, but in which the impurity was evenly distributed throughout the mass, were more resistant to corrosion than metals 99.9 per cent pure, but in which case the impurities were segregated.

The question naturally arises, "What is the outlook for the future?" We have been advocating that metals which are to be exposed to the atmosphere should be preferably annealed. If annealing is not feasible or practical, the surface of these metals should be equi-potentialized by chemical treatment, which is not difficult. In the application of paints to iron and steel it is likewise well to have the surface equi-potentialized before the prime coat is applied. Furthermore, this prime coat should form an intimate bond with the metal, just as in the case of hot galvanizing, in order to be of value.

We are still continuing our researches on corrosion, but, as stated above, we have yet to find an exception to the electrochemical theory advanced by Whitney thirty years ago.

W. H. HATFIELD.[10]

I would suggest the following as a definition of electrochemical corrosion:

"Corrosion is an electrochemical process when the metal passes into solution in the ionic form, its solution being accompanied by the discharge of an equivalent quantity of cations and the passage of an electric current, external to the solution, equivalent in amount to the metal dissolved."

This definition relates, of course, only to the underlying basic mechanism, and the number of factors which may bring about or modify the process is considerable. Thus, each case must be considered separately if any detailed account of the process at work is required. Although the particular factors operating may vary considerably from instance to instance, there would seem to be little doubt that the process is electrochemical rather than chemical. There is often a considerable divergence of opinion as to the detailed mechanism, however, which is not surprising in view of the number of factors which can influence attack.

Acceptance of the electrochemical theory in regard to the corrosion of a specimen in a uniform aqueous electrolyte necessitates, in my

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[10] Brown-Firth Research Laboratories, Sheffield, England.

opinion, the assumption of the existence of some variation in potential across the metal surface. There are several possible causes of such variations. There may, for example, be an oxide film over the surface of the metal, breaks in which provide anodic areas. (Such breaks or weak spots may result from strains or may be related to inclusions present in the steel). Again impurities present may act as cathodic areas, a fact which is often of considerable importance when the corrosion is largely of the hydrogen evolution type, and so on.

As implied in the above definition, I regard the passage of metal ions into solution as a necessary part of the mechanism of electrochemical corrosion.. The formation of compounds with anions present is therefore regarded as taking place in the solution as a reaction between ions.

The question of the degree to which the electrochemical theory is applicable is a difficult matter to decide. It is the more difficult because, as already indicated, it is a fundamental conception on which are based other less general hypotheses to explain the detailed operation in particular cases. Thus, there may even be rival theories which are yet alike in that they are based upon electrochemical theory, and it becomes a very difficult matter to design experiments of a sufficiently fundamental character to indicate whether the attack is chemical or electrochemical. Of course, cases where no electrolyte is present, as in reactions between gases and metals at temperatures such that no liquid can exist on the metal surface, must be regarded as chemical and not electrochemical corrosion, but with solutions the matter is much more difficult to decide. Nevertheless, there seems no reason why direct attack should not sometimes occur, even though most cases should prove to be largely or entirely electrochemical in character, and there are certain cases which are difficult to conceive of as other than instances of direct chemical attack. I think especially of the results obtained by M. Centnerszwer and W. Zablocki[11] in their work on the reaction between aluminum and hydrochloric acid. In this case the evidence clearly points to a reaction taking place between the molecules of hydrochloric acid and the metal. More work of this type is very desirable from the theoretical standpoint.

I have not so far entered into a discussion of the detailed mechanism of the attack in particular cases, and indeed I do not think it desirable to do so in a general consideration of the value and applica-

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[11] Z. physik. Chem., **122**, 455 (1926).

bility of the electrochemical theory, when, as is the case, the details vary so greatly from instance to instance.

FRANK N. SPELLER.[12]

"It may now be regarded as established that in substantially all cases of corrosion at ordinary temperatures the driving force of the corrosion reaction between metal and environment is electrochemical. The magnitude of this electrochemical potential, which varies with the environment and the metal, determines the tendency for the reaction to proceed; but the rate of corrosion is determined mainly by the resistance to continued progress of the reaction set up by certain of the corrosion by-products. In some cases such as where hydrogen sulfide is present in the absence of oxygen, the initial attack may perhaps be due to direct chemical reaction but as soon as the corrosion products are formed, the reaction is apparently accelerated by contact between the iron sulfide and the metal, with evolution of hydrogen.

"As to the origin of the two poles necessary in an electrochemical reaction, it is hard to conceive of a metal that does not have some points of differences of potential on the surface even though these are only the crystalline boundaries and the differences in orientation of the crystals. However, assuming that a metal surface can be found that has no differences of potential, the film that forms when the metal is exposed to the atmosphere is not permanent, and when broken causes differences in potential that localize corrosion. Granting differences of potential on the metal surface, it is easy to my mind to conceive of electrochemical action by the passage of electrically-charged ions from the metal into the solution and accompanying depolarization. Catalytic action may play an important part in oxygen depolarization.

"In corrosion of ferrous metals in contact with a solution, iron is usually dissolving at anodic areas, hydrogen being plated out at cathodic areas, whether on the iron itself or on other surfaces.

"In absence of oxygen, hydrogen gas can be slowly evolved even from neutral solutions. The author has found considerable hydrogen in hot water with a pH between 7.2 and 9 from which most of the free oxygen had been removed by contact with iron at 150° F. (65° C.) and at normal temperature has found smaller amounts of hydrogen in water freed from dissolved oxygen by contact with iron for a longer period of time.

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[12] Director, Dept. of Metallurgy, National Tube Co., Pittsburgh, Pa.

"Iron tends to corrode more rapidly in acid solutions. This effect of hydrogen ions is the opposite of that of ferrous ions because the latter oppose the iron going into solution, whereas the hydrogen ions favor hydrogen leaving the corroding media.

"Some metals and alloys, notably ferrous alloys of aluminum, chromium, silicon, copper, such as the group of stainless alloys, readily form a very adherent film under oxidizing conditions which is so impervious that the primary corrosion reaction (passage of metallic ions into solution) is considerably slower, no matter how great its tendency may be. These metals withstand corrosion not because they are really noble like gold and platinum, but by a self-healing protective insoluble film, in spite of the fact that some of them are less noble than iron.

"It has been found that the corrosion rate in most natural waters is determined by the rate of depolarization at cathodic areas and therefore by the rate at which dissolved oxygen reaches these portions of the metal surface."

Oliver P. Watts.

It is evident from a perusal of the opinions expressed above that to some the electrochemical theory of corrosion means that as a preliminary to flow of current and corrosion there must be, as in the voltaic cell, a difference of potential between two conducting surfaces in contact with an electrolyte. An e.m.f. is necessary to flow of current, and current is necessary for corrosion. Hence a really pure metal in a uniform electrolyte cannot corrode. Others hold that such initial differences of potential are not necessary, and that certain metals will continue to corrode in spite of perfect purity. In "Corrosion," p. 181, Speller presents this view: "The corrosion occurring, when dissimilar materials are in contact, is often spoken of as 'galvanic action.' This is generally due to the popular conception that the electric current, existing under conditions of 'galvanic action,' causes the corrosion. As a matter of fact, the current is the result of the corrosion taking place."

Evans says, "There is no evidence that impurities in the metal are needed for electrochemical corrosion in the presence of oxygen." Then he cites recent work by Palmaer, which "makes it difficult to avoid the conclusion that absolutely pure metal would be quite unattacked by oxygen-free acids." To refute this Bancroft cites pure sodium.

Except when otherwise specified, the statements which follow are claimed to apply only to aqueous solutions.

ELECTROLYSIS AND CORROSION.

It has been said of electrolysis that it splits a chemical reaction in two and permits the halves of the reaction to occur at different places. The beauty of this characterization can be appreciated only by those who are conversant with both electrolysis and corrosion. In ordinary cases of corrosion, such as the attack of zinc or iron by sulfuric acid, the two halves of an electrolytic reaction have been put together again, and the same piece of metal serves as anode and as cathode. The most fundamental law of electrolysis still applies, viz. Faraday's law, that the total of chemical changes at the anode, where metal tends to enter solution, equals the total changes at the cathode, where elements leave the solution. The amount of hydrogen displaced from sulfuric acid by zinc is equivalent to the quantity of metal dissolved. This seems to indicate that the nature of the processes by which metal passes into solution by chemical and by electrolytic corrosion is the same.

According to the old view, attack on a metal like iron by an acid such as hydrochloric is strictly a chemical process, the greater affinity of the iron for chlorine enabling this metal to rob the acid of its chlorine, thus displacing the hydrogen.

Today the majority of students of corrosion, and probably of chemistry also, appear to have accepted Nernst's view, that the dissolving of metals by acids or other corroding media takes place by ions (electrically charged atoms) leaving the surface of the metal. All that is needed for atoms of a metal to go into solution is that they be provided with tickets of admission, a number of positive charges equal to the valence of the metal in that particular solution. The former importance of the anion has vanished. Now it serves only for carrying current through the solution, and of itself contributes in no way to the dissolving of metal. The army of anions on reaching a soluble anode merely come to rest there and permit the metallic ions leaving the anode to pass peaceably through their ranks.

CORROSION CLASSIFIED.

Except for a single type, not often encountered, all corrosion of metals in aqueous solution is by displacement. For simplicity and convenience corrosion may be classified as follows:

1. *Corrosion without displacement of anything from the corroding solution,* e. g., the dissolving of iron or copper by a solution of ferric chloride.

II. *Corrosion by displacement of a metal,* e. g., the dissolving of iron by a solution of copper sulfate, or of zinc in the recovery of gold from cyanide solutions.

III. *Corrosion by visible displacement of hydrogen,* e. g., the dissolving of zinc by sulfuric acid.

IV. *Corrosion by invisible displacement of hydrogen,* following by its physical or chemical removal, e. g., the corrosion of iron by sea water or of copper by dilute sulfuric acid. This is often called corrosion by oxygen depolarization.

Type I. This kind of corrosion occurs only when there is in the corroding solution in one of its higher valences, a metal which is capable of existing in solution in at least two valences. Corrosion of this type is seldom met commercially, but is made use of in etching metallographic specimens with ferric chloride. Metal dissolves with equivalent lowering of the valence of the metal previously in the solution.

Type II. In arranging electrochemical series of the metals, this type of corrosion was extensively studied in the early part of the 19th century, although attention was then focused on the deposition of the one, rather than on the corrosion of the other of the two metals concerned in each case. The serious consequences of confining in a tank or pipe made of an active metal a solution containing a much more inert metal, is so well known that this type of corrosion is rarely encountered. One metal replaces the other in solution. Short of actual trial, tables of potentials and of solubilities furnish the best basis for prediction in regard to this type of corrosion.

Type III. Corrosion by visible displacement of hydrogen is possible only in those electrolytes from which the electric current deposits hydrogen, *i. e.,* water, and solutions of acids, alkalies and salts of sodium, potassium, aluminum, etc. Visible displacement of hydrogen occurs when the potential of the metal exceeds the discharge potential of hydrogen on that metal from that particular solution.

Type IV. Corrosion by invisible displacement of hydrogen is by far the most common type of corrosion, yet is least understood. This occurs only with those metals and in those solutions in which the discharge potential of hydrogen exceeds the potential of the metal. Corrosion by invisible displacement of hydrogen proceeds as follows: When the metal is immersed in the solution it begins to dissolve, displacing its equivalent in hydrogen. This continues until the counter e.m.f. set up by hydrogen equals the thrust of the metal to go into solution, when dissolving of metal and displacement of hydrogen cease. In the case of metals whose potentials lie far below the discharge potential of hydrogen on them, the contact surfaces of metal and electrolyte must be far from saturated with hydrogen.

Oxygen from the air dissolved in the electrolyte removes hydrogen by formation of water, thus lessening the force which prevented further displacement of hydrogen, so that dissolving of metal begins again. The speed of solution of metal is limited to the rate at which oxygen reaches its surface.

THE DISCHARGE POTENTIAL OF HYDROGEN.

In electroplating an inert cathode such as platinum or graphite with zinc, it is evident that when the cathode has been entirely covered, its potential must be that of zinc. Actually this potential is attained when but a small portion of the cathode surface has been covered by the deposit. Similarly the accumulation of hydrogen on a metallic cathode always alters its potential, and when enough hydrogen has accumulated for its visible discharge, a fairly definite potential, the discharge potential of hydrogen, is attained. The magnitude of this potential depends on the material and concentration of the electrolyte, and not only on the metal of the cathode, but also on the degree of smoothness of its surface. Time is also a factor, for so long as the cathode and the electrolyte in contact with it are not fully saturated with hydrogen, the potential continues to rise.

The two major factors which affect the magnitude of the discharge potential of hydrogen are the metal of the cathode and the hydrogen ion concentration of the electrolyte. Substitution of normal sodium sulfate for normal sulfuric acid causes a rise of 0.5 to 0.7 volts in discharge potential, depending upon what metal constitutes the cathode.

The rapid and visible attack of iron and commercial zinc by hydrochloric acid and the lack of visible action by sea water is due, not to a change in potentials of the metals, but to a rise in the discharge potential of hydrogen resulting from the lower hydrogen ion concentration in sea water.

The values of Table I were obtained by applying a voltage sufficient to cause rapid evolution of hydrogen on the specified metal cathode, and after ten minutes, lowering the voltage until hydrogen escaped very slowly. The potential of the cathode against a saturated calomel

TABLE I.

Potentials of Metals and Discharge Potential of Hydrogen on Them.

In N. H_2SO_4.

	Sat. Cal. = —0.5266			Hydrogen Electrode = 0.0	
	Potential	D. P. of Hyd.	Mil. amp.	Potential	D. P. of Hyd.
Zinc, amalg.	0.5604	0.5800	0.50	—0.8384	—0.858
Tin, rough	0.036	0.052	0.25	—0.914	—0.329
Tin, smooth	—0.056	0.054	0.30	—0.222	—0.332
s-Iron, rough	—0.010	Spont.	0.0	—0.268	....
s-Iron, smooth	—0.031	—0.022	2.50	—0.247	—0.257
s-Nickel, rough	—0.217	—0.139	1.3	—0.060	—0.139
s-Nickel	—0.244	—0.149	1.6	—0.34	—0.129
s-Copper	—0.417	—0.023	1.5	+0.137	—0.301
s-Copper, rough	—0.469	—0.022	1.0	+0.191	—0.256
Antimony, rough	—0.433	+0.114	2.5	+0.155	—0.392
Antimony	—0.449	+0.171	1.5	+0.171	—0.449
Bismuth	—0.491	+0.152	0.4	+0.213	—0.430
Gold	—0.505	+0.001	0.4	+0.227	—0.279
Arsenic, rough	—0.528	+0.021	1.3	+0.251	—0.299
Arsenic	—0.536	+0.083	0.3	+0.258	—0.361
Silver, rough	—0.525	+0.017	0.5	+0.247	—0.295
Silver	—0.566	+0.022	0.5	+0.288	—0.300
s-Platinum	—1.153	—0.195	3.5	+0.875	—0.083
Lead		+0.388	0.5		—0.666
Lead, rough		+0.393	0.5		—0.671

In N. Na_2SO_4.

	Potential	D. P. of Hyd.	Mil. amp.	Potential	D. P. of Hyd.
Zinc	0.556	+1.170	0.3	—0.8339	—1.295
Zinc, rough	0.556	+0.946	0.3	—0.834	—1.224
Zinc, Amalg.	0.535	+1.240	0.4	—0.813	—1.518
Cadmium, rough	0.285	+0.722	0.25	—0.563	—1.00
Cadmium	0.231	+0.886	0.25	—0.509	—1.164
Iron, rough	0.164	+0.569	0.7	—0.442	—0.842
Iron	0.1456	+0.571	0.5	—0.424	—0.849
Lead, rough	+0.063	+0.830	0.3	—0.3416	—1.108
Lead	+0.056	+0.948	0.25	—0.342	—1.222
Chromium, rough	—0.053	+0.634	0.5	—0.225	—0.912
Chromium	—0.038	+0.685	0.25	—0.240	—0.963
Tin, rough	—0.093	+0.744	0.3	—0.185	—1.022
Tin	—0.174	+0.893	0.3	—0.104	—1.171
Antimony	—0.215	+0.848	1.0	—0.063	—1.126
Antimony, rough	—0.227	+0.849	0.6	—0.051	—1.127
s-Nickel, rough	—0.317	+0.535	0.5	+0.039	—0.813
s-Nickel	—0.3922	+0.604	0.5	+0.114	—0.884
Arsenic, rough	—0.346	+0.798	1.5	+0.069	—1.076
Bismuth	—0.408	+0.877	0.3	+0.120	—1.155
s-Copper, rough	—0.501	+0.620	1.5	+0.223	—0.898
s-Copper	—0.504	+0.694	1.5	+0.226	—0.922
Silver, rough	—0.510	+0.790	0.4	+0.232	—1.068
Silver	—0.549	+0.803	0.6	+0.271	—1.081
Gold, rough	—0.514	+0.612	0.25	+0.236	—0.890
Gold	—0.544	+0.696	0.8	+0.266	—0.974
s-Platinum	—0.832	+0.657	0.25	+0.554	—0.935

All electrodes are 1 cm. sq. plated on copper, except for those marked (s), which are solid metal. Pt. = anode, 1 cm. distant. Data of R. W. Rummele & J. T. Sobota, June, 1932.

electrode was then read on open circuit by striking a key which opened the electrolyzing circuit and closed the galvanometer circuit in a single movement. The cathodes were polished except for those marked rough, which were scoured with fine emery paper. The values given should be considered as approximations only.

VOLTAIC OR GALVANIC ACTION.

Many speak of corrosion by voltaic action as if it were something different in principle and operation from ordinary corrosion of metals, and the mere mention of voltaic action seems to be considered a sufficient excuse for any amount of damage by corrosion. In the corrosion of a particular metal by a solution of an acid or of a sodium salt, all that contact with a more noble metal does is to provide additional surface on which hydrogen may be displaced, and from which it may either escape in the gaseous state or be removed by oxidation (depolarization). If there is no visible evolution of hydrogen from either metal before or after contact, the increase in corrosion of the more active metal induced by contact will not greatly exceed the increase in surface provided for displacement of hydrogen; but if hydrogen is evolved from the less active metal as a result of contact the increase in corrosion will be enormously greater than the added surface.

PURITY VS. CORROSION.

Will a perfectly pure metal corrode? This question has often been argued pro and con, usually with the result of leaving each of the disputants "of the same opinion still." The preceding portions of this paper show that several authorities on corrosion disagree on this seemingly simple question, which nevertheless involves the fundamental principles of corrosion.

A recent statement[13] says, "It has frequently been reasoned that if an element could be freed from all impurities and be perfectly homogeneous it would resist corrosion in every medium. It is known that as a metal is purified, its resistance to corrosion increases. The explanation for the greater insolubility of the purer metal is perhaps to be based upon the non-existence of local-action currents which are dependent on the presence of dissimilar metals or heterogeneity of structure. In other words if the metal is free of other elements and absolutely homogeneous, no potential can exist between one point on the surface

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[13] F. A. Rohrman, J. Chem. Education, p. 215 (1933).

and another; therefore no current can flow and the metal will not go into solution."

E. S. Hedges[14] says, "Whether perfectly pure metals will dissolve in acids with evolution of hydrogen is a question which is difficult to answer, and possibly it has not the importance which is often attached to it. All experience goes to show that the more highly purified a metal is, the more slowly it dissolves in acids, and the theory of 'local currents' between the anodic metal and cathodic impurities has received favor in proportion."

Many others have expressed the opinion that perfectly pure metals will not corrode—probably based on the behavior of zinc toward acids. That amalgamation stops visible evolution of hydrogen from dilute sulfuric acid by zinc is well known. All that has been accomplished by amalgamation is the elimination of one of the two processes by which the zinc was originally corroding. Initially the zinc was corroding rapidly by visible displacement of hydrogen, and very slowly by oxygen depolarization. Amalgamation stopped corrosion by the first process only. The favorite explanation for the apparent stopping of corrosion of commercial zinc by amalgamation is that the mercury covers up all impurities on the surface of the zinc and makes it uniform, so that there are no longer any voltaic couples on the surface, when, of course, according to their views, corrosion must cease since it is an electrochemical action. A more correct view is that amalgamating has left in contact with the electrolyte no material on which the driving force of zinc is capable of forcing out hydrogen to such a concentration that it escapes as gas. The discharge potential of hydrogen on mercury is the highest known.

No one has suggested that differences in material or potential are necessary on a cathode surface in order that an oxidizing agent may depolarize hydrogen accumulated there, nor that such differences are needed for depolarization by dissolved oxygen. Whether the metal is of ordinary commercial purity or absolutely pure, the force with which it tends to displace hydrogen from any particular solution is the same, and provided there is no visible discharge of hydrogen, the rates of corrosion in water will not be widely different.

The whole argument for cessation of the corrosion of metals, if they could be obtained perfectly pure, is based on the stopping of visible displacement of hydrogen by amalgamated zinc and by certain

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[14] Protective Films on Metals, p. 24.

samples of this metal of exceptional purity. No thought seems to have been given to the fact that corrosion by oxygen depolarization still goes on—that variety of corrosion which is responsible for the major part of the annual damage by corrosion.

Advocates of the necessity for voltaic couples, points of different potential, as an antecedent to corrosion apparently limit this claim to cases where anode and cathode consist of the same piece of metal. No one has yet claimed that there must be impurities in a metallic cathode in order that hydrogen may be displaced on it by electrolysis. With platinum electrodes in sulfuric acid everybody recognizes that whether or not hydrogen is evolved on the cathode depends, not on the presence of impurities on its surface, but on the magnitude of the e.m.f. applied to the cell. When certain persons insist that there must be impurities in metals in order that they be corroded by acids, they are merely asserting that the potential of every metal is too small to displace hydrogen on itself. This requires demonstration by experiment instead of mere assertion.

Should further experiments prove definitely that no perfectly pure metal is capable of visibly displacing hydrogen on itself from acids, which seems utterly incredible in the case of sodium, potassium, calcium, etc., nitric acid would still continue to dissolve absolutely pure zinc and copper, and corrosion of these metals in sulfuric acid by oxygen depolarization would go on, as would corrosion by displacement of other metals and by the method of type I of the author's classification. Metallurgists need not worry about zinc being made so pure that it will fail to precipitate gold from cyanide solution and sacrifice itself in doing so.

THE ROLE OF OXYGEN AND OXIDIZING AGENTS IN CORROSION.

It is observed that oxygen and oxidizing agents stimulate corrosion of metals. Early in the history of the voltaic cell it was discovered that unless an oxidizing agent was placed at the cathode, the current delivered by the cell quickly diminished through polarization by hydrogen—*i. e.*, deposition of hydrogen on the cathode caused its potential to approach that of the zinc, thus lowering the e.m.f. of the cell. With few exceptions the electrolytes of voltaic cells are those from which hydrogen is deposited at metallic cathodes when electrolysis occurs. To prevent this serious fall in e.m.f. during use, oxidizing agents are placed at the cathode either as a constituent of electrode or electrolyte. Studies of the Leclanche cell have shown that reduction of the manganese dioxide accounts for removal of only half the hydrogen deposited at the cathode; the remainder is removed by oxygen from the air dissolved in the electrolyte. In Volume 62 of the Transactions of this society a commercial air-depolarized cell is described. Polarization at the cathodes of primary cells has long been known, understood, and the removal of the polarizing hydrogen provided for by oxidizing agents, and finally by atmospheric oxygen.

About eighty years' study and experimenting in corrosion was required before this was recognized as electrochemical in character, and the function of oxygen in stimulating corrosion was not made clear for several year more. In any aqueous solution from which hydrogen is deposited on metallic cathodes, its deposition tends to displace the potential of the metal toward that of zinc. It is not necessary that there be enough hydrogen on the metal for visibility in order to cause this change in potential. It begins as soon as any e.m.f. is applied to the cell, and if the e.m.f. is gradually increased it continues until both electrode and electrolyte at the metal-electrolyte interface are saturated with hydrogen, and the gas begins to escape.

When a metal is placed in a solution of sulfuric acid or sodium chloride, it begins to dissolve by the only process possible, by displacing some other element from the solution. In acids and solutions of sodium and potassium salts the substance displaced is hydrogen, the element which is deposited at cathodes from these solutions by electrolysis. In a voltaic cell without a depolarizer, e. g., amalgamated zinc-sulfuric acid-copper, hydrogen is visibly evolved from the copper, and no one can doubt its displacement by the dissolving of the zinc. When copper is placed in dilute sulfuric acid it, too, starts to dissolve by displacing hydrogen, but the discharge potential of hydrogen on copper from dilute sulfuric acid exceeds the potential of copper in the same electrolyte; hence copper can continue dissolving only until hydrogen has accumulated on the metal to a concentration equivalent to the potential of copper; then there is equilibrium, and no more copper can dissolve until some of the hydrogen is removed, thereby lowering the opposition to its deposition. If air has access to the electrolyte, the oxygen slowly removes hydrogen and permits copper to dissolve at the exact rate necessary to replace the hydrogen as fast as it is removed. In the complete absence of oxygen copper does not corrode perceptibly in dilute sulfuric acid in years.

In April, 1926, the writer sealed in glass tubes in normal sulfuric acid inch-long (2.54 cm.) pieces of bright copper wire. The acid was boiled in the tube under diminished pressure and sealed under vacuum. One tube was left unsealed. The wire and liquid in this have completely disappeared, and in their place is dry copper sulfate. The acid in one tube became faintly blue after a month. Careful scrutiny showed a minute crack in the glass where sealed. Although the liquid has not evaporated, enough air has diffused through the crack to cause serious corrosion of the copper. In two other tubes the acid is still water-white, and the copper is as polished as when put into the tube seven years ago.

Not only does a zinc anode displace hydrogen on the cathode of a voltaic cell when they are connected, but it displaces hydrogen on itself. In neutral electrolytes, from which the discharge potential of hydrogen on zinc and its impurities exceeds the potential of that metal, no hydrogen is seen; but in acids where the discharge potential of hydrogen is much lower, it is necessary to amalgamate the zinc to prevent continuous evolution of hydrogen on the anode and corresponding waste of zinc. Although there is now no evolution of hydrogen on open circuit, corrosion by oxygen depolarization goes on. This corrosion of amalgamated zinc by depolarization of the invisible film of hydrogen always present on it was recognized years ago, and the zincs were removed from the single-fluid bichromate cell when not in use, to prevent waste through oxidation of the hydrogen film by the chromic acid.

OXYGEN CONCENTRATION CELLS OR CORROSION BY DIFFERENTIAL AERATION.

Corrosion by differential aeration has been much discussed. When two separate pieces of iron are placed in a neutral electrolyte and oxygen maintained at a higher concentration at one piece than at the other, the iron with the higher oxygen concentration corrodes faster and its potential is lower (more noble) than that of the other piece. When the electrodes are connected, each piece is privileged to displace hydrogen on the other as well as on itself. Enough current now flows from the metal where hydrogen is the more concentrated to raise the polarization by hydrogen of the other electrode until their potentials are equal, except for the e.m.f. required to drive the current through the cell. The corrosion of the two electrodes should differ by an amount equivalent to the current.

Two sheets of the same metal each 4 x 5 cm. were placed, one in normal sodium sulfate saturated with air, the other in the same from which the air had been removed by applying a vacuum to the hot solution and quickly covering it with a layer of melted paraffine, over which mineral oil was poured as soon as the paraffine had solidified. The two cells were connected by an agar bridge. Zinc, iron, copper and tin were also used. Five minutes after closing the circuit the current was about 0.00003 amp., about a half of the initial value. The high resistance of the agar bridge is partly responsible for the very small current. There was no agitation of either electrodes or electrolyte. The electrode in the vessel open to the air was always cathode.

Two explanations are suggested for corrosion by differential aeration. The first is that an oxide film is formed on the metal having the higher concentration of oxygen. "It is clear, therefore, that the formation of protective films on the aerated part of the metal does play a very considerable part in causing the aerated area to be cathodic."[15]

"The portions to which oxygen has least ready access are those where corrosion is greatest. This conclusion may at first sight seem almost paradoxical, but the action of oxygen is of the direct chemical type, giving at the aerated portions a uniform film having some protective qualities. These parts are thus ennobled and the parts sheltered from oxygen are relatively electronegative (more active) and dissolve by anodic attack of the ions in solution."[16]

The other explanation is that this is merely a case of ordinary corrosion by oxygen depolarization, except that the two portions of the same metal which act as anode and cathode happen to be connected by wires instead of being a single piece of metal. The initial differences in potential are characteristic of metals when the hydrogen concentration at the metal-electrolyte surface is changed. The following potentials were obtained in tenth molar potassium sulfate solution. previously saturated with hydrogen or with oxygen at 25° C.[17] The values are the difference between the metal and a saturated calomel electrode.

Metal	Oxygen	Hydrogen
Zinc	1.0655	1.1742
Nickel	0.1876	0.7276
Copper	0.0151	0.1603
Platinum	0.3837	0.7152

[15] Evans' Corrosion of Metals, p. 93.

[16] Hedges' Protective Films on Metals, p. 47.

[17] Unpublished work of A. J. Krombholtz, Chem. Eng. Labs., Univ. of Wis.

The greatest change in potential is in the case of platinum, where there can be no formation of an oxide. A cell consisting of copper and platinum electrodes in normal sodium sulfate, with the platinum in a porous cup, gave a current of 0.00012 amp.; on adding 2 drops of 30 per cent hydrogen peroxide to the cup, the current rose to 0.00065 amp. This would seem to be a case of direct depolarization of hydrogen.

It is generally considered that the velocity of corrosion by oxygen depolarization is controlled by the rate of diffusion of dissolved oxygen to the metal. This means that when the oxygen arrives at the metal surface hydrogen is already there, and the oxygen has a choice of uniting with hydrogen or metal. That an oxide should be formed in the presence of hydrogen, and later be reduced by hydrogen, seems an entirely unjustifiable, not to say unreasonable, assumption.

Granting that an oxide is formed, it should, like the copper oxide cathode of the Edison primary cell, prevent accumulation of hydrogen, and so promote continued flow of current. The only dissolving of metal either by the potassium chloride of Evans or the sodium sulfate of the last experiment, must be by displacement of hydrogen, and this hydrogen will be deposited where opposition is least, *i. e.*, where the hydrogen concentration is lowest. It is only a lower hydrogen concentration that makes one point on a piece of metal cathodic to another.

Dr. Blum makes the revolutionary suggestion that no hydrogen is displaced by metals dissolving by oxygen depolarization, but that "cathodic reduction of oxygen can be considered an electron reaction, which is much more likely to occur than the frequently assumed process of hydrogen evolution and subsequent reduction of oxygen by hydrogen."

ELECTROLYTIC PROTECTION.

In electrolytic protection the metal is made cathode and loaded up with hydrogen by an external e.m.f. so that there shall be no point on which the metal can itself push out hydrogen. In the Gunderson Process plating with arsenic insures that there shall be no corrosion of the steel by visible displacement of hydrogen, for the discharge potential of hydrogen on arsenic, even from acids, exceeds the potential of iron.

RESIDUAL CURRENT AND CORROSION.

Residual current is that microscopic current which flows in an electrolytic cell at any voltage below the e.m.f. of decomposition without visible products of electrolysis. It is the current-equivalent of the rate of depolarization of the electrodes by the electrolyte. At a constant voltage the current diminishes with time, but never ceases. It has been studied both with platinum electrodes and an e.m.f. external to the cell, and with electrodes of different metals, in which case the cell supplies its own e.m.f.

In 1902 S. L. Bigelow, at 1 volt with platinum electrodes in $N/200$ sulfuric acid, obtained a residual current of 64 microamp. at the end of 24 minutes, which fell to 0.22 microamp. in 32 days.

With iron and copper electrodes in normal air-saturated potassium sulfate, A. J. Krombholz obtained the following data:

Time	E. M. F.	Microamperes
4 min.		
0	0.580	0
4 min.	0.0097	20.3
60 min.	0.0056	12.5
8 hr.	0.0043	8.8
24 hr.	0.0040	8.4

In less than 4 minutes the iron by dissolving had displaced enough hydrogen on the copper to raise its potential to equal that of the iron, except for the IR drop through the cell due to the current flowing. In this case the anode is soluble, its potential is approximately constant, and the current is equivalent to the rate of depolarization of the cathode by dissolved oxygen from the air.

Corrosion of type IV is the same phenomenon, except that here a single piece of metal serves both as anode and cathode; but the corrosion is controlled by the rate of removal of hydrogen by dissolved oxygen, just as both current and corrosion in the experiment cited are fixed by the rate of depolarization of the cathode. A thorough study of residual currents under various conditions should throw much light on corrosion of type IV.

METALS ALWAYS IN EQUILIBRIUM WITH A FILM OF HYDROGEN.

Metals, when placed in acids or solutions of sodium salts, must displace on themselves a concentration of hydrogen equal to their own potentials, else there would be no acceleration of corrosion by oxygen depolarization. Copper, silver and other inert metals which are incapable of visibly displacing hydrogen from dilute sulfuric acid, corrode very slowly when allowed to stand in the acid. Sheet copper with a total exposed surface of 50 cm.^{2}, submerged in normal sulfuric acid for 131 hours lost 0.016 g. per dm.^{2} per day. The surface area of the liquid was 32.15 cm.^{2}. Silver foil in normal sulfuric acid to which a few drops of hydrogen peroxide had been added was strongly etched in twenty minutes.

When a gradually increasing e.m.f. is applied to platinum electrodes in dilute sulfuric acid the potentials of the electrodes move apart until at a difference of 1.7 volts, oxygen and hydrogen are evolved. With each increase in e.m.f. a momentary polarizing current flows, depositing hydrogen and oxygen in strict accord with Faraday's law, until it has built up a polarization equal to the impressed e.m.f., when it drops to zero except for the residual current. Only when the electrodes and electrolyte in contact with them are saturated do gases escape, and any appreciable current becomes permanent. It is evident that the polarization, change in potential of the electrodes, was due to hydrogen on the cathode and oxygen on the anode. When copper sulfate is substituted for the acid, the general phenomena are the same, except that copper is found on the cathode instead of hydrogen at the end of the experiment. Although no hydrogen is seen, for the greater part of the experiment, polarization of the cathode was due to hydrogen not to copper, the latter being deposited only when the potential of the cathode had been brought nearly to that of copper by deposition of hydrogen on it. In the presence of air copper dissolves slowly in solutions of sulfuric acid and of copper sulfate. In the absence of air it has been proved not to dissolve in sulfuric acid, and undoubtedly will not do so in a solution of copper sulfate.

In normal copper sulfate a sheet of copper with 15 cm.^{2} of surface was short-circuited with a platinum wire a fiftieth of its area. The initial current was 0.000031 amp.; after 20 hours it had fallen to 0.000013 amp. At a magnification of 100 diameters no copper could be detected on the wire—another case of depolarization of hydrogen.

It is only at the potential of copper in sulfuric acid, for example, that there can be equilibrium between copper and hydrogen; at any potential more noble than this if copper began to deposit on a cathode, it must re-dissolve with displacement of hydrogen until equilibrium is reached. So very minute currents of the order of magnitude of residual currents deposit hydrogen, not copper, from air-saturated solutions of copper sulfate.

AN INSULATING FILM OF HYDROGEN.

In the early days of the study of corrosion the mistake was made of attributing the stopping of corrosion by the film of hydrogen to its insulating power, and in some quarters this erroneous opinion is still held. It is the polarization (counter e.m.f.) produced by it, not its resistance, that reduces corrosion and the current in voltaic cells. In one case the residual current between nickel and iron was found to be 1/20,000 of the current density usually used in chromium plating, where a storm of hydrogen is evolved at 6 to 8 volts. The resistance of the films of hydrogen encountered in corrosion are negligible.

NERNST'S OSMOTIC PRESSURE AND HELMHOLTZ'S ELECTROLYTIC DOUBLE LAYER.

"According to the well-known classical theory of Nernst, each metal has a definite solution pressure, which is a measure of the tendency of the metal to pass into aqueous solution in the form of ions. This solution pressure is opposed by the osmotic pressure of the metal ions, which tends to drive them out of solution, depositing them on the metal. With the reactive metals, such as zinc, the solution pressure is greater than the osmotic pressure, positively charged zinc ions go into solution, and the metal acquires a negative charge. When the solution pressure is less than the osmotic pressure, as is the case of copper and the 'nobler' metals in solutions of their salts, ions of the metal are deposited, giving a positive charge to the electrode, whilst the solution in the vicinity is negatively charged by the corresponding anions. The surface of the electrode is thus the seat of an electric double layer."[18]

The solution pressure of zinc is stated to be 9.9×10^{18} atmospheres, or five million-billion tons per square inch, and that of copper 4.8×10^{-20}, a quantity unimaginably small.

"In accordance with Nernst's assumption, when a bar of zinc is placed in water, zinc atoms each give up two electrons to the bar of metal and pass into the water as positively charged ions. In this way an electric double layer is formed at the junction of the metal and liquid. That but an exceedingly minute quantity of zinc enters the water in the form of ions, notwithstanding its enormous electrolytic solution pressure, is due to the electrostatic attraction of the negative charges which accumulate on the bar of metal. Evidently the relative

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[18] Hedges' Protective Films on Metals, p. 12 (1932).

values of the osmotic pressure and the electrolytic pressure determines whether ions leave or enter solution."[19]

Helmholtz's double layer is a myth. Not only is it stated above that metal ions pass into solution without displacing their equivalent in other positively charged ions, but the very existence of a double layer depends on their doing so. If metals dissolve by displacing on themselves, or another conductor in electrical contact with them, their equivalent in positively charged ions, there can be no accumulation of electric charges on either metal or electrolyte! Experience shows that, except for type I, all corrosion of metals is by displacement.

Nernst's conception of the "osmotic pressure" of the ions of the metal already in solution as equalizing or even overcoming solution pressure, chemical affinity, or whatever name is applied to the force which causes metals to dissolve, is also untrue. A sheet of copper 48 cm.^{2} in area, immersed for 12 days in 250 cc. of normal copper sulfate, *lost* 0.1386 g. in weight! According to Nernst, as quoted above, copper tends to *deposit* from solutions of its salts.

How can osmotic pressure and an electrolytic double layer be reconciled with this corrosion of copper in a strong solution of copper sulfate by oxygen depolarization? Yet modern texts on physical and electrochemistry continue to present Nernst's theory of osmotic pressure and Helmholtz's double layer as "law and gospel," to be swallowed by embryo scientists, greatly to the impairment of their scientific digestions! These figments of the imagination were created to explain the practical stopping of corrosion of the anode in certain primary cells when the circuit is opened, and the fact that metals of high potential fail to dissolve quickly and completely when placed in neutral electrolytes. Now that it is known that their supposed job of limiting corrosion is performed by hydrogen, and that they were never capable of doing it in the first place, they should be plainly labeled as scientific conceptions that have outlived their usefulness. Both Helmholtz and Nernst conceived the dissolving of metal to consist solely in the passage of metal ions into the electrolyte, unaccompanied by displacement of an equivalent of some other element, i. e. they ignored Faraday's law.

After thirty years, Whitney's statement that corrosion is electrochemical in nature still stands as our best definition of the electrochemical theory of corrosion.

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[19] Creighton & Fink's Electrochemistry, 1, p. 172 (1924).

DISCUSSION.

W. Blum[20] (*Communicated*): If in Dr. Watts' discussion, and especially his conclusion (p. 150) that "except for type I, all corrosion of metals is by displacement", he means direct, local displacement, this is equivalent to a complete rejection of the electrochemical theory of corrosion. The latter explanation of corrosion involves two processes, occurring at finite distances, and involving respectively the loss and gain of electrons. Solution or attack of metal, by the usual chemical definition, represents oxidation. Electrochemically, oxidation results from the loss of electrons from neutral atoms to form positively charged ions. To proceed continuously, this anodic process must be accompanied by one or more cathodic processes, in which electrons are consumed, i. e., reduction occurs. The most common cathodic processes are:

(1) Combination of electrons with positive ions to form atoms, e. g., of hydrogen or metals. This corresponds to the displacement referred to by Dr. Watts in classes II and III; but it should be noted that the hydrogen or other metal is not discharged where the corroding metal is dissolving, but at some other point.

(2) Reduction in valence of a positive ion, e. g., from ferric to ferrous ion. (Class I of Dr. Watts).

(3) Reduction of non-metallic atoms, e. g., of oxygen or chlorine to form negatively charged ions. (Class IV of Dr. Watts).

The words of J. W. Richards that "the cathode does not know what is going on at the anode" (or vice versa) apply as well to corrosion as to any other electrolysis. All that is necessary to permit continued corrosion of a metal is to remove electrons from it, regardless of what process is used to consume the electrons.

Which of several possible processes that consume electrons will occur at a cathode depends upon (a) their respective equilibrium potentials for the concentrations present, and (b) their polarizations (overvoltages) for the current densities involved. The fact that copper dissolves in sulfuric acid in the presence (but not in the absence) of oxygen, is merely an evidence that under those conditions free oxygen can be more readily reduced by electrons than can hydrogen ions. Contrary to the statement on p. 141, it is almost axiomatic (p. 126) that the potential required for continued reduction of oxygen at an electrode surface is likely to be affected by the composition and physical condition of the metal, though not necessarily to the same extent as is hydrogen evolution.

It is commonly assumed by many authors, including Dr. Watts, that hydrogen is first discharged by combination of electrons with hydrogen ions and that then the hydrogen atoms (or molecules) combine with the dissolved oxygen. This explanation overlooks the fact that, by definition, an electron (i. e. a negative charge) is the strongest conceivable reducing agent, and that therefore direct reduction of oxygen by electrons is much more probable than a secondary reduction by hydrogen. This suggestion, far from being "revolutionary," is a necessary corollary of the electrochemical theory of corrosion as defined by most of the persons quoted in this paper. It is believed that all the observed phenomena can be more simply explained by this mechanism than by secondary reduction.

If, as stated by Dr. Watts, when a metal is placed in acid, hydrogen is discharged on (but not necessarily evolved from) its surface, it is difficult to explain how the presence of (neutral) hydrogen atoms or molecules can make the potential more negative (less noble). The latter condition is, by definition, merely an evidence of an increased concentration of electrons (negative charges) on the metal. If this concentration of electrons is sufficient to cause continued hydrogen evolution under the existing conditions, this occurs. If some other reduction is possible at this potential, it occurs. If no electronic reduction can take place, the anodic solution of the metal ceases automatically because no more electrons can flow to the cathodic portions with the existing potentials.

Oliver P. Watts (*Communicated*): In reply to Dr. Blum I would say that I meant displacement without any restriction as to distance. The nature of the process can hardly be altered by the distance which separates the point where an atom

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[20] Chemist, Bureau of Standards, Washington, D. C.

leaves the metal surface and the point at which its equivalent in some other element is deposited as a result of the passing of the first-mentioned atom into solution. I cannot agree with Dr. Blum when he makes the definition of electrochemical action a matter of distance. I contend that all corrosion in aqueous solutions is electrochemical in nature to the extent that it is in accord with Faraday's law, and that the metal atoms carry the same electric charges as when corrosion occurs in the voltaic or electrolytic cell, where it is possible to measure the relationship between the amount of chemical change and of electricity involved. All other conditions being equal, Ohm's law requires that the depositing atom alight as closely as possible to the point where its equivalent of the corroding metal enters solution. The only condition which can ever make displacement occur at a point remote from that at which the displacing atom enters the electrolyte is that deposition is enough easier at the far point to offset the greater IR-drop through the electrolyte to it. I would restrict the term "electrolytic corrosion" to that which occurs when an external electromotive force is applied, as in electroplating and the refining of metals.

The voltaic cell is the standard example of electrochemical corrosion. Its action consists in the corrosion of zinc and the displacement from the electrolyte of an amount of some other element equivalent to the quantity of zinc dissolved. In order that the electric charges carried by the ions may be utilized, it is necessary that the displacement take place on some conductor other than the zinc. Displacement of any constituent of the electrolyte on the zinc results in its corrosion without the possibility of utilizing the electric energy involved in the chemical changes. For this reason our forebears, who originated voltaic cells, chose in the main electrolytes such that slight, if any, continuous displacement on the zinc occurred. If an electrolyte was used from which continuous displacement on the zinc was possible, it was kept from contact with the zinc by a diaphragm or, in one cell, by gravity. In order to secure action when the circuit was closed, a material was chosen for the other electrode (the cathode) such that the driving force of zinc was capable of continuously displacing on it some element from that portion of the electrolyte with which it was in contact.

Although the electric charges carried by the reacting ions cannot be unilized when zinc dissolves in sulfuric acid or when iron is corroded by a solution of copper sulfate, that fact, in the writer's opinion, is not a valid argument for believing that the elements which enter and leave solution under such conditions do not carry electric charges. Faraday's law still holds to the extent that the quantity of material which enters solution is equivalent chemically to that which is displaced. The nature of the process has not been changed by the fact that dissolving and displacement take place on a single piece of metal, instead of on two separate pieces. In the writer's opinion, such corrosion is electrochemical in nature.

As originally stated, Faraday's law included only the relation between the quantity of electric current and the amount of metal deposited. Today it is recognized as of wider application, and it may be stated: "The total of chemical change at the anode, where metals tend to enter solution, equals that at cathodic areas, where elements tend to leave the electrolyte, and at each is proportional to the current, to the time, and to the chemical equivalents of the substances concerned." Faraday's law is a fundamental law of the electrolyte, not merely of the ordinary process of electrolysis, where a current is forced through an electrolyte by application of an external electromotive force. In the dissolving of zinc by dilute sulfuric acid and in the recovery of copper from mine waters by means of scrap iron, the dissolving of the zinc and iron is conditioned on the displacement of their chemical equivalents of hydrogen and of copper, respectively. Stop displacement and you prevent corrosion. This is seen in the writer's experiment with copper in air-free sulfuric acid, where absence of depolarizing oxygen stops continued displacement of hydrogen by copper, and has prevented detectible corrosion of the copper for seven years.

In regard to the academic, yet important, question of whether or not perfectly pure metals, when and if ever obtained, will corrode, it is evident from this paper that electrochemists are divided in their opinions. In the voltaic cell, is the current the cause of the corrosion, is corrosion the cause of the current, or are corrosion and current simultaneously occurring phenomena that have a common origin in the chemical affinities of the reacting substances?

Dr. Blum says, "There can be no corrosion except as there is a difference of potential between two parts of the surface." Others agree with him. On the other hand, is it credible that points of different potential are initially necessary on the surface of a sheet of purest iron or zinc in order that they may be corroded by solutions of platinum chloride or copper sulfate? Will perfect purity prevent corrosion of zinc and copper by nitric acid? Will perfect purity in the metal permit the storage of dilute sulfuric acid in a copper tank that is open to the air? How then can a difference of potential between points on a metal surface be considered the fundamental and prerequisite condition that must be met before corrosion can start? It is true that contact with another metal often stimulates or renders continuous the corrosion of a particular metal; but contact may lessen corrosion of the same metal, depending on the metals and electrolytes concerned.

Dr. Blum takes exception to the writer's statement that when a metal is placed in an acid it begins to displace hydrogen on itself. As a reason for this disbelief he says, "It is difficult to explain how the presence of hydrogen atoms or molecules can make the potential less noble." In place of an explanation the writer will give examples of just such changes in potential produced by hydrogen on the surface of metals: In making up a "hydrogen electrode", so called, a strip of platinized platinum is placed in dilute sulfuric acid of a definite strength and hydrogen is bubbled through the solution. The saturation of the contact surfaces of metal and electrolyte with hydrogen causes the potential of the platinum to become less noble by several tenths of a volt. Such a change of potential by hydrogen is not confined to platinum, but occurred with every metal of Table I, when hydrogen was deposited on it by electrolysis. This is seen on comparing the potentials of the metals with the discharge potentials of hydrogen on them.

A paper presented at the Sixty-seventh General Meeting, held at New Orleans, La., March 21, 1935, Dr. H. S. Lukens presiding.

12

VOLTAIC COUPLES AND CORROSION.[1]

By Oliver P. Watts.[2]

Abstract.

The author presents his views on certain phases of corrosion, and in the experimental part of the paper gives the effect on corrosion of the removal of air from electrolytes in which metallic couples are short-circuited. For the metals and couples used, removal of air stops corrosion.

The electrochemical theory of corrosion now seems to have been adopted as agreeing better with the known facts of corrosion than any of the theories previously proposed. It appears to the author that the concensus of opinion among authorities on corrosion is that in order for corrosion to occur there must be as a prerequisite an electromotive force between the metal and some other conductor in contact with it, or that there be points of different potential on the surface of the metal itself. This view is shown by the quotations which follow.

Bengough and Stuart[3] in presenting the current theory of corrosion say, "These differences in solution pressure are presumed to be due to chemical or physical differences in the condition of the metal, and even in highly purified metal are supposed to be large enough to cause local currents of sufficient magnitude to account for all corrosion phenomena; consequently all corrosion is considered to be of the anodic-cathodic (*i. e.*, galvanic or electrochemical) type, and to result from such currents. An ideally pure and homogeneous metal is presumed to be incorrodible."

"According to the electrolytic theory there can be no corrosion except as there is a difference in potential between two parts of the surface, due either to an initial difference in composition, in physical condition, or in the surrounding mediums."[4]

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[1] Manuscript received February 16, 1934.

[2] Associate Professor of Chemical Engineering, Univ. of Wisconsin, Madison, Wis.

[3] Sixth Report to Corrosion Research Committee, J. Inst. Metals, 28, 54 (1922).

[4] Wm. Blum, Trans. Electrochem. Soc., 52, 432 (1927).

"It now seems justifiable to express the opinion that an absolutely chemically pure metal possessing an absolutely homogeneous surface would not be dissolved by acids."[5]

"In other words, if the metal is free of other elements and absolutely homogeneous, no potential can exist between one point on the surface and another; therefore no current can flow and the metal will not go into solution."[6]

"Acceptance of the electrochemical theory in regard to the corrosion of a specimen in a uniform aqueous electrolyte necessitates, in my opinion, the assumption of the existence of some variation in potential across the metal surface."[7]

The author does not accept this view that voltaic action is essential to corrosion. Contact of one metal with another in an electrolyte usually increases the rate of corrosion of the more active metal. In such cases lessening the area of the more inert metal diminishes corrosion. It does not follow from this, however, that there *must* be a lack of homogeneity in either metal or electrolyte in order that a metal may corrode.

Will perfect purity in the metal and uniformity in the electrolyte prevent corrosion of—

(a) Zinc, copper and silver by nitric acid?

(b) Gold and platinum by aqua regia?

(c) Copper, zinc and iron in dilute sulfuric acid open to the air?

(d) Iron and zinc by solutions of copper sulfate, silver nitrate, platinum and gold chlorides?

(e) Copper, iron and many other metals by an acidulated solution of ferric chloride?

Does increase in purity of the metals lessen the velocity of corrosion in the above cases to such an extent that one is justified in believing that with complete absence of impurities corrosion would cease?

The author finds that the crystals of silver deposited in the electrolytic process of refining that metal dissolve rapidly in nitric acid, although the metal is 999.9 fine. Is it reasonable to conclude that the vigorous attack, which takes place all over the surface, is due solely to the minute traces of foreign materials present, and that the removal of these would render the silver immune to attack by the acid?

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[5] The Corrosion of Metals, pt. II, p. 194, W. Palmaer, Stockholm (1931).
[6] F. A. Rohrman, J. Chem. Education, p. 215 (1933).
[7] W. H. Hatfield, Trans. Electrochem. Soc., 64, 123 (1933).

In reply to inquiry by the author, the Director of the U. S. Mint says, "There does not appear to be a noticeable difference in the rate of solubility of gold between 995. and 999.9."

If corrosion of a metal depends on electric currents generated by voltaic action between the metal and impurities, it is evident that to promote corrosion the impurities must be cathodic to the metal. What metal can constitute the 0.01 per cent of cathodic impurity which causes gold 999.9 fine to dissolve rapidly in aqua regia? What of platinum and other metals of the platinum group? Some one of these must be cathodic to all others, and this metal, even though impure, should be utterly insoluble in all media!

It is unfortunate that generalizations regarding the effect of impurities in metals on their corrosion have been so largely drawn from observations on zinc and iron in non-oxidizing acids and salts. The selection of zinc as a criterion for the behavior of the metals in general is particularly unfortunate. Zinc is relatively active chemically and, except for magnesium and aluminum in certain electrolytes, has a greater potential than other commonly used metals. The discharge potential of hydrogen on zinc is probably greater than on any other metal except mercury.[8] The result of this situation is that any carbon, silicon or metallic impurity present in zinc promotes corrosion to a far greater extent than it could do in most other metals. The impurity affords points on which the discharge potential of hydrogen is much less than on zinc. Besides accelerating corrosion by oxygen depolarization, the low discharge potential of hydrogen on such impurities may change the process of corrosion from oxygen depolarization (type IV, below) to the far more rapid one of visible displacement of hydrogen (type III). With less active metals impurities rarely, if ever, cause such change from one type of corrosion to another more rapid one. This is illustrated by placing in dilute sulfuric acid, but not in contact, a strip of copper and of so-called C. P. zinc or amalgamated zinc, and stirring in a few drops of a solution of platinum chloride. There is visible evolution of hydrogen from the zinc but not from the copper. The discharge potential of hydrogen on platinum from dilute sulfuric acid is greater than the potential of copper but less than the potential of zinc; hence the results observed.

Progress in the natural sciences has been greatly aided by classification of the phenomena of each science; but heretofore this aid has

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[8] Trans. Electrochem. Soc., 64, 139 (1933).

been notably lacking in studying the host of individual cases encountered in the corrosion of metals in aqueous solutions. To supply this lack the author has proposed[9] a classification into which he believes every case of the corrosion of metals in aqueous solutions can be fitted.

CORROSION CLASSIFIED.

Type I. Corrosion without displacement of anything from the corroding solution, e.g., the dissolving of iron or copper by a solution of ferric chloride.

Type II. Corrosion by displacement of a metal, e.g., the dissolving of iron by a solution of copper sulfate.

Type III. Corrosion by visible displacement of hydrogen, e.g., the dissolving of commercial zinc by dilute sulfuric acid.

Type IV. Corrosion by invisible displacement of hydrogen, followed by its physical or chemical removal, e.g., the corrosion of iron by sea water or of copper by dilute sulfuric acid.

These four types of corrosion are not exclusive of each other, but the same piece of metal may be corroding by two or more of them simultaneously. When oxygen or an oxidizing agent is present in the solution, corrosion of type III is always accompanied by type IV, although the latter may contribute only a small per cent of the total corrosion, unless the solution is stirred.

The process of corrosion in voltaic couples does not, in the author's opinion, differ in its nature from the corrosion of a single metal. Except for type I, in either case the metal enters solution only by displacing its equivalent of other cations.

In contending that the presence of voltaic couples is not necessary to corrosion, the author does not mean that voltaic couples and impurities in metals are without effect on corrosion. Far from it! Contact with another metal or introduction of impurities into the metal itself usually localizes corrosion, even if it does not increase its amount. Such contact or impurities may, with certain metals and electrolytes, change the process of corrosion from type IV to type III, thus greatly increasing the rate.

EXPERIMENTS WITH VOLTAIC COUPLES.

The experiments here presented were undertaken to show that voltaic couples may exist in good electrolytes without corrosion of either metal

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[9] Trans. Electrochem Soc., 64, 136 (1933).

provided the oxygen normally present in aqueous solutions be removed. Generally the couples were made by plating a strip of one metal, 4 x 1 cm. with the second metal desired in the couple, although in several cases the two metals were interlocked or soldered.

Several methods of removing air and sealing were tried. In the first method the test tube was nearly filled with the electrolyte, closed by a rubber stopper carrying two glass tubes, the air removed as far as possible by a Cenco Hy-vac pump (supposed to give a vacuum of 0.0006 mm. of mercury, but of course in these experiments never getting below the tension of aqueous vapor), the tube heated while steam was passed into the solution, the stopper removed, the passage of steam continued, and the metal couple dropped in. After further steaming under partial vacuum to remove any air carried down by the specimen, the stopper was lifted, and while steam passed, melted paraffin was poured in to the depth of an inch or more.

Later the dry tubes were coated inside with melted asphalt for an inch (2.5 cm.) where the seal was intended to be, and still later asphalt was used in place of paraffin for sealing. There were many failures, indicated by tarnished spots or dulling of the luster of the polished metal surfaces. Finally pyrex tubes were made by a glass blower. These were 10 in. (25.4 cm.) long, with side tube sealed on 4 in. (10 cm.) from the open end. One and a half inches (3.8 cm.) below the side tube the main tube was bent to an obtuse angle. To use, the tube was partly filled with electrolyte, clamped with the upper end horizontal, the couple inserted, but left lying in the horizontal part of the tube out of the electrolyte. The main tube was then sealed in a flame, the pump applied to the side tube for ten or fifteen minutes and the side tube sealed under vacuum.

The electrolyte was prepared for use by subjecting it to a vacuum in a filtering flask or large pyrex test tube, and passing either carbon dioxide or nitrogen through it for about thirty minutes. Before filling the specimen tube with electrolyte a vacuum was applied to this and it was then filled with the same gas with which the electrolyte had been saturated. The electrolyte was forced in by gas pressure and a stream of gas was passed into the side tube while the main tube was being sealed. Finally the side tube was sealed under vacuum.

Application of the vacuum usually caused boiling of the liquid, and after visible escape of dissolved gas had ceased care had to be taken that the tube was not broken by the water-hammer effect. An inch (2.5 cm.) of electrolyte would be projected against the far end of the tube, and strike with a sharp metallic click. Chilling of the tube was often resorted to to prevent this.

Single metals and over 150 couples were sealed in electrolytes from which the air had been removed as completely as could be achieved by the methods outlined. The metals were polished in order that any corrosion might easily be seen, and all experiments rejected in which a single dark or tarnished spot appeared on a metal surface. In comparison tests in open tubes with electrolytes from which the air had *not* been removed, couples with iron as anodic member showed corrosion in a few hours; with less active metals 20 hours might be required, while with an inert metal like copper a week might elapse before etching of the metal or a blue color in the electrolyte indicated corrosion.

TABLE I.

Corrosion in Sodium and Ammonium Chlorides.

No.	Couple	Electrolyte	pH	Time in Days
36C	Fe-brass	$0.5\ N$ NaCl + CO_2	3.9	232
50C	Fe-brass	$0.5\ N$ NaCl + CO_2	3.9	211
36D2	Fe-Cu	$0.5\ N$ NaCl + CO_2	3.9	232
68D	Fe-monel	$0.5\ N$ NaCl + CO_2	3.9	212
68E	Fe-monel	$0.5\ N$ NaCl + CO_2	3.9	212
3A	Fe	$0.5\ N$ NH_4Cl	6.4	270
77-3	Cu	$0.5\ N$ NH_4Cl + CO_2	4.4	176
77-8	Cu	$0.5\ N$ NH_4Cl + CO_2	4.4	176
3C	Ni	$0.5\ N$ NH_4Cl + steam	6.4	270
83-4	Fe-Au	$0.5\ N$ NH_4Cl + CO_2	4.4	163
83-1	Fe-Cu	$0.5\ N$ NH_4Cl + CO_2	4.4	163
81-8	Fe-Cu	$0.5\ N$ NH_4Cl + CO_2	4.4	166
109-1	Brass-Pt	$0.5\ N$ NH_4Cl + CO_2	4.4	124
109-2	Brass-Pt	$0.5\ N$ NH_4Cl + CO_2	4.4	124
109-3	Brass-Pt	$0.5\ N$ NH_4Cl + CO_2	4.4	124
11A	Cu	$0.5\ N$ NH_4NO_3	5.4	260
52A	Cu-Au	$0.5\ N$ NH_4NO_3 + CO_2	4.4	221

CORROSION IN SODIUM AND AMMONIUM CHLORIDES.

Six couples in which Armco iron was one member were sealed in a sodium chloride solution, 35 g./L., and saturated with carbon dioxide. Removal of air and saturation with carbon dioxide lowered the pH from 5.8 to 3.9. Although this lowering of the pH also lowered the discharge potential of hydrogen, thereby rendering the iron more liable to corrosion, visible corrosion did not take place.

Not only is ammonium chloride the electrolyte most used in commercial primary cells, but it has a well-earned reputation for promoting the rusting of iron and steel. Three metals and nine couples have been sealed in 0.5 N NH_4Cl for periods of 124 to 270 days, without visible evidence of corrosion. Particulars of specimens in these two electrolytes are shown in Table I, along with a few specimens in 0.5 N NH_4NO_3.

THE ACID THEORY OF CORROSION.

One of the several theories which man has devised to explain the corrosion of metals is the acid theory,[1] the immediate predecessor of the present reigning electrochemical theory. Advocates of the acid theory held that in addition to water and oxygen an acid was necessary for the rusting of iron, but that so weak an acid as that resulting from the dissolving of carbon dioxide from the atmosphere was sufficient to cause corrosion.

TABLE II.

0.5 N Sulfuric Acid.

No.	Couple	pH	Days
X	Cu alone	$(N.H_2SO_4)$	3,113
Y	Cu alone	$(N.H_2SO_4)$	3,113
5	Cu-Au	0.65	269
20A	Cu-C	0.65	246
20A2	Cu-C	0.65	246
99-4	Cu-C	0.9	146
101-5	Cu-C	0.65	140
102-1	Cu-C	0.65	138
102-2	Cu-C	0.65	138
102-3	Cu-C	0.65	138
34A	Cu-Pt	0.65	238
75-1	Cu-Pt	0.65	177
75-2	Cu-Pt	0.65	177
75-3	Cu-Pt	0.65	177
104-1	Cu-Pt	0.65	134
104-2	Cu-Pt	0.65	134
104-3	Cu-Pt	0.65	134
106-2	Cu-Pt	0.65	132
36F	Cu-Au	0.9	232
75-14	Cu-Ag	0.9	177
75-15	Cu-Ag	0.9	177
75-16	Cu-Ag	0.9	177

"Dry ice," the solid carbon dioxide now obtainable in many localities, was a convenient source of the gas, and was used as an aid in expelling air from electrolytes and in keeping it out during sealing of the tubes. In most cases the carbon dioxide was pumped out before sealing, but where it is indicated in the tables, the electrolyte was saturated with this when sealed, and whatever corrosive effect this may have was added to that of the original electrolyte.

PLATINUM AND GRAPHITE AS CONTACT MATERIALS.

In 1822 Faraday[10] studied the effect on the rate of corrosion by sulfuric acid of alloying with steel several metals of the platinum group. He found that 1 per cent platinum in steel increased the rate at which it displaced hydrogen from sulfuric acid 200 to 300 fold. Experience since Faraday's time has but enhanced the bad reputation of platinum as a stimulator of corrosion. In applying the Marsh test for arsenic, difficulty is often encountered because of the very slow rate at which the C. P. zinc is attacked by sulfuric acid. Addition of a few drops of a solution of platinum chloride causes a rapid evolution of hydrogen.

TABLE III.

Corrosion in De-Aerated Sea Water.

		Days			Days
101-3	Fe	140	93-1	Fe-monel	156
86-1	Fe	162	93-2	Fe-monel	156
86-2	Fe	162	94-2	Fe-monel	155
109-8	Watch spring	124	94-4	Fe-monel	155
102-4	Brass	138	110-1	Fe-Sea Call	122
109-1	Brass	124	110-2	Fe-Sea Call	122
109-2	Brass	124	119-2	Fe-Sea Call	104
109-3	Brass	124	119-3	Fe-Sea Call	104
102-5	Brass-Au	138	110-3	W. spring-Sea Call	122
102-6	Brass-Au	138	119-1	W. spring-Sea Call	104
102-7	Brass-Au	138	119-4	W. spring-Sea Call	104
102-9	Brass-Pd	138	119-5	W. spring-Sea Call	104
101-1	Fe-graphite	140	107-1	Medley of Metals	127
101-2	Fe-graphite	140			

Contact with graphite and amorphous carbon, the latter the cathode most used today in voltaic cells, is blamed for the rapid destruction of metals in many cases of corrosion.

Couples of copper with platinum, graphite, silver and gold in 0.5 *N* sulfuric acid are shown in Table II, along with a few other combinations. Two specimens of copper in normal acid are included.

To prevent corrosion by the air held in the pores of the graphite rods, these were boiled in paraffin under vacuum, and allowed to cool under the paraffin. The surface of the graphite was then scoured with emery paper and washed with benzol as a preliminary to electro-

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[10] Phil. Trans. Roy. Soc., p. 263 (1822).

plating half its length with copper from a copper sulfate solution. Another type of couple was made by plating each end of the graphite rod (diameter 1.6 mm.) with copper, bending upward each end of a strip of copper slightly longer than the rod, and soldering the upturned ends to the coppered rod.

Iron-graphite couples were made similarly by soldering polished strips of Armco iron to the coppered ends of graphite rods. These were sealed in air-free sea water and are listed in Table III. The iron was in contact with graphite, solder and copper; the copper with graphite and solder. In the manufacture of many dry cells care is taken that no solder gets inside the can, where it would form a couple with the zinc; in these air-free electrolytes no trouble was anticipated from the exposed solder, and none has been experienced.

CORROSION IN SEA WATER.

The corrosiveness of sea water toward iron in its commercial forms has been attested by thousands of cases of the destruction of wrought iron, cast iron and steel. Brass, at present widely advertised for durability, is destroyed by "dezincification" after a few years in sea water. The most remarkable case of voltaic action in modern times, and probably in the entire history of the world, occurred in sea water, and resulted in the scrapping of the half-million dollar yacht, Sea Call, in 1915.

The vessel's plates were made of monel (approximately 70 per cent nickel and 30 per cent copper), but the keel, stem, stern post and rudder frame were steel. Intended to be the world's most durable vessel, voltaic action between these dissimilar electrical conductors, with the water of the Atlantic Ocean as electrolyte, resulted in the perforation of steel 0.75 in. (19 mm.) thick in less than three months, and the yacht was broken up as unseaworthy.

Armco iron, steel watch springs, and one of these coupled with brass, monel, platinum and graphite were sealed in ocean water obtained ten miles at sea off the Maine coast. Not only was iron coupled with commercial sheet monel, but iron and watch-spring steel was soldered (solder left uncovered) to pieces of monel cut from one of the original plates of Sea Call, which had previously contributed its share to the destruction of that expensive vessel. No corrosion is yet visible to the naked eye in the experiments listed in Table III. Exp.

107-1—In a single tube containing air-free sea water the following were placed:

2 watch springs, 2 Armco iron, cold rolled for half their length.
2 Ag, half rolled, half annealed.
1 watch spring, annealed and twisted to a spiral.
1 Armco, rolled, bent flat and straightened.
2 brass, rolled for half its length.
2 stainless iron.
2 monel, half rolled, half annealed.
2 Allegheny metal, half rolled, half annealed.

No corrosion is visible after 127 days.

Sea water loses its corrosive powers for these metals and voltaic couples when deprived of its dissolved oxygen, as far as can be observed by the naked eye and for the duration of these experiments.

THE CORROSION OF METALS AS DOUBLE SALTS.

In the deposition of metals by electrolysis, electrolytes in which the metal is supposed to be present as a double salt are credited with special and peculiar properties:

(a) They are claimed to yield smoother deposits than are obtained from solutions of single salts.

(b) It is frequently possible to plate from these solutions a particular metal which cannot be successfully plated in the solution of a single salt, e.g., the plating of iron and zinc with copper can be done in a cyanide copper solution, but not in the sulfate.

(c) The very process of deposition from double salts has commonly been held to differ from deposition from solutions of single salts in taking place by "secondary deposition,"—some other metal is first deposited, and this then displaces from the electrolyte the metal which constitutes the electroplate.

The author is merely presenting (c) as a view commonly held regarding deposition from cyanide and other double-salt solutions, without believing or upholding it himself. Concerning plating with copper from a cyanide solution, W. E. Hughes says,[11] "At the cathode the potas-

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[11] Modern Electroplating, p. 115, W. E. Hughes, London (1923). Similar views are given in the following: Manuel pratique de Galvanoplastie, p. 75, Andre Brochet, Paris (1908); Electrodeposition of Metals, p. 56, George Langbein, Trans. from the 6th German ed. (1909); Principles of Electrodeposition, p. 185, S. Field, London (1911); Electroplating, p. 200, Barclay and Hainsworth, London (1922); Chem. & Met. Eng., 19, 83 (1918); Industrial Electrometallurgy, p. 51, E. K. Rideal, London (1919); Die elektrolytischen Metallniederschlage, p. 105, W. Pfanhauser, Jr., Berlin (1922).

sium that is set free reacts with the undissociated complex salt and liberates copper, which is deposited on the cathode." With such outstanding differences in the process of deposition credited to solutions of double salts, it might be expected that the dissolving of metals in them would also differ from their solution in other electrolytes.

Sodium cyanide and potassium oxalate were chosen for the formation of double salts. Because of the action of carbon dioxide on cyanide solutions, nitrogen was used instead of that gas as a help in the removal of air. In the former, twelve couples in six tubes and in the latter, only six couples in three tubes have survived, and are listed in Table IV.

These experiments reveal no difference in the nature of the corrosion process in these solutions and in acids and other electrolytes in which single salts are formed. Oxygen or other depolarizer appears to be necessary for corrosion when the discharge potential of hydrogen on the metal, and on any other conductor which touches it, exceeds the potential of the metal itself. Corrosion, in these solutions also, is conditioned on ability of the metal to displace some other cation from the electrolyte.

TABLE IV.

Corrosion of Metals as Double Salts.

In 0.1 *N* NaCN			In 0.1 *N* $K_2C_2O_4$		
		Days			Days
111-10	Ag-Fe	120	121-8	Fe-Au	101
111-11	Ag-Fe	120	121-7	Fe-Au	101
132-5	Ag-Fe	80	133-2	Fe-Au	79
132-4	Ag-Pt	80			
115-3	Ag-Pt	115			
132-3	Au-Fe	80			

For cyanide solutions, this result was anticipated from the practice of aerating the dilute cyanide solutions used in dissolving gold and silver from their ores, and from the proved beneficial effect of removing the air[12] from solutions before applying the reverse process of displacing the precious metals from solution by zinc.

CORROSION IN ALKALINE SOLUTION.

Triethanolamine is an alkaline, organic liquid of high boiling point, which attacks many metals. To nine parts by volume of 0.5 *N* NH_4Cl one volume of triethanolamine was added, and the metals and couples

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[12] The Crowe Process, Chem. & Met. Eng., 19, 283, 652 (1918).

of Table V were sealed in the solution by the usual methods. Nitrogen was used instead of carbon dioxide when the pH of 8.9 is shown. Like ammonia, triethanolamine imparts an intense blue color to aqueous solutions of copper salts. In the absence of oxygen corrosion in this solution was not apparent to the unaided eye.

In solutions of sodium and potassium hydroxide arsenic, antimony, tin and lead dissolve to form arsenites, stannates, etc., in which the metal is supposed to take a position in the acid-radical similar to that of sulfur in sulfates and nitrogen in nitrates. Couples of these with iron and copper, which are less readily attacked by these solutions, are listed in Table V. Nitrogen was used instead of carbon dioxide. Again removal of air prevented corrosion, as observed by the naked eye.

TABLE V.

Corrosion in Air-Free Alkaline Solutions.

In 9 vols. 0.5 *N* NH_4Cl + 1 vol. triethanolamine			In 0.5 *N* NaOH		
		Days			Days
79	Cu	180	128-2	As-Cu	96
85-3	Cu-Ag	166	131-8	As-Cu	85
134-5	Cu-Fe	82	131-9	As-Cu	85
134-4	Cu-Fe	82	128-4	As-Fe	96
134-6	Cu-Fe	82	128-5	As-Fe	96
134-8	Cu-Fe	82	127-6	Sb-Fe	97
			127-7	Sb-Fe	97
			127-8	Sb-Fe	97

All couples numbered above 101 have two specimens in each tube unless stated otherwise.

THE EFFECT OF TEMPERATURE DIFFERENCE.

The blueing was removed from eight watch springs by dipping for a few seconds in concentrated hydrochloric acid containing formalin, the springs were polished, cut to a length of 13⅞ in. (35 cm.) completely immersed in air-free sea water and sealed in four pyrex glass tubes. Nitrogen was used to assist in removing oxygen, and the tubes were sealed under vacuum.

The lower ends of the tubes rested on the bottom of a metal can containing ice-water to the depth of five in. (12.5 cm.), and the upper five in. of the portion of the tube filled with electrolyte was heated to 95° F. (35° C.) by a winding of nichrome wire through which an electric current was passed. The winding was heat-insulated on the outside by sheet asbestos. Inside the asbestos, with its bulb insulated from the winding and tube by a tiny pad of asbestos, a thermometer was placed. The can was set inside a much larger heat-insulated vessel, with two in. (5 cm.) clearance around and beneath the can. This space was kept filled with chipped ice.

A temperature difference of 63° F. (35° C.) was maintained between the end portions of the springs for 26 days with no visible evidence of corrosion.

THE EFFECT OF STRAIN ON CORROSION IN AIR-FREE ELECTROLYTES.

It is well-known that severely cold-worked steel is rendered anodic to the unstrained metal.[13]

Pieces of annealed Armco iron, copper, brass and watch spring were cold-rolled and sealed in the air-free electrolytes indicated in Table VI, in which "thickness" is the ratio of the final to the original thickness. The portion of the watch spring which was rolled was annealed previous to rolling. Experiments numbered 102 and higher carried two specimens, except that 118-5 had three. The total number of specimens was thirty-six.

Specimen 86-1 consists of Armco iron 6 x 0.3 cm. twisted six full turns; 86-2 is 9 cm. long and twisted sixteen full turns.

The Old Bent Spring Conundrum: What becomes of the energy stored in a bent spring when the spring is dissolved in acid? The usual answer is that it appears as extra heat of solution, and that the potential of the bent spring is greater than that of the unbent spring. In Exp. 118-5 three short pieces of watch spring were bent opposite to the natural curvature of the spring until the two parts touched and were tied in this position. The ends beyond the thread were unstrained while at the middle of the loop the steel was under severe strain. After 62 days one spring broke. Is not this a case of embrittlement caused by absorption of *invisible* hydrogen? No corrosion was visible to the unaided eye after sixty-six days.

THE EFFECT OF SURFACE FINISH.

It is generally believed that a rough metal surface corrodes more readily than a smooth surface. U. R. Evans says,[14] "There seems to be no doubt that the general effect of polishing is to diminish corrosion. Common experience has taught that polished articles exposed to the ordinary atmosphere start to corrode at places where the surface has been scratched or indented."

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[13] Trans. Electrochem. Soc., 13, 32 (1908); 33, 176 (1918).

[14] The Corrosion of Metals, p. 141.

A contributing factor in the more rapid corrosion of rough than of smooth metal is the lower discharge potential of hydrogen from the rough surface. In normal sulfuric acid the discharge potential of hydrogen was found to be from 1 to 60 millivolts lower on a rough than on a smooth surface, depending on the metal. In sodium sulfate the maximum and minimum differences were 200 and 2 millivolts for a larger list of metals.[15] With some metals this difference is too small to have a noticeable effect on the rate of corrosion, except as corrosion of type IV is increased by the enlarged surface produced by roughening; but the larger changes might in some cases alter the corrosion process from type IV to type III, with a great increase in rate.

TABLE VI.

The Effect of Strain on Corrosion.

No.	Metal	Electrolyte	Thickness	Time in Days
86-1	Iron	Sea water	....	166
86-2	Iron	Sea water	....	166
109-8*	Watch spring	Sea water	0.6	128
104-4	Copper	0.5 N H_2SO_4	0.20	138
104-5	Copper	0.5 N H_2SO_4	0.15	138
104-6	Cu-Pt	0.5 N H_2SO_4	....	138
105-4*	Copper	0.5 N H_2SO_4	0.16	136
102-7	Brass	Sea water	....	142
103-1	Brass	Sea water	0.41	140
105-5	Brass	Sea water	0.09	135
109-1	Brass	Sea water	....	128
109-2	Brass	Sea water	....	128
109-3	Brass	Sea water	....	128
118-5	Watch springs	Sea water	Bent	111

Strips of polished metal were ground on an emery wheel for an inch (2.54 cm.) at one end and sealed in air-free electrolytes. Exp. 104-11 consists of such strips of Armco iron and watch spring in sea water. There has been no corrosion visible to the naked eye in 93 days. The two experiments starred in Table VI combine the effect of cold work with a roughened surface on a portion of the specimen.

No experiments have been made on differences in concentration. In normal sodium sulfate the potential of iron as measured in the presence of air lacks 0.4 volt of being able to displace hydrogen on itself.[16] In sea water in the presence of air the relationship is probably about the same.

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[15] Trans. Electrochem. Soc., 64, 139 (1933).

[16] Trans. Electrochem. Soc., 64, 139 (1933).

WATERLINE CORROSION.

Localized corrosion at or near the waterline is often observed in the case of metals partly immersed in electrolytes for considerable periods, and is referred to as waterline corrosion. In thirteen of the experiments listed in preceding tables the metal projected above the waterline. The failure of corrosion to be observed may indicate that when corrosion of type IV is stopped by removal of oxygen, whatever other influences ordinarily produce waterline corrosion are no longer able to cause this variety of corrosion. The experiments are: 99-4, 101-4-5, 102-1-2-5-6-7, 103-1, 104-3-6, and 105-1-2.

METAL-OXIDE COUPLES.

It was thought that metals coupled with conducting oxides in air-free electrolytes should be corroded to a limited extent at once. A few couples of metal with lead peroxide were made and sealed under vacuum.

Exp. 106-1. Two strips of copper were plated on one end with lead peroxide by using as anode in a solution of sodium plumbite, and sealed in 0.5 N H_2SO_4. When the seal was finished the copper was found to be etched in a narrow band above the lead peroxide. The remainder of the copper has kept its polish for 88 days.

Exp. 109-4. Two strips of cold-rolled brass were annealed for a third of their length, a part of the other end plated with lead peroxide, and sealed in air-free sea water. As soon as sealed a line of copper showed next the lead peroxide, due to dezincification. There has been no further visible evidence of corrosion in 133 days.

Exp. 109-5. Two strips of iron were plated with lead peroxide for three minutes at 0.06 amp. each (current density $= 2$ amp./dm.^{2}) and sealed in sea water. The iron was immediately tarnished for an inch above the lead peroxide, but no rust has appeared in 128 days.

THE TESTIMONY OF AMALGAMATED METALS.

The remarkable effect on the corrosion of zinc in acids produced by amalgamation has been known for a century and profitably utilized in voltaic cells. Explanations for this effect are:

"Faraday explained the effect of impurities in zinc in causing it to dissolve in acid in the following lucid terms: 'The cause is that when ordinary zinc is acted on by dilute sulfuric acid, portions of copper, lead, cadmium and other metals which it may contain are set free upon its surface; and these, being in contact with the zinc, form small but very active voltaic circles, which cause great destruction of the zinc and evolution of hydrogen, apparently on the surface of the zinc, but really upon the surface of these incidental metals. . . . It is probable that the mercury acts by bringing the surface, in consequence of its fluidity, into one uniform condition and preventing those differences in character between one spot and another which are necessary for the formation of the minute voltaic circuits referred to.'[17]

"By the very nature of local action we should naturally expect such a remedy as that of amalgamation to be ineffective, for the process consists practically in adding an electro-negative impurity to the zinc. The protection afforded by mercury is often said to be due to a film of hydrogen which is formed by local action, and which adheres to the amalgam, thus preventing the liquid from coming into close contact with the plate. If this were really so, it is difficult to see why the electrolyte should be able to come into closer contact when the circuit is closed, and therefore why voltaic action should take place at all.

"It has been suggested by Grove[18] that the protection is due to polarization, the hydrogen that is evolved combining with the mercury and rendering it electropositive."[19]

If the protection afforded by amalgamation is due to the production of a uniform surface, the presence or absence of oxygen should have no effect; if due to a polarizing film of hydrogen, in the presence of oxygen, corrosion should continue. Because of the color imparted to aqueous solutions by small amounts of dissolved copper, this metal was chosen for amalgamation in preference to zinc.

Exp. 139-1. A sheet of copper was heavily amalgamated and suspended horizontally in 0.5 *N* H_2SO_4, open to the air. In 24 hours a drop of the acid gave a faint blue color with ammonia. In five days the acid was very faintly blue, and in seven days it was distinctly blue. Amalgamation was perfect and brilliant at the end of the test.

Exp. 139-2. A similar piece of copper was placed in a solution of 9 volumes of 0.5 *N* NH_4Cl plus 1 volume triethanolamine. In 24 hours the solution was blue, and in a week the blue was extremely intense. The amalgamation appeared to be perfect.

However uniform the surface of amalgamated metals may be, this uniformity does not prevent corrosion of type IV, by oxygen depolarization.

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[17] Essays on the Art and Principles of Chemistry, p. 168. H. E. Armstrong.

[18] Phil. Mag. 3rd series, 15, 81 (1839).

[19] Primary Batteries, p. 25, W. R. Cooper, London (1916).

CONCLUSION.

The term air-free as used in this paper means that the electrolyte has been subjected to the processes described for removal of air.

Whether corrosion of metal takes place in a solution of sodium chloride, ammonium chloride, sea water, sulfuric acid or alkali, or the metal dissolves as a double salt, these experiments disclose no difference in the nature of the corrosion process—as far as can be detected with the naked eye, removal of air prevents corrosion. In these particular cases, either for a single metal or for a couple of two or more metals in contact, *corrosion appears to depend on the ability of the metal to displace hydrogen from the electrolyte.*

Oxygen is the depolarizer generously and universally supplied by Nature. Although necessary to man, this supply of oxygen greatly shortens the useful life of many metals. Were free oxygen absent from the world, the author believes that steel ships and other metallic structures exposed to the ocean would never need painting or application of other protective coating, but, unprotected, would last indefinitely, so far as corrosion by sea water itself is concerned.

ACKNOWLEDGMENT.

The author gratefully acknowledges his indebtedness to the Wisconsin Alumni Research Foundation for relief from teaching duties, which has made this research possible. For help with a portion of the experimental work the author is indebted to J. O. Iverson and Geo. W. Thompson, C. W. A. Research Assistants.

DISCUSSION.

COLIN G. FINK[20]: Dr. Watts, when you say the potential difference between two metals was as much as 0.8 volt, I assume you made that measurement in sealed oxygen-free tubes—is that so?

O. P. WATTS: No.

COLIN G. FINK: You assumed that this 0.8 volt which you obtained in the presence of air applies likewise in the absence of air. Is that right?

O. P. WATTS: I would not say that if I measured and found 0.8 volt in air and then applied a vacuum and pumped the oxygen out, I would have exactly 0.8 volt, but I will guarantee that we still have a difference in potential.

COLIN G. FINK: But potential alone does not suffice! There must be chemical, electrochemical action. Without electrochemical action, no voltaic action, and therefore no "voltaic couples".

F. A. ROHRMAN[21] (*Communicated*): It is not my intention to take issue with the author on his very conclusive evidence relating to the importance of oxygen in

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[21] Asst. Prof. of Chemistry, Michigan College of Mining and Technology, Houghton, Mich.

corrosion reactions. I think it is the consensus of opinion among electrochemists that oxygen is necessary for certain corrosion reactions. I do disagree with the author, however, when he states that voltaic couples are not necessary for corrosion.

A piece of metal, say iron, when placed in sea water, tends to corrode. According to the orthodox electrochemical theory of corrosion, differences in potential exist on the surface of the metal due to differences in homogeneity or purity. In the early part of his paper Dr. Watts states that he does not accept this view.

It is difficult for me to visualize or conceive of any solution of metal taking place if there was not a greater solution tendency for one atom than its neighbors. If the atoms are all identical, and under the same environment, then each atom would have just as great a tendency to remain as metal rather than ion, consequently no corrosion could possibly occur. If a Maxwell's demon could be created and instructed to crawl over the surface of the submerged metal and plug his voltmeter from groups of atoms to groups of atoms, he might settle this question easily. This was done on an enlarged scale by Fink and Kenny[22] when they explored the surfaces of submerged metals with a fine capillary-calomel cell and found differences in potential existing over the surfaces. I believe that the author will agree that a corroded metal is always corroded non-uniformly. Microscopic examination will show a pitted or striated structure. This is true for the pure as well as the impure metal, indicating the greater and lesser tendencies toward solution that must prevail.

As for getting a metal free from impurities and absolutely homogeneous, that is another question. It so happens that different crystal faces of the elements have different potentials, thus one plane will have a greater tendency to go into solution than another plane. Just because a metal of great purity has been prepared does not necessarily connote that the metal will not go into solution. The local action couples also exist due to differences in physical make-up. In answer to the author's questions on page 236, I should say that perfect purity (actually a hypothetical state) will not prevent the corrosion of the metals in the media mentioned, due to the influences of the differences in physical conditions just mentioned.

The author has cited numbers of experiments with different couples he has constructed showing no corrosion in the absence of oxygen. I hardly feel this is convincing proof for the non-acceptance of the local action theory. Just because there is no corrosion is hardly reason for discarding this theory. Corrosion indicates that current has passed, but just because no current has passed is no proof that a potential between two couples did not exist. The potentials between couples were undoubtedly opposed by polarization potentials which, in turn, can be reduced to nil by circulation and the presence of depolarizers such as oxygen. In conclusion, may I ask one question? Was any attempt made to measure the potentials between couples in the solutions in the absence of oxygen? A definite potential should exist for each experimental couple.

M. deKAY THOMPSON[23]: Before discussing "corrosion" it would be well to define what is meant by this term. According to Funk and Wagnalls' dictionary, corrosion is "the action of eating or wearing away by slow degrees," and that is the usual technical meaning. However, this word is also frequently extended to include the rapid solution of metals in strong acids. The second is the meaning adopted in this paper, and in the following remarks.

Professor Watts seems to me to be inconsistent in the statements on page 236 that he "does not accept this view that voltaic action is essential to corrosion," and on the last page that "corrosion appears to depend on the ability of the metal to displace hydrogen from the electrolyte," for this displacement of hydrogen is voltaic action. This last statement is also inconsistent with (e) of page 236 where it is pointed out that corrosion of "copper, iron and many other metals" is produced by an acidulated solution of ferric chloride, for the assumption of the deposition of hydrogen ions is not necessary to explain corrosion in this solution.

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[22] Trans. Electrochem. Soc., 60, 235-65 (1931).

According to the electrolytic theory, corrosion depends on the ability of a metal to go into solution as ions, which means it must deprive some other ions of their charges. Whether these are hydrogen or ferric ions, or any other kind, makes no difference. Usually it is hydrogen ions that are involved because they are the most easily dischargeable cations present.

The presence of oxygen is necessary for corrosion only when the free energy decrease of the reaction $M + \nu F = M^{\nu +}$ is not sufficient to deposit hydrogen from the solution at atmospheric pressure. In the case of iron, this free energy decrease is enough to deposit hydrogen on itself from strongly acid solutions where the activity of the hydrogen ions is high. In neutral solutions the free energy decrease of this reaction is able to deposit hydrogen on iron only at pressures less than one atmosphere; consequently the solution of iron is slowed down because it takes time to remove the hydrogen by diffusion and depolarization by oxyyen. Various other variables affect the rate of corrosion, such as the hydrogen overvoltage of the corroding metal or of any metal in contact with it, the electrolytic potential of any other metal in contact, the conductivity of the solution in which corrosion takes place, and whether protecting scale is formed. This paper shows a number of metal couples which have not enough difference in potential to deposit hydrogen on the more electropositive metal, and therefore do not corrode in the absence of oxygen.

It is purely a matter of fact, and not of theory, that some metals can dissolve in acids and deposit hydrogen at atmospheric pressure.

Professor Watts quotes without approval a number of opinions to the effect that "an absolutely chemically pure metal possessing an absolutely homogeneous surface would not be dissolved by acids," and points out that pure metals do dissolve. There can be no such surface as this, however, any more than there could be a rope equally strong at all points, for it would either never break under tension, or would break into the molecules of which the rope is made. Such speculations, therefore, do not prove that voltaic action is not present when a pure metal dissolves.

I would like to add that recently I have come across an interesting paper published by Humphrey Davy, in 1824, on "The Corrosion of Copper Ship Bottoms,"[24] in which he implied the electrolytic theory of corrosion. He protected ship bottoms by placing them in contact with zinc, and showed that copper does not corrode in sea water in the absence of oxygen. It seems to me that he has covered the fundamentals of corrosion pretty well in that early paper.

G. D. **Bengough and F. Wormwell**[25] (*Communicated*): It seems to us that the question raised by Professor Watts as to the necessity for a variation of potential along a metallic surface, if corrosion is to occur, may be answered as follows:

1. Potential differences are usually present when corrosion occurs, and may be due to the presence of local variations in either the metal (e. g., due to difficult phases or strains) or in the environment (e. g., concentration differences).

2. Potential differences are not always the *sole* requirement, a depolarizer may be necessary.

3. In the presence of powerful oxidizing agents several highly purified and annealed metals have been found to corrode with a speed that is of the same order as that of less highly purified and unannealed metals. It seems to follow either that small and not easily detectable potential differences are sufficient to start corrosion under otherwise favorable conditions, or that such differences are not necessary.

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[23] Prof. of Electrochemistry, Massachusetts Institute of Technology, Cambridge, Mass.

[24] Proceed. Royal Soc., Jan. 22, 1824. Annales de Chim. et Phys., **29**, 187 (1825). Collected Works of Sir Humphrey Davy, Vol. 6, London, 1840, p. 273. On page 275 we find: "Copper in sea water deprived of air by boiling or exhaustion, and exposed in an exhausted receiver or an atmosphere of hydrogen gas, underwent no change."

[25] Dept. of Scientific and Industrial Research, Chemical Research Laboratory, Teddington, Middlesex, England.

4. It is probable that a choice between these alternatives cannot be made with certainty until it is possible to experiment on an atomic scale, since differences on such a scale may suffice to start corrosion.

If the decision is made that some potential difference is necessary, the amusing question has been propounded by Professor Riley and others, how does the last, and presumably, most cathodic atom of a metal enter solution? Or does it wander forever alone and inviolable?

Our own opinion may be expressed as follows: Corrosion of immersed metals is an oxidation process which usually takes an electrochemical course and is, therefore, associated with differences of potential and the spatial separation of electrodes; we cannot say at present that this is the only possible course. In actual experiments there will usually be sufficient potential differences present along a metallic surface to produce corrosion in conditions otherwise favorable.

Amongst Professor Watts' interesting experiments we find one that is rather surprising, namely, the absence of attack by NH_4Cl on iron either alone or coupled with gold or copper. We have found that when a piece of turned mild steel was exposed to $0.5N$ NH_4Cl solution in the presence of air-free argon, corrosion occurred with evolution of hydrogen gas. The corrosion/time curve was of parabolic form, which seemed to be due to the gradual building-up of an inhibiting film of ferrous hydroxide. On the admission of oxygen to the corrosion vessel, a great increase in the rate of hydrogen evolution occurred and oxygen absorption began; no doubt the oxygen destroyed the inhibiting film. No less than 15 ml. of hydrogen were collected before the admission of the oxygen, or about 150 times the amount detectable in the apparatus used, so that the result is not in doubt. The appearance of the metallic surface had slightly darkened before the admission of the oxygen.

We note that Professor Watts' specimens were polished and not turned like ours, and this may have affected the overpotential of the metal; he used carbon dioxide instead of argon, so that his corroding liquid had a pH value of 4.4, and was much more acid than ours (about 6.5), but this would encourage hydrogen evolution. Possibly the carbon dioxide had some film-forming effect, or perhaps hydrogen evolution was not detectable by the method used.

We can confirm Professor Watts' experiment on the action of sea water on iron in the absence of oxygen. We could observe no hydrogen evolution when mild steel was exposed to sea water beneath argon for a prolonged period; this is the more surprising because a notable proportion of the total corrosion in presence of air is due to hydrogen evolution.

O. P. WATTS (*Communicated*): Since 170 days have elapsed since this paper was presented, the times given in the tables may be increased by this amount,—except for Nos. 121-7 of Table IV, 128-4 and 5 of Table V, and 86-2 of Table VI, which now show corrosion.

As further evidence of the prevailing view regarding the cause of corrosion, C. L. Mantell[26] says, "An essential condition for electrochemical corrosion is some departure from uniformity, such as in a metallic article of a heterogeneous character on a coarse scale through contact of dissimilar metals and on a fine scale through contact of alloy constituents, or by the unequal access of oxygen to different parts of the metallic article."

Lest it be thought that whether or not voltaic couples are necessary for corrosion is of small importance, the author would point out that on the answer to this question depends the direction in which the metallurgist should work in order to produce corrosion-resistant metallic materials. If all types of corrosion are due to voltaic couples, it is obvious that purity in metals should be the first aim of the metallurgist, and when perfect purity is attained, one metal will be as good as another for resisting corrosion. On the other hand, if corrosion can take place without the presence of voltaic couples, perfect purity in metals offers no hope, and the metallurgist should direct his efforts to the compounding of impure metals,—

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[26] Industrial Electrochemistry, p. 99, McGraw-Hill Book Co., New York and London (1931).

alloys which will be protected by film formation in the particular electrolyte in which resistance to corrosion is desired. In corrosion of type III voltaic couples may have a great effect on the rate of corrosion, but in type IV their effect is usually negligible except as the surface exposed to the electrolyte is increased or made rougher.

In the opinion of Professor Rohrman and many others, cathodic areas in contact with a metal are absolutely necessary to corrosion. These cathodic areas may consist of another metal, impurities in the metal itself, portions of the metal surface in contact with a part of the electrolyte which differs from the main body in material, concentration, content of dissolved oxygen, or in temperature.

In corrosion by oxygen-depolarization, the type which causes the major part of the damage due to corrosion, all that such a cathode surface does is to furnish a portion only of the surface on which depolarization of hydrogen takes place. In the case of iron in contact with copper in sea water, not only is hydrogen deposited on the copper and removed therefrom by oxygen, but the same process occurs on the surface of *metallic* iron as distinct from any impurities in it. This is indicated by the experiments of Whitman and Russell[27] on the corrosion in natural waters of bare steel and of the same three-fourths plated with copper. The rate of corrosion of the steel was unchanged, although plating with copper must have increased the cathode area at least twenty-five fold. The author has measured the corrosion in half-normal ammonium chloride of Armco iron, 5 x 30 mm., half-plated with copper, and of pieces 5 x 60 mm. with the same area of copper plate as in the smaller specimens. Addition of an area of iron equal to that of the original half-and-half specimen doubled the loss in weight by corrosion. Here, again, corrosion is proportional to the total surface of the couple, regardless of the proportion between the two metals. Increase of the iron surface was just as effective in promoting corrosion of this couple as would have been the addition of an equal area of copper.

If, as is generally believed, corrosion of the iron is due solely to voltaic action between the iron as anode and the impurities in it, plus similar action of any cathodic metal also in contact with the iron, the one per cent or less of impurity in the iron must be a hundred times as effective per unit of surface exposed as is copper. In the author's other paper presented at this meeting, on the effect of arsenic in corrosion, it is shown that in sea water corrosion is practically the same whether the iron is bare or is half-plated with gold, silver, copper or arsenic. When equal areas of these different cathodic materials produce the same effect on the corrosion of iron in contact with them, it would be strange indeed if the impurities in Armco iron were a hundred times as potent as copper in accelerating corrosion by oxygen-depolarization. There seems no escape from the conclusion that in natural waters, sea water, ammonium chloride, and probably also in similar neutral solutions of sodium and potassium salts, the surface of the iron itself is as effective in promoting depolarization by dissolved oxygen as is an equal surface of copper or of the impurities normally present in commercial iron. It follows that in the case of an iron-copper couple in sea water, where the total exposed surface of copper and impurities in the iron equals the area of metallic iron, if it were possible to remove all cathodic areas, thereby cutting the surface of the specimen in half, this would reduce corrosion of the iron only fifty per cent. How, then, can contact of iron with some cathodic conductor be considered necessary to corrosion?

Professor Rohrman contends that, even if all impurities were removed from a metal, differences in strain and differences of potential of crystal faces are sufficient to account for the continuing of corrosion in the cases of page 236 of this paper.

The author cut strips of annealed copper and of annealed "Horse Head" zinc (the latter noted for its purity), cold-rolled one end to twenty per cent of its original thickness, bent to a U-shape, and immersed both ends simultaneously in electrolytes having more noble metals in solution. The zinc was plunged into an

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[27] Ind. Eng. Chem., 16, 276 (1924).

acidified solution of copper sulfate and withdrawn as quickly as possible. In the fraction of a second that the zinc was in contact with the liquid, copper was deposited on both ends as a black coat which was easily rubbed off. No difference could be detected between the two coatings. Similarly, but more slowly, coats of silver were produced on the copper from solutions of silver nitrate and of the double cyanide of silver and sodium. Like hydrogen in corrosion by oxygen depolarization, in this corrosion of type II metal is deposited on anodic as well as on cathodic areas—and cathodic areas can be no more necessary for corrosion here than in corrosion of type IV.

Twenty years ago this deposition of metal by immersion on anodic surfaces proved most disappointing to the inventor of a process for operating plating shops without dynamo, motor, cables, or the customary anodes, thus making a great saving in the capital invested. In this simplified practice the articles to be plated were placed in a plating barrel with pieces of a magic alloy, covered with plating solution, and the barrel slowly revolved, when the articles became plated with metal from the solution. It was claimed that the alloy did not become coated with metal; but in tests by the author, this and all other alloys which the inventor could furnish became coated with metal and ceased to function.

A month ago another scheme for plating by use of a metal more active than that which it is desired to deposit was sent to the author for testing. This has a better chance for financial success than the other, since the anodic metal is a powder, and the process is intended merely for patching places where electroplate has worn off from large apparatus, and the interruption of service and cost of sending parts to a plating shop would be a serious matter.

Professor Rohrman says, "It is difficult for me to visualize or conceive of any solution of metal taking place if there is not a greater solution tendency for one atom than its neighbor." If the author's classification of corrosion is correct, except for type I, all corrosion is by displacement from the corroding solution of an amount of hydrogen or metal chemically equivalent to the metal which dissolves. Since atoms enter solution individually and not in groups, the author fails to see how similarity of an atom with its neighbors can prevent that particular atom from displacing from solution a metal more noble than itself. Zinc dust precipitates gold and silver from solution quite as readily as does sheet zinc. If a particle of zinc dust could be comminuted to atoms, would its power of precipitating gold and silver be lost? If its action depends on the presence of voltaic couples we must conclude that single atoms of zinc could not precipitate gold and silver, although millions on millions of dollars worth of gold recovered by the corrosion of zinc has been precipitated by the action of zinc, atom by atom.

There remains as the cause of that voltaic action which is supposed to be the root of all corrosion, the "difference in potential of different crystal faces of the elements." How tremendous must this be to account, in the main, for the violent action of sodium on water!—sodium, a metal so pure that no detectable residue remains when much of the metal is dissolved in water, and a soft, cast metal in which strains should be at a minimum. How minute, if not really zero, must be the differences in potential of different crystal faces of iron and copper, built on the equi-axed cubic system!

If contact of copper with iron (e.m.f. = 0.26) does not increase the total of corrosion in sea water more than does contact with a piece of iron of the same size, how can the infinitesimal e.m.f. between the crystal faces of iron be held responsible for the corrosion which occurs? The hypothesis of an e.m.f. between the crystal faces of metals lends but feeble support to the theory that voltaic couples are necessary for the corrosion of metals.

Of the several possible explanations mentioned by Dr. Bengough for the evolution of hydrogen in his experiments with iron in oxygen-free ammonium chloride and its absence in the author's experiments, the difference in overpotential (discharge potential of hydrogen) on rough and on smooth metal appeals most to the author,—who found it necessary to polish the cut edges of certain metals in order to prevent evolution of hydrogen there. Regarding the evolution of hydrogen by iron in ammonium chloride,—in one experiment the test tube was sealed by a layer of paraffin an inch (25.4 mm.) thick. After fifteen months no gas can be seen, even when the tube is inverted.

May not the evolution of hydrogen observed by Dr. Bengough with iron in sea water, open to the air, be due to a lowering of the discharge potential of hydrogen as a result of the roughening of the iron? As corrosion proceeds by oxygen depolarization there is added to this, corrosion by visible displacement of hydrogen.

O. P. WATTS (*Communicated*): Professor Thompson points out what he terms inconsistencies. To prove the first he says, "for this displacement of hydrogen is voltaic action." Does he mean with or without voltaic couples as a necessary preliminary to displacement? If the former, his view is the same as those quoted at the beginning of this paper; if the latter, this would seem to be a new and private definition of voltaic action, and is not acceptable until it has been generally adopted and approved by usage. The second apparent inconsistency is produced by Professor Thompson's omission from the second quotation of that portion of the sentence which limited the author's statement to particular experiments, all of which are of types III and IV. The complete sentence is not in conflict with the third quotation, which concerns corrosion of type I only.

The author is in agreement with Professor Thompson's statement, "Corrosion depends on the ability of a metal to go into solution as ions, which means that it must deprive some other ions of their charges." In different words, this is the substance of Faraday's law as it applies to corrosion and appears in the Transactions of this Society.[28]

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[28] Trans. Electrochem. Soc., 64, 152 (1933).

A paper presented at the Sixty-seventh General Meeting, held at New Orleans, La., March 21, 1935, Dr. H. S. Lukens presiding.

13

EFFECT OF ARSENIC ON THE CORROSION OF IRON BY SULFURIC ACID.[1]

By Oliver P. Watts.[2]

Abstract.

Tests are reported on the effect of arsenic on the rate of corrosion of iron alone and when coupled with other metals in dilute sulfuric acid and in sea water. It is only when it is dissolved in the electrolyte that arsenic inhibits the corrosion of iron, and it has this effect only in solutions in which iron dissolves mainly by visible displacement of hydrogen. It is without effect on the corrosion of iron by oxygen depolarization.

It has been known for many years that the addition of arsenic to sulfuric acid greatly lessens attack of iron and steel by the acid. Along with the experiments on the effect of removal of air on the corrosion of metals and couples in several electrolytes,[3] a number of experiments were started with iron, and couples of iron and arsenic in sulfuric acid containing arsenic. After more than a year had elapsed the specimens were weighed, and the results are reported for the first time in Table I. The couples were formed by plating the 4 x 1 cm. pieces of armco[4] iron for half their length with the other metal. The specimens were submerged in the electrolyte in test tubes, which were either open to the air or sealed. Before sealing, the air was exhausted by an air pump as previously described.[3] A comparison of the loss of weight in the open and in the sealed tubes shows the usual effect of excluding oxygen where hydrogen is not visibly displaced from the electrolyte by the metal —corrosion is reduced to a negligible amount. This absence of corrosion in the sealed tubes indicates that arsenic in the acid has in some manner stopped corrosion of the iron by visible displacement of hydro-

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[1] Manuscript received February 20, 1935.

[2] Assoc. Prof. of Chemical Engineering, Univ. of Wisconsin, Madison, Wis.

[3] See page 235 of this volume.

[4] An American Rolling Mill product, very low in impurities: Si, 0.002; S, 0.02; P, 0.005; C, 0.1; Mn, 0.02; Cu, 0.03.

gen, the process which is ordinarily responsible for the major portion of the corrosion which occurs in acid of this strength. In the experiments of long duration open to the air, arsenic has failed to prevent corrosion of the iron.

To obtain more definite information than was afforded by these experiments, a series of short-time experiments has recently been carried out in electrolytes open to the air. Results are recorded in the tables which follow.

TABLE I.

Effect of Arsenic on the Corrosion of Iron in Sulfate Solutions, With and Without Access of Air. Also of Iron Half-plated With Arsenic.

Expt. No.	Metal	Time (days)	Electrolyte	Air	Loss g.	Loss Mg/cm.²
1	Fe	385	$N.H_2SO_4 + .5$ g./L. As_2O_3	None	0.0022	0.28
2	Fe	385	$N.H_2SO_4 + .5$ g./L. As_2O_3	"	0.0014	0.18
3	Fe	368	$N.Na_2SO_4$	"	0.0002	0.03
4	Fe	375	$N.Na_2SO_4$	"	0.0008	0.10
5	Fe	375	$N.H_2SO_4 + .5$ g./L. $As_2O_3 + NaAsO_2$	Saturated	0.1365	17.0
6	Fe	375	$N.H_2SO_4 + .5$ g./L. $As_2O_3 + NaAsO_2$	"	0.1235	15.4
7	Fe	357	$N.H_2SO_4 + .5$ g./L. As_2O_3	"	0.2788	34.9
8	Fe	356	$N.H_2SO_4 + .5$ g./L. As_2O_3	"	0.4174	52.2
9	Fe	375	$N/2\ Na_2SO_4$	"	0.1240	15.5
10	Fe	375	$N/2\ Na_2SO_4$	"	0.1428	17.8
11	Fe	364	$N/2\ Na_2SO_4$	"	0.1830	22.8
12	Fe	364	$N/2\ Na_2SO_4$	"	0.1843	23.0
13	Fe-As	357	$N/2\ H_2SO_4$	"	0.2557	32.0
14	Fe-As	357	$N/2\ H_2SO_4 + As_2O_3$	"	0.3505	43.8
15	Fe-As	357	$N/2\ H_2SO_4 + As_2O_3$	"	0.3912	48.9

Inspection of Table II shows that addition to half-normal sulfuric acid of 0.5 g./L. of As_2O_3, which does not entirely dissolve, cuts corrosion to 5-10 per cent of the original value in the case of iron; has no effect with copper (which is incapable of displacing hydrogen visibly from the acid) and increases the corrosion of cadmium, as it is also known to do with zinc.

Whether iron in half-normal sulfuric acid is coupled with arsenic, antimony, copper, gold or silver, corrosion is practically the same. Platinum produces a slight acceleration, and tin alone of the metals tested protects iron by contact with it. It is only when arsenic is a constituent of the electrolyte that it protects iron from corrosion by acids. Careful inspection of the cathodic elements of the couples failed to show any arsenic on them, although the presence of arsenic on the iron was proved. When an iron-silver couple is dropped into a solution of copper sulfate, copper is deposited on both silver and iron. When electroplating articles composed of several metals whose potentials differ considerably, there is usually difficulty in plating over some of them, the preference being for the deposit to form on the more noble metal.

TABLE II.

Corrosion in N/2 H_2SO_4 Without and With 0.5 g./L. As_2O_3.

Single metals 5 x 30 mm., couples formed by crimping together the two metals, except that arsenic, gold, antimony and platinum are plated on copper. Air saturated solutions.

Expt. No.	Metal	In N/2 H_2SO_4			In N/2 $H_2SO_4 + As_2O_3$		
		Time	Loss in grams	Loss Mg/cm.^{2}	Time	Loss in grams	Loss Mg/cm.^{2}
16	Fe	25 hr.	0.0254	8.4	25 hr.	0.0010	0.33
17	Fe	24 hr.	0.0229	7.6	24 hr.	0.0005	0.17
18	Fe	24 hr.	0.0264	8.8	24 hr.	0.0005	0.17
19	Fe	24 hr.	0.0257	8.6	5 days	0.0012	0.40
20	Fe	24 hr.	0.0267	8.9	......	.....	...
21	C. I.	24 hr.	0.1845	..	24 hr.	0.0002	...
22	C. I.	28 hr.	0.2150	..	28 hr.	0.0013	...
23	Cd	3 days	0.0033	1.1	3 days	0.0151	5.0
24	Cu	7 days	0.0036	1.2	7 days	0.0039	1.3
25	Cu	24 hr.	0.0007	0.2	......	.....	...
26	Fe-Cu	24 hr.	0.3689	61.5	24 hr.	0.0003	0.05
27	Fe-Cu	24 hr.	0.3411	56.8	24 hr.	0.0003	0.05
28	Fe-Au	24 hr.	0.4027	67.1	24 hr.	0.0006	0.10
29	Fe-Au	24 hr.	0.3887	64.8	24 hr.	0.0008	0.13
30	Fe-As	24 hr.	0.3757	62.6	24 hr.	0.0006	0.10
31	Fe-As	24 hr.	0.3919	65.3	24 hr.	0.0005	0.08
32	Fe-Ag	24 hr.	0.3875	64.6	24 hr.	0.0006	0.10
33	Fe-Ag	24 hr.	0.4109	68.5	24 hr.	0.0003	0.05
34	Fe-Sb	24 hr.	0.3494	58.2	24 hr.	0.0003	0.05
35	Fe-Sb	24 hr.	0.3720	62.0	24 hr.	0.0009	0.15
36	Fe-Sn	24 hr.	0.0039	0.65	24 hr.	0.0000	0.00
37	Fe-Sn	24 hr.	0.0041	0.7	24 hr.	0.0007	0.10

An explanation for the mysterious absence of a deposit of arsenic from the more noble metal of these couples was found in a statement in Foerster's Elektrochemie wässeriger Lösungen, p. 382, "that in dilute acid or alkaline solutions of arsenious acid, with a platinum cathode all the arsenic can be removed as arseniuretted hydrogen by electrolysis." Experiments soon showed that electrolysis gave no deposit of arsenic from the solutions here employed. If current produced by an external electromotive force can deposit no metal on cathodes, it is not to be expected that current produced by the voltaic action of iron within the cell will prove any more effective. That arsenic is displaced from these solutions by iron means that this exchange of metals takes place without the intervention of hydrogen.

Of all the metals coupled with iron, tin alone gave evidence of protecting by voltaic action. No. 24 indicates that the corrosion of copper by dilute sulfuric acid is not affected by the presence or absence of arsenic in the electrolyte. This was to be expected, since copper cannot displace arsenic from solution and in this electrolyte copper corrodes only by oxygen depolarization.

TABLE III.

Corrosion in Sea Water Without and With Addition of 0.5 g./L. As_2O_3, Open to Air.

All specimens 5 x 30 mm. Couples formed by plating half the iron with the other metal. Time, 7 days.

Expt. No.	Metal	Sea water alone		Sea water + As_2O_3	
		Loss grams	Mg/cm.^{2}	Loss grams	Mg/cm.^{2}
38	Fe	0.0042	1.4	0.0023	0.77
39	Fe	0.0049	1.7	0.0034	1.13
40	Fe	0.0047	1.6	.....	...
41	Fe-Cu	0.0036	1.2	0.0029	1.0
42	Fe-Cu	0.0025	0.8	0.0017	0.6
43	Fe-Ag	0.0039	1.3	0.0047	1.5
44	Fe-Ag	0.0039	1.5	0.0035	1.2
45	Fe-Au	0.0036	1.2	0.0034	1.1
46	Fe-Au	0.0040	1.3	0.0039	1.3
47	Fe-As	0.0047	1.5	0.0039	1.3
48	Fe-As	0.0043	1.4	0.0041	1.4
49	Fe-Pt	0.0044	1.4	0.0040	1.3
50	Fe-Pt	0.0051	1.7	0.0057	1.9

Among the many substances, called inhibitors, which may be added to sulfuric acid to lessen corrosion of metal and consumption of acid in the pickling of steel, are formalin and dimethylaniline. Although these are effective in inhibiting the corrosion of steel, the writer has found them of no value in pickling gray cast iron. In Experiments 21 and 22 small pieces of cast iron were ground to a rough finish and dropped into the electrolytes indicated. It is seen that arsenic in the acid strongly inhibits the corrosion of cast iron.

It is seen in Table II that the coupling of iron with equal areas of copper, silver, arsenic, etc., increased corrosion of the iron in sulfuric acid twelve to fifteen fold, and that addition of arsenic reduced corrosion of the couples to a fraction of one per cent, without covering up the cathodic member of the couples!

Taking into consideration the variations in corrosion of identical specimens in Table III, it appears that corrosion in sea water is proportional to the total area, regardless of the cathodic member of the couple. Whitman and Russell[5] had already found this to be true for the corrosion in natural waters of iron partly plated with copper. It is now confirmed for the corrosion of iron in sea water, and for other cathodic metals than copper.

In sea water, as in sulfuric acid, contact with arsenic has the same effect as copper or silver; but dissolved in the electrolyte, arsenic lacks the inhibiting power which it possesses in the acid. Arsenic in the electrolyte is without effect on the corrosion of iron by oxygen depolarization.

TABLE IV.

Corrosion of Iron in $N/2$ H_2SO_4 With Various Additions Open to the Air.

Specimens 5 x 30 mm., except for about 1.5 sq. cm. additional surface of mercury in Nos. 62-65. Fe-Ag and Fe-Cu couples made by plating half the iron with the other metal. Time 24 hours except for 25 hours in Nos. 54, 55.

Expt. No.	Metal	Addition to acid	Gain-Loss grams	Mg/cm.^{2}
51	Fe	2 g./L. $SnCl_2$	0.0007 gain	....
52	Fe	2 g./L. $SnCl_2$	0.0005 "	....
53	Fe	2 g./L. $SnCl_2$	0.0007 "	....
54	Fe	1 g./L. Sb-tartrate	0.0209 loss	7.0
55	Fe	1 g./L. Sb-tartrate	0.0232 "	7.7
56	Fe-Cu	0.9 g./L. Sn	0.0007 "	0.23
57	Fe-Cu	0.9 g./L. Sn	0.0008 "	0.26
58	Fe-Ag	0.9 g./L. Sn	0.0009 "	0.30
59	Fe-Ag	0.9 g./L. Sn	0.0007 "	0.23
60	Fe	5 cc. N.$CuSO_4$/100 cc.	0.0464 "	15.4
61	Fe	5 cc. N.$CuSO_4 + As_2O_3$	0.0402 "	13.3
62	Fe-Hg	None	0.0294 "	....
63	Fe-Hg	None	0.0271 "	....
64	Fe-Hg	None	0.0226 "	....
65	Fe-Hg	Sat. $HgSO_4$	0.0063 "	....
66	Fe	Excess HgO	0.0088 "	2.8
67	Fe	Excess HgO	0.0087 "	2.7

By comparing the amounts of corrosion in Table IV with results for the same metals or couples of Table II, the effects of the additions to sulfuric acid in Table IV may be seen.

Antimony in the electrolyte appears to be without effect on the corrosion of iron. This was a surprise, for both the potential of antimony and the discharge potential of hydrogen on it are in the same relation

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[5] Ind. Eng. Chem., 16, 276 (1924).

to the potential of iron as are the corresponding properties of arsenic. It was expected that the action of antimony would be similar to that of arsenic, though perhaps differing in degree.

Experiments 60 and 61 show that copper dissolved in the acid increases the corrosion of iron, and that addition of arsenic inhibits this accelerative action of copper but little, if at all. In No. 60 the iron was covered with copper in ten seconds, but in No. 61 it was free from copper at the end of five minutes, although later a deposit of copper was formed. It is this delay in the deposition of copper on iron "by immersion" that makes possible the electroplating of iron and steel from the acid copper sulfate solution by use of the "arsenic dip"[6]—immersion of the article which is to be plated in a strong solution of arsenic in hydrochloric acid for a minute immediately before rinsing and hanging it in the plating bath.

TABLE V.

The Current in Milliamperes Between Iron and Either Tin or Arsenic.

The arsenic electrode consists of a deposit of arsenic on solid silver. To avoid waterline effects, each electrode was covered with wax at and near the waterline, leaving exposed to the electrolyte the standard surface, 5 x 30 mm. x 2. In E both electrodes were smooth; in D they were roughened by emery paper. The plus sign indicates that iron is cathode.

Electrolyte Electrodes Hours	A 30% H_2SO_4 2 g./L. $SnCl_2$ Fe, Sn	B N/2 H_2SO_4 2 g./L. $SnCl_2$ Fe, Sn	C N/2 H_2SO_4 Fe, As	D N/2 H_2SO_4 Fe, Sn	E N/2 H_2SO_4 Fe, Sn
0	+0.350	0.050	0.050	+0.004	0.011
1	+0.060	0.002	0.026	0.036	0.050
3	....	....	....	0.014	0.022
7	....	....	....	0.010	0.006
13	....	+0.016	0.044	....	....
19	+0.061	....	....	....	....
26	....	+0.018	0.050	+0.002	+0.003
30	....	+0.021	0.051	+0.020	+0.042
46	+0.115	....	....	....	....
49	....	....	....	+0.056	+0.056
51	....	+0.014	0.035	....	....
66	+0.090	....	....	....	....
70	+0.116	....	0.050		
74	+0.170	+0.033	0.040		
90	+0.170	....	....		
93	....	+0.065	0.050		
97	+0.155	....	....		
100	....	+0.065	0.055		
Loss in wt.	Fe 0.0012 Sn 0.0334	Fe 0.0027 Sn 0.1842	Fe 0.0918 As 0.0009	Fe 0.0089 Sn 0.0095	Fe 0.0042 g. Sn 0.0120 g.

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[6] Trans. Electrochem. Soc., 35, 265 (1919).

Experiments 62 to 65 consisted of iron 5 x 30 mm. with a fine projection on one end by which contact was made with a layer of mercury in the bottom of the test tube. Contact with mercury added about 1.5 sq. cm. to the metallic surface, but appears to have little effect on the corrosion of iron, although the potential of mercury in sulfate solution lies between those of copper and silver. The explanation is that this contact with mercury does not affect the visible discharge of hydrogen at the iron surface, no hydrogen escapes from the mercury, and its only contribution to corrosion is that due to the very slow depolarization by oxygen which takes place on its surface.

When mercury sulfate or oxide is added to the acid (No. 65-No. 67), a small quantity of mercury goes into solution and the iron is found to be amalgamated at the end of the test. The result is that all corrosion is now of type IV, by oxygen depolarization, and consequently the total is greatly lessened. The writer has found that amalgamated iron in dilute sulfuric acid loses its amalgamation in a few hours, the mercury gathering into droplets and leaving the exposed iron to corrode at full speed like the iron-mercury couples of No. 62-No. 64. To protect iron, mercury, like arsenic, must be dissolved in the electrolyte, and even then it is less effective than arsenic or tin.

Probably based on the rusting of tin cans when exposed out of doors, it is generally thought that tin, unlike zinc, exerts no protective effect on iron by contact with it. Experiments 36 and 37 of Table II, seem, however, to indicate protection by contact in 0.5 *N* sulfuric acid. A limited protective action of tin by contact is indicated in some cases of Table V, in which the current between iron and tin in several electrolytes is recorded. The reversals of current show that reversals of e.m.f. between iron and tin can occur in sulfuric acid, as well as in the fruit juices investigated by Kohman and Sanborn.[7] When tin was anode (Expts. A and B) it was deeply etched. That corrosion of the cathode occurred where there had been no reversal of current, indicates that the flow of current was insufficient to overcome the natural rate of corrosion of the cathode metal by the electrolyte. Although anodic action by tin explains the occasional protection of iron by contact with tin, it but deepens the mystery of the protection produced by addition of tin salts to the acid. If tin were cathodic to iron, it might be expected to deposit on the iron and have the same effect as arsenic; but so long as tin is anodic to iron, such deposition cannot take place.

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[7] Ind. Eng. Chem., 20, 76 (1928).

SUMMARY.

Arsenic dissolved in dilute sulfuric acid practically stops that portion of the corrosion of iron or steel which takes place by visible displacement of hydrogen.

Against corrosion by oxygen depolarization, arsenic has no value either as a contact electrode or when dissolved in the electrolyte.

As a contact electrode, arsenic has no protective value in the corrosion of iron by dilute sulfuric acid; on the contrary, it acts as an accelerator to about the same degree as copper or silver.

Unlike those other inhibitors of the corrosion of iron and steel, formalin and dimethylaniline, which fail to protect gray cast iron in sulfuric acid, arsenic has been shown to be nearly as effective an inhibitor for cast as for wrought iron.

Addition of nitric acid to 0.5 *N* sulfuric acid has been found to promote the corrosion of iron in spite of the presence of arsenic. Other oxidizing agents will probably act similarly in acid solutions.

These experiments confirm the writer's hypothesis of over twenty years ago[8] that this protection of iron and steel against acids is due to the deposition of a film of arsenic on the metal. Although this film is not water-tight, and iron is still in contact with the acid through microscopic holes and cracks, there is no longer an appreciable extent of surface on which iron is capable of discharging hydrogen,—hence corrosion proceeds only by the slow process of oxygen depolarization.

Cushman and Gardner[9] cite an interesting industrial application of arsenic to prevent corrosion of the water jackets and pipe lines of a copper blast furnace at Cananea, Mexico, in 1905. When all other remedies had failed and corrosion had become so serious that it was difficult to keep the furnace in operation, the addition of arsenious oxide to the water cured the trouble, which was due to absorption of sulfur dioxide from the smelter fumes that blew across the water spray in the cooling tower.

Although the use of arsenic for preventing corrosion of steel by nonoxidizing acids is not likely to become general for obvious reasons, it is probable that other valuable special applications will be found for it, besides the one just mentioned. In any attempt to use arsenic for lessening the corrosion of steel by acids, it should be kept in mind that arsenic is a dangerous poison for the human organism and that arseniuretted

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[8] Trans. Electrochem. Soc., 21, 340 (1912).

[9] Corrosion and Preservation of Iron and Steel, p. 296 (1919).

hydrogen (AsH_3), which is always mixed with hydrogen when the latter is evolved from solutions containing arsenic, is still more deadly.

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DISCUSSION.

J. T. MacKenzie[10]: I would like to ask Professor Watts if he knows anything about an alloy of arsenic with iron or steel. I know we have some pig iron with the arsenic content running up around 0.4 per cent.

O. P. Watts: I have not experimented on that alloy myself, but I have read reports of others on that quite a long time ago, and they have found that arsenic in the steel itself does not protect; arsenic in solution, however, protects against acid corrosion.

J. T. MacKenzie: I never made any tests on the alloy. The only test I have made is in dissolving for sulfur determination. The steel does not seem to take any longer to dissolve in 1:1 hydrochloric acid with arsenic present than without arsenic.

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[10] American Cast Iron Pipe Co., Birmingham, Ala.

14

A paper read at the Ninth General Meeting of the American Electrochemical Society, Ithaca, N. Y., May 2, 1906. President Bancroft in the Chair.

STRUCTURE OF ELECTRO-DEPOSITS.

BY CHARLES F. BURGESS AND OLIVER P. WATTS.

It is a well-known fact that electro-deposits may be made to exhibit a great variety of physical structures; in fact, it has been suggested that all forms of vegetation may be imitated in metal, deposited electrolytically. It is not the reproduction of the various forms of vegetation, but rather the prevention of their formation that measures the success of deposition for technical purposes.

The factors which influence the structure are, current density, temperature, circulation of solution, composition of electrolyte, gases, or other impurities dissolved in the electrolyte, and the thickness of the deposit.

It is not the purpose of this paper to discuss in detail the influence produced by a variation of each of these factors, but rather to point out some peculiarities of the physical structure of electrolytic iron. These observations are incidental to an investigation of the production and properties of electrolytic iron now in progress under a grant from the Carnegie Institution of Washington.

With suitable adjustment of the factors above named, it has been found that the deposition of iron in thick layers may be carried on with almost the same ease and rapidity as is the case with copper and some other metals.

One of the difficulties which may be encountered in the deposition of iron or other similar metals is vertical grooving, as illustrated in Fig. 1. This appears to be due to the upward flow of the electrolyte at the cathode surface, the dilute solution flowing upward through channels which conform to and start from protuberances near the bottom of the cathode. Among the methods of preventing this grooving are agitation of the solution and the proper choice of solution density and composition. The addition of an inert salt will diminish the changes of specific gravity of the electrolyte in the neighborhood of the cathode, due to depletion of electrolyte by deposition of the metal.

Another troublesome feature is that caused by gas bubbles adhering to the deposited metal. These bubbles insulate the portions of the plate beneath them, thus producing pitting, and the metal may even pile up around the bubbles so completely as entirely to enclose them. Fig. 2 illustrates a surface in which the influence of gas bubbles is apparent, the light portions representing the ridges between bubbles. It is commonly assumed that these gas bubbles are due to the liberation of hydrogen, but it is the belief of the authors that air may be equally responsible with, or more so than, hydrogen in giving rise to this trouble. In the deposition of iron, it has been found that the gas pitting is more pronounced with a solution freshly prepared than it is after the current has been flowing for some time. Also that after allowing the solution to stand idle for some time, the gas bubbles will be copiously liberated when the cell is again started. Agitation of the electrolyte by blowing air through it, is not practicable, through the increased liberation of the gas

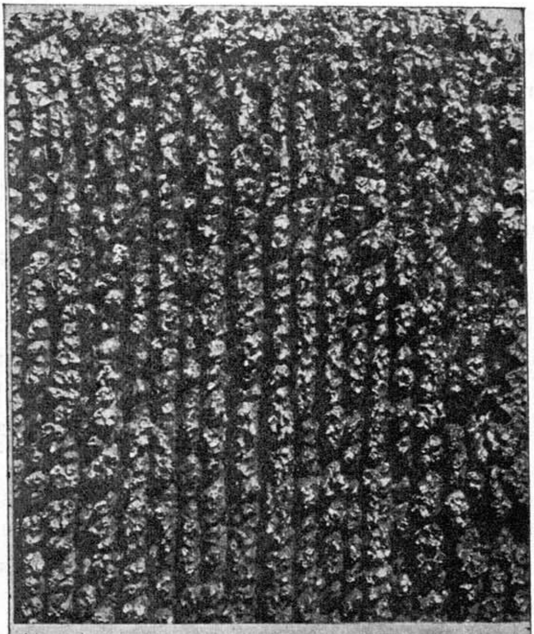
Fig. 1. Vertical Grooving.

Fig. 2. Pitting Produced by Gas Bubbles.

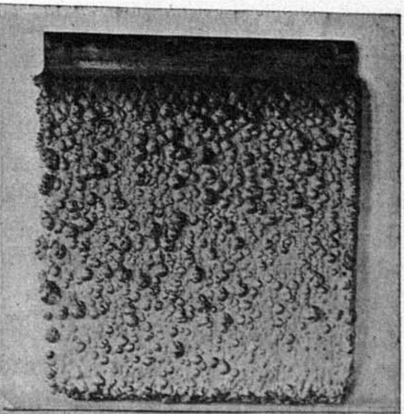

Fig. 3. Iron Cathode, two months growth.

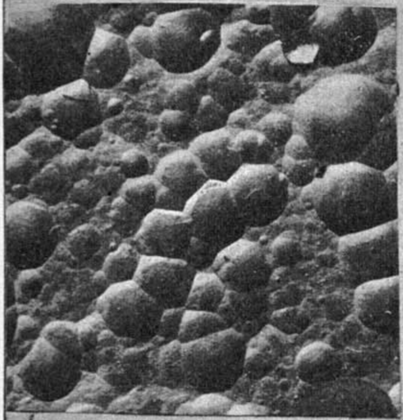

Fig. 4. Cathode Nodules.

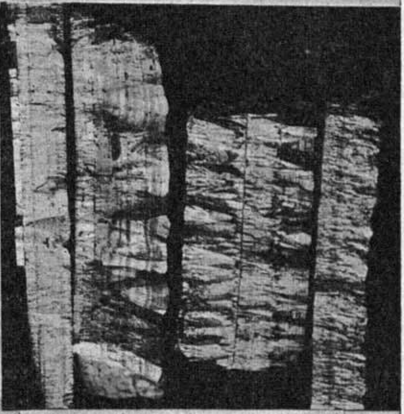

Fig. 5. Surfaces of Fracture.

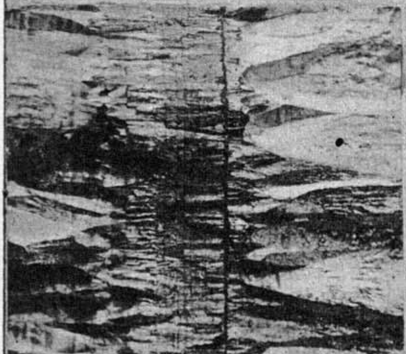

Fig. 6. Fractured Surface Magnified about 4 diameters showing starting sheet.

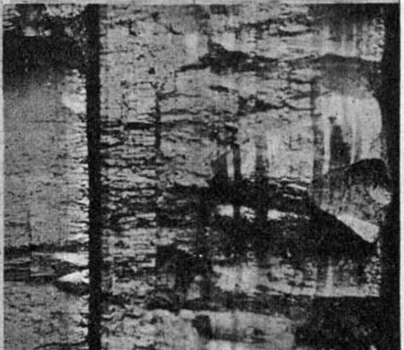

Fig. 7. Fracture showing conical growths.

caused by it; and, in fact, the deposition proceeds most satisfactorily if air is kept, as far as possible, away from the solution. It is well known that air is soluble to a certain extent in various solutions, and it appears that the flow of the electric current has the effect of driving this air out of the electrolyte onto the cathode. A remedy which may be used for overcoming this defect, at least in the case of iron, is to boil the solution, driving out the air as far as possible.

Employing a current density of about ten amperes per square foot, temperatures between 20° and 30° C., a solution of ferrous sulphate and ammonium chloride, with a centrifugal pump for circulating the electrolyte through the series of tanks, and, observing precautions for the exclusion of dissolved gases, it has been found possible to deposit iron to a thickness of at least 1 inch. The thickness is usually limited by the degree of roughness on the surface. The iron made during the first few days of deposition appears smooth; later, small irregularities may become apparent, and these increase in number and size as the process is continued.

Fig. 3 illustrates a cathode of iron in which the deposition has proceeded for two months.

Fig. 4 illustrates more in detail the appearance of the surfaces, showing nodules in various stages of development. The convex hummocks vary in size from those which require a microscope to detect them to those which measure ½ inch or more across. The natural form of these growths is of a circular cross section, the diameter increasing steadily with the thickness of deposit. Where two of these growths interfere, deformation takes place, producing a honey-comb appearance, as shown in the group near Fig. 4.

Just what produces these characteristic growths is perhaps, a matter of speculation. The ideal deposit is one which is dense, homogeneous, and smooth on the surface. It is possible that the roughness of the iron deposit just referred to, may be due to minute particles of impurity suspended in the electrolyte, which attach themselves to the surface receiving the deposit. The current tends to cover up such particles, and the hump thereby produced, steadily increases in magnitude. This is commonly offered as the explanation, though we have been unable to find such particles with a microscope.

Fig. 5 illustrates the fracture of four different iron cathodes, the lower one being a dense and rather smooth deposit and the one above showing how such dense deposit may assume that peculiar structure which makes itself apparent on the surface in Fig. 4. The third section in Fig. 5 shows a deposit in which the cones grow in both directions from the starting sheet. The difference in thickness on the two sides of the starting sheet, is due to the variation in the current density on the respective sides. The top section shows an electrolytic deposit which is of a fibrous nature.

Fig. 6 shows a larger magnification of the fracture, and the growths which appear to take root near the surface of the starting sheet and extend onward, are quite apparent.

Fig. 7 shows two fractured cathodes, the larger illustrating the characteristic tooth-like growth, and the other demonstrating that by acidifying the solution, the conical growths may be suppressed until the plate has attained a considerable thickness. If the nodular deposits are struck a sharp blow with a hammer, some of the conical-shaped growths will become separated from the main body of the metal, leaving cavities sometimes ½ inch or more in depth. A group of these teeth which were collected in breaking up an iron cathode is illustrated in Fig. 8. It will be noted that some of them are almost perfect cones, while the sides of others show interferences produced by adjacent growths.

Another characteristic which is prominent in most of the figures referred to, is shown by the lines parallel to the starting sheet, which indicate surfaces of cleavage along which the metal is liable to separate when mechanically disintegrated. These surfaces of cleavage seem to be produced when any marked change in or interruption of the depositing process occurs. If the current is interrupted for a time, or if the cathodes are removed from the tank and exposed to the air, a cleavage surface may be produced. It is also believed that a sudden change in the current density may have the same effect. The differences in structure produced by variations in the current density are illustrated in Fig. 9, which is a fracture at right angles to the surface of deposition, which had been polished, etched, and magnified to seventy-one diams. The strata which are shown and which average 2 mm. in thickness, indicate the thickness of iron deposited each day of twenty-four hours. Striations are the

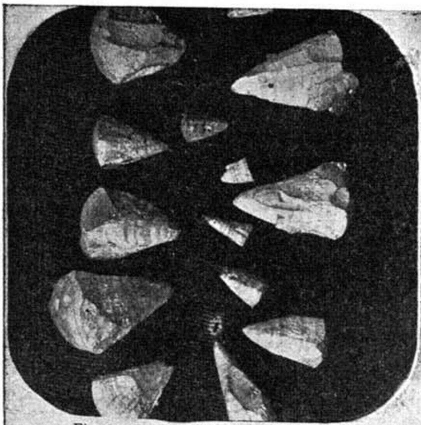

Fig. 8. Conical growths within deposit.

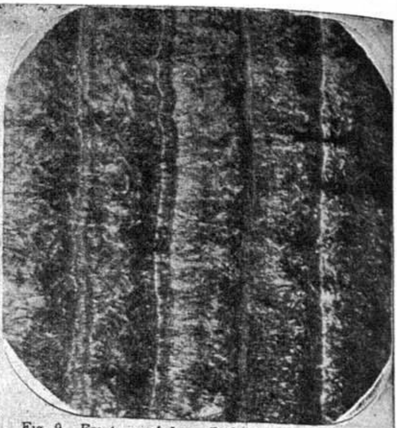

Fig. 9. Fracture of Iron Cathode, magnified showing layers deposited each day.

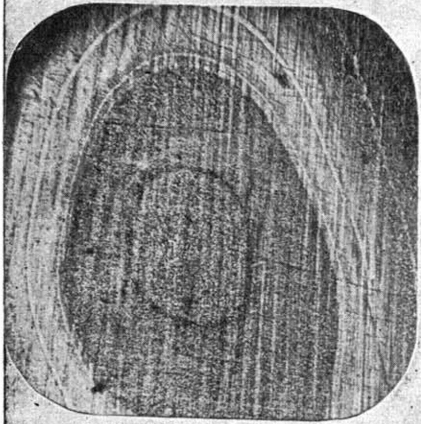

Fig. 10. Polished Section of Nodule.

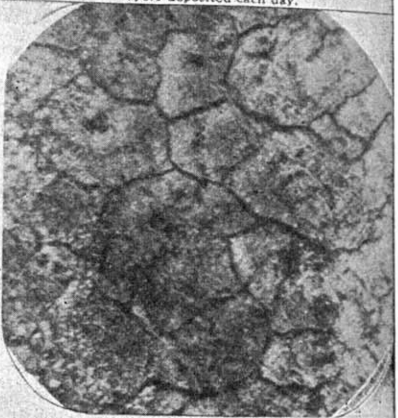

Fig. 11. Section of Electrolytic Iron magnified 250 diameters.

Fig. 12. Electrolytic Iron heated.

Fig. 13. Swedish Iron.

result of varying the current density, due to the method of operating the plant, which consisted in charging storage batteries in series with the iron cells for eight hours, and discharging at a lower current density for the remainder of the twenty-four hours.

Fig. 10 shows a polished and etched section of one of the nodules, such as are illustrated in Fig. 8. This reveals the laminated structure of the nodule, the magnification being twenty diams. and not sufficient to show the granular elements of the mass, as in Fig. 11, which is a magnification of the previous section to 225 diams. This reveals the fact that the mass of the iron is made up of grains bearing a striking similarity to ferrite, but differing from the normal ferrite structure in the absence of visible orientation of crystals composing the grains. The characteristic ferrite structure may be developed, however, by heating electrolytic iron; Fig. 12 shows such structure produced by heating electrolytic iron to about 1,000° C., polishing and etching the section, and magnifying to 132 diams. The light and dark patches are due to the different orientation of the crystals which go to make up the separate grains of ferrite. The unrefined iron, when subjected to the same treatment and magnification, is illustrated in Fig. 13, in which we have the typical ferrite grains. The black spots distributed throughout and between these grains are attributed to slag fibres which are contained in the Swedish iron, and which are entirely absent from the electrolytic iron.

That the characteristic nodular structure of electrolytic deposits is not peculiarly an electrolytic phenomenon is shown by the striking similarity of these deposits to those which are produced in nature. Figures 14 and 15 show two surface photographs taken from electrolytic iron and hematite. Fig. 16 is a similar photograph of the surface of a mass of manganite. Several other minerals that have resulted from deposition from a solution show a similar appearance.

This striking similarity of structure between certain minerals deposited by natural processes and some of the products of electrolytic deposition are not confined to the surface, but extend throughout the materials, as is seen in Figures 17, 18, and 19, which are photographs of fractured specimens of hematite, of limonite, and of electrolytic iron, respectively.

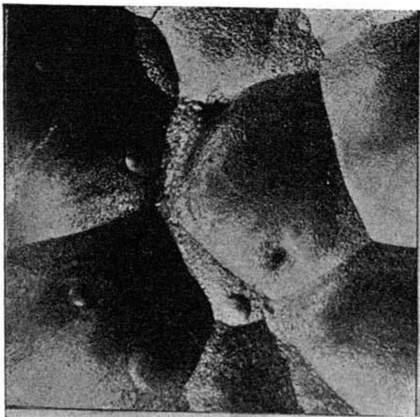

Fig. 14. Electrolytic Iron Nodules.

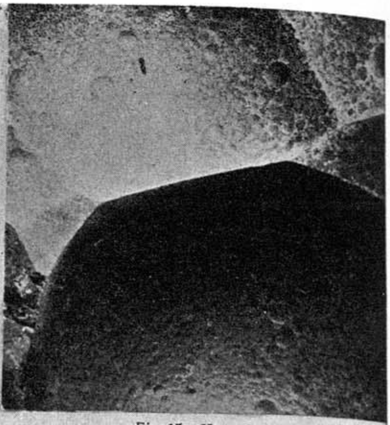

Fig. 15. Hematite.

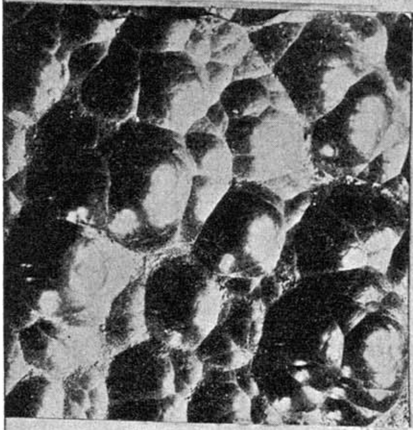

Fig. 16. Manganite.

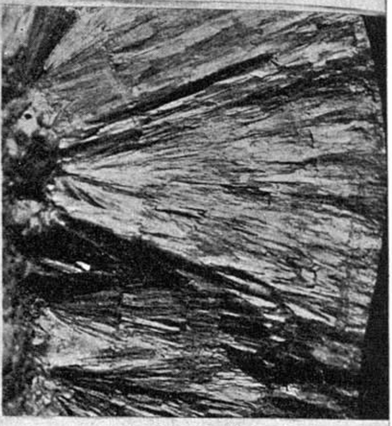

Fig. 17. Fracture of Hematite.

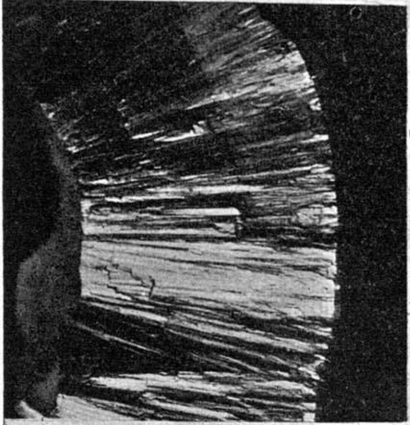

Fig. 18. Fracture of Limonite.

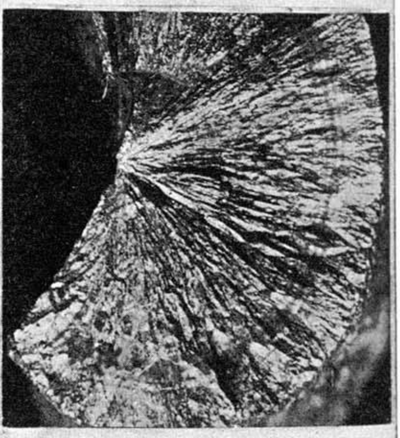

Fig. 19. Fracture of Electrotytic Iron.

Manganite has a similar fracture. In view of these facts, the time may yet come when the geologist, seeking better understanding of the natural deposition of minerals from solution, will experiment in the laboratory, and with the aid of the electric current, be able to observe during their growth and obtain, in a few weeks, forms which in nature required years for their production. It is well, too, that the electrochemist should keep in mind that the process of deposition, as carried out by means of the electric current in the laboratory, although an artificial process, is yet closely related to such examples of natural depositing as have already been cited, and, in so far as the two processes are alike, must be subject to the same laws.

Laboratory of Applied Electrochemistry,
University of Wisconsin.

DISCUSSION.

MR. S. S. SADTLER: I would like to ask what differences in the structure are noticed by increasing the rapidity of deposition of the iron,—whether you succeeded in getting much smoother deposits.

PROF. C. F. BURGESS: That was one of the problems we had to meet—to find the current density that would give us the best deposit; and we found that that range was rather small, lying between 5 and 15 amperes per square foot. Of course, the current density had to be adjusted in conjunction with the other variable factors; and the influence on the physical structure which a change in the current density would make, depends upon what your adjustments of temperature, circulation and other factors are. It is hard to state what the effect of current density is on the physical structure.

MR. SADTLER: The range is not quite as great as in copper or silver depositing, is it?

PROF. BURGESS: Well, I think it is. The trouble comes in getting thick plates. We can use a great range of current density for iron if we want to get only a film of it; but when we come to get thick plates the trouble develops.

President Bancroft: Is your commercial scale so colossal that you could not afford to stir your solutions vigorously?

Prof. Burgess: We stir by circulating it. By putting a stirrer in each tank we would agitate the solution so much that it breaks up the film that forms on the surface, thereby letting in too much air.

15

A paper presented in the Symposium on Electrodeposition of Metals, at the Twenty-Third General Meeting of the American Electrochemical Society, at Atlantic City, N. J., April 5, 1913, President W. Lash Miller in the Chair.

THE ELECTRODEPOSITION OF COBALT AND NICKEL

By Oliver P. Watts.

In accordance with a request from the President of the Society, this paper was undertaken with the intention of including all solutions used for the deposition of cobalt and nickel. Lack of time, however, has prevented such a thorough search of the periodical literature as could insure this result. Because of the difficulty of making intelligible yet brief abstracts of lengthy metallurgical processes in which electrolysis is often but a single step, the various processes and patents which deal with the extraction of these metals from their ores have been omitted.

ELECTRODEPOSITION OF COBALT.

Cobalt and nickel present such striking similarities in both physical and chemical properties that it is not surprising to find similarities in their behavior under electrolysis. In this connection Langbein[1] says: "For plating with cobalt, the baths given under 'Nickeling' may be used by substituting for the nickel salt a corresponding quantity of cobalt salt."

Hollard et Bertiaux[2] says: "In our numerous analyses we have never found any difference in electrolytic properties between nickel and cobalt." Many other writers give similar testimony.

While there is a general agreement in regard to the similarity of conditions and solutions suitable for the electrodeposition of cobalt and nickel, there is the widest disagreement concerning the relative hardness, color, etc., of these metals, as shown by the quotations which follow:

Brochet[3] says: "Cobalting has been proposed in place of nickeling when a deposit of the greatest hardness is desired."

McMillan[4] says: "The deposit of cobalt is similar to that of nickel; it is equally brilliant, but is somewhat harder."

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[1] For references, see the end of the paper.

On the other hand, Langbein says: "Cobalt precipitated from its chloride solution does not yield a hard coating."

Watt[6] says: "When deposited by electrolysis under favorable conditions, cobalt is somewhat whiter than nickel, but acquires a warmer tone after being exposed to the air for some time." . . . "Gaiffe says that, when deposited from a solution of the double sulphate of cobalt and ammonium it is 'superior to nickel in hardness, tenacity and beauty of color.' Wahl remarks: 'The electro-deposits of this metal which we have seen equal, if they do not surpass, those of nickel in whiteness and brilliancy of lustre.' Electrolytic cobalt[7] is somewhat softer than nickel."

S. P. Thompson[8] finds that articles plated with cobalt tarnish much less quickly in the atmosphere of London than silver or nickel plate; while Watt[9] quotes Stolba to the effect that cobalt salts treated like nickel "yield metallic deposits of a steel gray color, less lustrous than nickel and more liable to tarnish." In the same article Watt says: "I have invariably found that, while cobalt admits of being burnished without difficulty with a steel burnisher, nickel yields but little to the tool."

In the account of the deposition of nickel many authorities will be quoted in regard to the extreme difficulty or impossibility of obtaining deposits of that metal more than a few hundredths of a millimeter in thickness. E. Bouant[10] says: "Electrolytic deposits of cobalt are easily obtained, even of very great thickness, so that the electrodeposition of cobalt is as easy as that of copper."

A partial explanation of the above contradictions is given by Watt:[9] "The whiteness of electro-deposited cobalt depends greatly upon the nature of the electrolyte employed. Again, the density of current influences the color of the deposit; the strength of the solution also greatly affects the color of the deposit." It is evident that not only is the color of the deposit influenced by these and other factors, such as temperature, acidity, alkalinity, etc., but also that the hardness, brittleness and other physical properties of both cobalt and nickel are dependent upon the conditions above mentioned.

ELECTROPLATING WITH COBALT.

Concerning cobalt plating solutions, Watt says:[9] "Nearly all those who have devised formulæ for cobalt baths for electrodeposition prefer to employ solutions which are either neutral or more or less alkaline, but, so far as I am aware, in no case acid. . . . I have found that certain solutions were greatly improved when put in a faintly acid condition. . . . In working solutions which are more or less acid some little care is necessary to prevent the film from stripping or peeling off the receiving surface."

For ease of comparison the original composition of the baths which follow has been re-calculated to the basis of grams of solid taken per liter of water, where they were not already expressed in this way. Current densities are given in amperes per square decimeter, and temperatures on the centigrade scale.

1. Becquerel's solution:[11] 37.5 grams of cobalt chloride, neutralized by ammonia or potassium hydroxide, gives a brilliant, white, hard and brittle deposit. A very weak current must be used.

2. G. W. Beardslee's solution[12] consists of 30 to 45 grams of cobalt chloride per liter of water, made very faintly alkaline with ammonia. He claims that this bath gives a thick deposit which is very white, exceedingly hard, tenaciously adherent and not liable to tarnish. "I do not, however, limit myself to the precise method or agents above described, but employ any others which will produce similar results in substantially the same manner. What I claim and desire to secure by letters patent is: Electroplating with the metal cobalt so as to form a useful coating of this metal that is tenacious, compact, adherent, and flexible, and of sufficient thickness to protect the surface upon which it is deposited." Although plating with cobalt had been known for thirty years, the United States Government at this late date seems to have turned the practice over exclusively to Mr. Beardslee.

3. Boettger's solution[11] consists of 400 g. cobalt chloride, 200 g. ammonium chloride, 200 g. ammonia. It is claimed to give a brilliant deposit.

4. Watt[11] (page 519) recommends 37.5 grams of cobalt chlo-

ride, without any additions, as giving good deposits at low current density, but states that heavy deposits become dull.

5. Another solution by Watt[11] (page 519) consists of 37.5 grams cobalt chloride and 22.5 grams of ammonium chloride per liter. This gives a very white and very bright deposit, but requires a smaller current than No. 4.

6. The substitution of an equal weight of sodium chloride for the ammonium chloride causes the deposit to continue bright longer than in bath No. 5.

7. E. D. Nagel[13] patents the following for plating with cobalt, nickel, or both metals in combination:

"Four hundred parts by weight of pure sulphate of the protoxide of nickel (or cobalt) is combined with 200 parts by weight of pure ammonia to form a double salt, which I dissolve in 6,000 parts of distilled water, and add 120 parts ammoniacal solution of specific gravity 0.909. A platinum anode is used, and the solution is heated to 38° C."

8. Watt[11] (page 354) gives 30 to 45 g. of the double sulphate of cobalt and ammonium, made alkaline by ammonia, and states that the solution gives a fine white deposit.

Isaac Adams[14] says: "I have found that a solution made and used in the manner described in the books will not produce such a continuous and uniform deposit of cobalt as is necessary for the successful and practical electroplating of metals with cobalt. . . . I have found, further, that the simple salts of cobalt, such as are recommended by Becquerel and others, are not such salts as can be used in practical electroplating with cobalt. I have found out, also, that the simple salts of cobalt, when associated with another electrolyte—such as the chloride of ammonium, or the sulphate of ammonia, or the chloride of magnesium, or the sulphate of magnesia—can be used so as to produce good results in practical cobalt-plating.

"I have found, further, that, in order to produce the best results, the cobalt solutions should, in use, be neutral, and (except in covering poorly conducting surfaces) in no case acid. I find, further, that when solutions of cobalt are used—such as are mentioned in Smee—and contain an excess of ammonia, they become changed, by contact with the air, into such salts of cobalt as are not suitable for practical electroplating with cobalt. I have found, further, that the electrodeposition of cobalt does not necessarily take place in solutions in which exist salts of alkalies—such as the nitrates of soda or potash, or free nitric acid."

Adams' solutions:[14]

9. 22.5 g cobalt chloride.
   15 g. ammonium chloride.
10. 22.5 g. cobalt chloride.
   15 g. magnesium chloride.
11. The sulphates of cobalt and ammonia.
12. The sulphates of cobalt and magnesia.

13. Watt[11] (page 354) gives 30 to 45 g. of cobalt ammonium sulphate, made alkaline by ammonia, and states that this gives a fine white deposit.

14. Watt[11] (page 518) also gives 37.5 cobalt sulphate per liter, and specifies a current density of 0.2 to 0.4 ampere per square decimeter.

15. Brochet[3] recommends 100 grams of the double sulphate of cobalt and ammonium, making 21 grams of cobalt per liter. Specific gravity 1.057. Specific resistance 22.1 ohms.

S. P. Thompson's[15] solutions:

16. 60 g. cobalt sulphate.
   30 g. magnesium sulphate.
   60 g. or less ammonium sulphate.
17. 100 g. double sulphate of cobalt and ammonium.
   50 g. magnesium sulphate.
   6.2 g. citric acid.
   12.5 g. ammonium carbonate.

These solutions are claimed to give "deposits of greater tenacity, density, and brilliance of tint, than have heretofore been obtainable with certainty." . . . "The solution for the deposition of cobalt may consist of the sulphate or chloride of cobalt, or of the double sulphate or chloride of cobalt and ammonium, to which has also been added the sulphate or chloride of magnesium, or other suitable soluble salt of magnesium, or a mixed soluble salt of magnesium and ammonium may be added to the solution of cobalt salts. Citrate of magnesium is a useful salt.

. . . Citrate of ammonium, or simply citric acid, may be added to the solution."

18. Maigne and Mathey[16] give:

28.6 g. cobalt chloride.
14.3 g. potassium cyanide.
143 g. sodium thiosulphate (hyposulphite).

The first two are dissolved separately, the solutions are mixed, the cobalt cyanide is washed, collected and dissolved in a solution of the thiosulphate in one liter of water.

19. The same authors (p. 334):

20 g. cobalt chloride.
10 g. potassium sulphocyanide.

20. Kayser's[17] solution:

67 grams cobalt sulphate.
67 grams ammonium sulphate.
33 grams boric acid per liter.

21. Langbein's[5] solutions consist of:

40 grams of the double sulphate of cobalt and ammonium.
20 grams boric acid.

At an E. M. F. of 2.5 to 2.75 volts, and a current density of 0.4 ampere per square decimeter, this bath is claimed to give a hard deposit suitable for electrotypes.

22. The solutions of Joseph Vandermersch[18] for the deposition of cobalt, nickel, copper, brass, manganese, cadmium, zinc and other metals are claimed to give deposits of any thickness and any weight. He says: "Heretofore in depositing nickel on iron and copper it has been possible to get only thin coatings (0.01 to 0.02 mm.). I obtain thick deposits by adding to a solution of nickel (or cobalt, etc.) sulphate as a base, one or several acids—benzoic, salicylic, boric, gallic, pyrogallic, and others of similar qualities—which gives a perfectly pure and white nickel deposit, but still in thin films only.

Therefore I add to the above bath 10 drops per liter, more or less, of sulphuric acid, and get deposits of any thickness and of any weight. I may also add sulphurous, perchloric, chloric, formic, lactic, acetic, or other acid instead of sulphuric and get a similar effect. But sulphuric acid is best.

The same results are obtained with cobalt.

The process applies not only to nickel sulphate, but also to nickel chloride, nickel nitrate and all other nickel salts.

Instead of benzoic acid, etc., any compounds of these acids may be used, *e. g.*, calcium benzoate, etc. The chlorides, bromides, iodides, or other compounds of these acids may be used instead.

In the second operation, the sulphuric, sulphurous, or other acid may be replaced by compounds of salts of these acids, *e. g.*, sulphates. The sulphuric, lactic and other acids may be replaced by any other acid, provided they contain oxygen, and not only acids may be used for this purpose, but also all bodies capable of being added to the bath, provided they contain oxygen, such as alcohols, ethers, aldehydes, gums, sugars, creosote, glycose, glycerine, etc.

The second operation may take place before the first, the same result being obtained.

Acids capable of furnishing in a single operation the deposit of required thickness may, if desired, be employed, *e. g.*, phosphoric, permanganic, manganic, or other acids which are highly oxygenated, and which, when added to the nickel salts of any kind, give an unlimited deposit; but this result is far from equaling that of benzoic, aromatic and oxygenated compounds, superoxygenated by another body as above described. . . . It is however in all cases required as a total result that the bath be so constituted that it forms an ether, an alcohol, or an oxygenated acid, or an oxygenated compound in such a manner that hydrogen produced in consequence of decomposition of water by the electric current, is absorbed by the composition of the bath."

23. M. Kugel[19] deposits "tough, rollable, cobalt or nickel of any desired thickness by adding to any desired nickel-salt (or cobalt) solution, a strong mineral acid which is not changed in its chemical composition by the current. The most suitable acids are perchloric, perbromic and sulphuric. The acid concentration ranges from 2 to 20 percent normal or 1 to 10 grams per liter. The temperature must be kept above 30° C., and

current densities of 10 to 20 amperes per square decimeter may be used without harm to the deposit,—"a correspondingly lively movement of the electrolyte, in order to mix well, being of course necessary."

24. Alexander Classen[20] deposits more rapidly and compactly than has heretofore been possible, the metals cobalt, nickel, copper, iron, zinc, cadmium, bismuth, lead, tin, and antimony, by converting solutions of the chlorides or sulphates, by means of a solution of neutral potassium oxalate, into soluble potassium double salts. A suitable bath for cobalt consists of:

50 grams cobalt sulphate.
80 grams ammonium oxalate.
20 grams potassium oxalate.
1 liter water.

The baths are used hot.

25. E. Placet and J. Bonnet[21] claim the employment of polyatomic acid salts, alone or mixed with neutral salts, to obtain deposits of cobalt, nickel, chromium, aluminum, copper, iron, tungsten, molybdenum, antimony, tin, silver, etc., and the alloys of these metals electrolytically. They specify particularly the use of the bisulphates, biphosphates and biacetates" (?), and give the following bath for the deposition of chromium:

100 to 150 g. chrome alum.
100 to 150 g. acid sulphate of potassium, sodium, or ammonium, per liter of water.

It is evident at a glance that several of the metals listed cannot be deposited from these baths, and there is, from the chemical standpoint, no reason why the use of an acid salt should prove any more beneficial than equivalent amounts of the free acid and normal salt. The substitution of acid salts for free acid is claimed as the particular merit of the invention.

Watt[22] experimented with many different solutions for the deposition of cobalt. Those which he considered best were published in his book, and have already been mentioned in this paper. The others follow:

26. Cobalt acetate faintly acid gives a deposit which, at the end of an hour, is very bright, and pure white.

27. Cobalt and ammonium acetates gives a dull, brownish deposit.

28. The same as No. 27, made slightly alkaline, gives the same result as No. 27.

29. The same as No. 27, strongly acidified by acetic acid, gives a brilliant white deposit for two hours.

30. Cobalt citrate, acidified, gives a bright, but slightly yellowish deposit, and good anode corrosion.

31. Cobalt and ammonium citrates, neutral, gives a dull and dark deposit.

32. The same as No. 31, but acidified, gives a bright deposit. After 12 hours deposition the deposit is dark gray and nodular. The single citrate is better.

33. Cobalt borate, neutral, gives a bright and very white deposit, which finally loses its lustre and becomes dull. Gas is evolved at the cathode.

34. Cobalt tartrate, neutral, gives a deposit which turns black at the end of 10 minutes.

35. Cobalt tartrate, acidified, gives a bright and white deposit, and good anode corrosion.

36. Cobalt and potassium tartrates made by dissolving cobalt carbonate in a hot solution of cream of tartar, gives a white deposit, streaky on the front, but good on the back of the cathode. The result was the same in three different trials.

37. Cobalt phosphate gives only hydrogen at low current density. At higher currents a good deposit is obtained and much hydrogen is evolved.

38. Cobalt carbonate dissolved in a solution of ammonium carbonate gives at first a brilliant white deposit, becoming dull in 10 minutes. There is a vigorous evolution of hydrogen.

39. Cobalt salicylate gives a dark, but polished deposit.

40. Cobalt nitrate, a weak solution, gives on brass a malachite-green deposit of great beauty, which falls from the plate in transparent flakes.

41. Cobalt and ammonium nitrates gave a thick green deposit on brass.

42. Cobalt carbonate and sodium pyrophosphate were heated together, producing a solution of faint pink color. This gives a very adherent, dark deposit along with much hydrogen.

43. 42 g. cobalt sulphate and 30 g. potassium sulphate per liter, heated, gives a bright deposit, which peels off in 20 minutes. Gas is evolved at both electrodes.

44. 42 g. cobalt sulphate and 18 g. magnesium sulphate per liter gives a bright and remarkably white deposit which becomes dull after a long time. No gas is evolved.

45. Excess of oxalic acid, added to a solution of cobalt sulphate, gives no deposit at low currents, but a bright deposit with evolution of hydrogen at high current.

46. Cobalt oxalate digested with a warm solution of ammonium carbonate gives no deposit of metal with one or two Daniell cells, but with three cells gives a brilliant, silver white deposit, and much hydrogen. In 15 minutes the deposit is streaked and in 30 minutes it is covered with dark streaks except on the edges.

47. Cobalt carbonate and potassium carbonate evolves much gas and yields a dark, smooth deposit of cobalt.

48. Cobalt sulphate and excess of ammonia gives a dark deposit. No gas is evolved.

49. Cobalt hydrate is very sparingly soluble in a strong solution of potassium cyanide, and three Daniell cells give only a trifling film of cobalt, and much gas.

50. Cobalt sulphocyanide. Potassium sulphocyanide, dissolved in alcohol, was added to a solution of cobalt sulphate, the clear solution decanted from the potassium sulphate, evaporated to dryness, and the residue dissolved in water. Three cells gave a slight deposit of cobalt on brass.

Many "per-salts" were tried. Calcium hypochlorite solution was added to a solution of cobalt sulphate, and the precipitate was washed and dissolved in the desired acid.

51. Cobalt per-citrate, tartrate, oxalate, acetate, chloride, sulphate, phosphate and borate all give bright, adherent deposits with three cells. Gas is evolved.

Gaiffe[5] has proposed the use of cobalt instead of nickel for facing valuable electrotypes on account of the complete solubility of the former metal in dilute sulphuric acid, thus permitting the removal of the film of cobalt and its replacement by a fresh deposit without injury to the copper.

DEPOSITION OF AN ALLOY OF COBALT AND NICKEL.

Owing to the difficulty of separating cobalt and nickel electrolytically as well as chemically, it should be an easy matter to deposit an alloy of the two metals. Nagel[23] deposits an alloy of the metals from a mixed solution of their ammonium double sulphates, made alkaline by ammonia, and heated to 40° C. He uses a platinum anode.

A similar trial was made in the experimental laboratory of the Brass World[24] for the purpose of getting a deposit harder than nickel, "since alloys are always harder than pure metals." The electrolyte consisted of a solution of 70 parts nickel sulphate, 30 parts cobalt sulphate, with ammonium sulphate sufficient to form double salts, acidified by boric acid and made up to 6° Bé (sp. g. 1.0432). E. M. F., 2 volts. The deposit contained both nickel and cobalt, and was very hard. It was suggested for facing electrotypes, as the electrolytic iron commonly used, rusts.

The writer found in his filing cabinet another bath, from an unknown source, which is claimed to deposit the hardest alloy of the two metals, consisting of 75 percent nickel and 25 percent cobalt. The bath consists of:

Nickel ammonium sulphate	147	grams
Cobalt ammonium sulphate	40	"
Ammonium sulphate	56	"
Water	1,000	"

The following bath is given by Langbein[5] (p. 307):

Nickel ammonium sulphate	53	grams
Cobalt ammonium sulphate	13	"
Boric acid, cryst	22	"
Water	1,000	"

The only obstacle to the general use of cobalt in place of nickel for plating appears to be its high price. Rumors have frequently reached us that cobalt was about to be put on the market at the same price as nickel. Fink[25], in 1912, says that cobalt can be bought for less than one-third what it cost ten years ago, yet in that same year the metal purchased for use in the writer's laboratory cost $5 per pound, just a dollar higher than it cost two years before, while in 1889 Watt, in England, bought the metal in the form of anodes for only $3.90 per pound.

In an account of the Cobalt mining district Gibson[26] says: "The enforced production of cobalt from these mines has brought about a reduction in the price of cobalt oxide and is likely to lead to still further reductions."

ELECTROCHEMICAL ANALYSIS.

Solutions for Estimation of Cobalt:

52. The double oxalate of ammonium and cobalt according to Classen:[27]

0.3 g. cobalt, present as sulphate.
4 to 5 g. ammonium oxalate.
120 c.c. in volume.
1 ampere per square decimeter.
2½ to 3½ hours at 60 to 70° C.
3.1 to 3.8 volts.

Perkin[28] (page 98) states that the deposit contains carbon.

53. Solution of Fresenius and Bergmann. Classen[27] gives:

0.5 g. cobalt as sulphate.
5 to 6 g. ammonium sulphate.
40 c.c. ammonia (s. g. 0.96).
150 to 170 c.c. in volume.
0.7 ampere at 20° to 25° C.

The presence of chlorides, nitrates, fixed organic acids and magnesium compounds acts injuriously. Neumann[29] (page 113) states that this is the only solution employed in practical analysis.

54. Cobalt and ammonium chlorides have been proposed by Oettel. According to Neumann[29] (page 112) a suitable solution is:

1 g. cobalt chloride (0.248 g. cobalt).
5 g. ammonium chloride.
30 c.c. ammonia.
150 c.c. total volume.
1.5 amperes.
5 to 6 hours.

For the determination of cobalt a larger amount of ammonium chloride is required than in the case of nickel. The presence of nitrates is harmful.

55. Cobalt potassium cyanide is stated by Smith[30] (p. 129) to give complete precipitation. He adds 0.1 g. more of potassium cyanide than is necessary for precipitation and re-solution.

2 g. ammonium carbonate.
150 c.c. in volume.
1.5 amperes at 60° C.
6 to 6.5 volts.
3½ hours.

Neumann[29] (p. 113) states that it is impossible to secure a quantitative separation of cobalt from solutions containing an excess of potassium cyanide.

56. Neumann[29] (p. 112) states that exact results are given by:

1 g. cobalt sulphate (0.21 g. cobalt).
15 g. ammonium carbonate.
2 to 4 c.c. ammonia.
150 c.c. total volume.
1 ampere at 3.7 to 3.9 volts.
2½ to 3½ hours at 50° to 60° C.

57. Perkin[28] (p. 97) adds 3 g. ammonium tartrate to the solution of the cobalt salt, begins electrolysis at 0.2 ampere, and after an hour increases the current to 1 ampere per square decimeter. Time, 4 to 5 hours. The deposit often has a brilliant, burnished appearance. The results are slightly high, owing to a small amount of carbon being deposited with the cobalt.

58. Perkin[28] (p. 98) claims that the most accurate results are obtained by adding to the solution of the cobalt salt:

2 c.c. of a 5 percent solution of phosphoric acid,

20 to 25 c.c. of a 10 percent solution of di-hydrogen, sodium phosphate, stirring during the latter addition to prevent precipitation of a double phosphate. Hydrogen di-sodium phosphate cannot be used on account of the formation of an almost insoluble cobalt salt. Electrolysis should begin at 0.2 ampere in the cold solution. After an hour the current may be raised to 1 ampere and the solution warmed to 60° C. If a brown deposit forms on the anode it may be removed by adding 0.1 to

0.2 gram of hydroxylamine sulphate or chloride. Formaldehyde acts more slowly. Time, 4 to 6 hours. The deposit is usually brilliant.

59. Vortmann[30] adds tartaric or citric acid and an excess of sodium carbonate to the solution of the cobalt or nickel salt, then electrolyzes at 0.3 to 0.4 ampere. The deposit may contain traces of carbon.

60. Smith[30] (p. 129) obtains perfectly satisfactory results by adding an alkaline acetate to the cobalt solution. For rapid precipitation with a rotating anode he uses (p. 135):

Cobalt sulphate = 0.331 g. metal.
25 c.c. ammonia.
10 c.c. acetic acid, 20 percent.
5 amperes at 6 volts for 25 minutes.

The deposit is brilliant, and there is no precipitation on the anode.

61. Sodium formate is a very satisfactory electrolyte.[30]

Cobalt sulphate = 0.3535 g. metal.
2.5 g. sodium carbonate.
4 c.c. formic acid, 98 percent.

Heat to boiling, remove the flame and electrolyze with rotating anode at 5 amperes and 6 volts. Time, 30 minutes. The deposited cobalt is brilliant. A slight anode deposit may be removed by a few drops of a mixture of 5 c.c. glycerine, 45 c.c. alcohol, 50 c.c. water. A few drops of formic acid should be added from time to time to prevent the solution from becoming alkaline.

62. Lactic acid or a lactate makes an excellent electrolyte.[30] No precipitation occurs on the anode, and the cobalt deposit is exceedingly brilliant and adherent. A large excess of lactic acid retards precipitation.

2.2 g. sodium carbonate.
5 c.c. lactic acid, conc.
5 amperes at 8 volts precipitates 0.32 g. cobalt in 25 minutes.

63. Ammonium lactate is even superior to the preceding electrolyte.[30]

0.331 g. cobalt as sulphate.
30 c.c. ammonia.
7 c.c. lactic acid.
125 c.c. in volume.
6 amperes at 5 volts.
25 minutes is sufficient for complete precipitation.

64. Smith[30] uses a mercury cathode for the rapid determination of cobalt from its sulphate or chloride. At 4 amperes, 6 volts and 1,000 R. P. M. of anode, 0.35 g. of cobalt is precipitated in 15 minutes. It is necessary to add 10 c.c. of toluene or xylene to the chloride solution to prevent attack of the platinum anode.

65. Ammonium succinate can be employed, but some carbon is apt to be precipitated with the cobalt. Sodium succinate should not be used.

Separation of Cobalt and Nickel: Several solutions have been proposed for the difficult problem of separating cobalt and nickel by electrolysis.

66. Basse and Selva[31] add to the neutral or feebly acid solution of the metals an organic substance, such as tartaric or citric acid, glycerine, dextrose, etc., to prevent precipitation of the metals by excess of alkali; a large excess of caustic soda is added, and the solution is electrolyzed at a current of 0.3 to 1 ampere (per square decimeter?). Cobalt, iron and zinc are deposited, while nickel remains in solution. Ammonium carbonate is then added to the solution, and the nickel is deposited electrolytically.

67. G. Vortmann[32] adds to a neutral solution of the sulphates of the metals alkali or alkali-earth sulphates, and about 1 percent sodium chloride, and electrolyzes with frequent reversals of the current. Nickel remains in solution, and cobalt separates as hydroxide.

Neumann[29] (p. 215) says that this method is not suited to quantitative analysis.

68. Vortmann[29] also proposes to electrolyze solutions containing tartrates of the alkalies and a little potassium iodide. Neumann condemns this process also, and states that there is no reliable method for the electrolytic separation of cobalt and nickel.

Classen[27] (p. 241) ascribes to Vortmann the use of a solution containing sodium potassium tartrate, strongly alkaline by sodium hydroxide, but says that the essential data for repeating his experiments are lacking.

Bancroft[33] tested Vortmann's separation in an alkaline tartrate solution. He states that in this solution "the decomposition voltage of cobalt is about one volt lower than that of nickel." He finds that cobalt peroxide tends to precipitate at the anode, but this can be remedied by a high current density at the anode or by the addition of a few drops of concentrated nitric acid. In the latter case a little nickel peroxide may precipitate at the anode at low current densities. With a Classen dish as cathode and an E. M. F. of 1.9 to 2.0 volts between the electrodes, a good deposit of cobalt is obtained which gives no test for nickel, but some cobalt is always left in solution. If the voltage is raised to take out the last traces of cobalt, some nickel is also deposited. Heating the solution makes matters worse. The addition of potassium iodide, as recommended by Vortmann, is unsatisfactory. Addition of hydroxylamine sulphate, hydrogen peroxide, formaldehyde or sodium bisulphite helps a little, but does not remove the last traces of cobalt in a reasonable time. Nickel peroxide precipitates more readily the more carbonate and the less tartrate there is present, but, as cobalt peroxide tends to come down with the nickel peroxide, it is best to deposit nearly all the cobalt first, then to add sodium carbonate, and electrolyze with low current density at the anode. Proceeding in this way it was possible to separate one gram of cobalt from 0.1 g. nickel in eight days' electrolysis.

69. A. Coehn and E. Salomon[31] electrolyze neutral solutions of the sulphates or nitrates of cobalt and nickel, when the cobalt separates at the anode as peroxide.

70. A. Coehn, in a later patent,[35] by the addition of a persulphate to the former electrolyte, secures the precipitation of cobalt alone.

71. A. Coehn and E. Salomon,[36] to prevent cobalt and nickel from precipitating on the cathode when carrying out the above process, add to the solutions some metal more easily precipitated, *e. g.*, copper. In this case cobalt precipitates as peroxide on the anode, nickel remains in solution, and copper is deposited on the

cathode. Nitrate and sulphate solutions are well adapted to the process; which works better at elevated temperatures, e. g., 60° C. E. M. F. 1.5 to 2 volts. Current 0.1 ampere per square decimeter.

72. Perkin[28] (p. 170) says: "Many attempts have been made to separate cobalt and nickel electrolytically, but none of the methods so far published can be said to give very satisfactory results. The only method which can be at all recommended is that of A. Coehn and M. Glaser:[37] "The process depends upon the simultaneous deposition of the two metals—nickel at the cathode and cobalt at the anode. . . . The cobalt must be prevented from being precipitated on the cathode. Now, as hydrogen is only deposited 0.22 volt higher (lower?) than cobalt, too high an E. M. F. must not be employed, or else one must employ some method in which the deposition takes place at a lower potential than that at which the H ions are discharged, *e. g.*, the addition of a carbonate to the solution." To the neutral solution, containing not more than 0.1 g. cobalt, add 0.1 to 0.2 g. potassium dichromate and 3 to 4 g. potassium sulphate, make up to 500 c.c., and electrolyze at 0.10 to 0.15 ampere for 10 hours. E. M. F. 2.3 to 2.4 volts. All the nickel is deposited as metal at the cathode, and all the cobalt as peroxide at the anode. The peroxide is dissolved in acid, neutralized and precipitated as metal.

73. Balachowsky's method. Classen[27] gives:

0.3 g. of the metals in acetic acid solution.
3 g. ammonium sulphocyanide.
1 g. urea.

Ammonia to neutralize the free acid.

0.8 ampere per sq. decimeter, 1.0 volt, at 70 °to 80° C. Time, 1½ hours to precipitate the nickel. This contains sulphur, and should be dissolved in nitric acid, filtered and re-precipitated. The solution containing cobalt is boiled with nitric acid, filtered, and the cobalt deposited by any regular method.

Smith[30] (p. 266) uses:

10 g. ammonium sulphocyanide.
3 g. urea.
300 to 350 c.c. total volume.

After removal of the nickel the solution containing cobalt is evaporated to dryness several times with nitric acid, and the residue taken up with water, before depositing the metal.

74. Method of Alvarez.[38] The salts of cobalt and nickel are dissolved in cold water, recently boiled, and saturated at 0° C. with sulphur dioxide, forming a yellow cobalto-cyanide, $Ni_2CO(CN)_6$, which becomes green after washing and drying. Dissolve 0.5 g. of this salt in 100 c.c. of water, add 40 c.c. of ammonia of sp. g. 0.927 and 5 g. of ammonium sulphate. Electrolyze at 4 amperes per square decimeter and 3.4 to 4 volts for 2 hours. A brilliant deposit of nickel is obtained, free from cobalt, but containing carbon.

At 50 to 60° C., 1 ampere at 3.8 volts, in one hour precipitates both metals from a solution of:

1 gram of $Ni_2Co(CN)_6$ in 100 c.c. water.
50 c.c. ammonia.
10 g. ammonium sulphate.

P. Brulylants[39] criticises the method as not detailed enough for successful use. He obtains both metals in the deposit and also in the residual solution.

Smith[30] obtained unsatisfactory results with this process.

To sum up, it appears that all electrolytic methods so far devised for separating cobalt and nickel fail in the hands of all save their inventors.

ELECTRODEPOSITION OF NICKEL.

The quotations which follow give the opinions of different authorities upon the nature of electro-deposited nickel, and some of the difficulties encountered in plating with this metal.

Langbein[5] (page 246) says: "Hot fats strongly attack nickel, while vinegar, beer, mustard, tea, and other infusions produce stains; hence the nickeling of culinary utensils or the use of nickel-plated sheet iron for that purpose cannot be recommended." Bouant[10] (page 186): "After having considered nickel as dangerous in the preparation of food, it is now recognized, on the contrary, to be harmless. Nothing prevents the extension of nickeling to utensils of copper, an operation doubtless more expensive than tinning, but giving much more durable results."

"To decrease the resistance of the nickel solutions, conducting salts are added to them, which are also partly decomposed by the current. . . . The use of sodium acetate, barium oxalate, ammonium nitrate, ammonium-alum, etc., we consider unsuitable, and partly injurious, and are of the opinion that with few exceptions potassium, sodium, ammonia, or magnesia, are best for bases of the conducting salts. The presence of a small amount of free acid effects without doubt the reduction of a whiter nickel than is the case with a neutral or alkaline solution. Hence a slightly acid reaction, due to the presence of citric acid, etc., with the exclusion of the strong acids of the metalloids can be highly recommended. . . . An alkaline reaction of nickel baths is absolutely detrimental."—Langbein.[5]

"Lowering of the acidity, and elevation of the temperature, current density and nickel content of the bath tend to produce a fine-grained and matte deposit. Addition of alkalies and salts of magnesium have a beneficial effect. Addition of ammonium salts hinder the production of thick deposits. . . . Deposits from chloride solutions are always crystalline and coarser grained than those from sulphate solutions. Their hardness is about the same. The observation that the deposit from a chloride solution deteriorates more readily than one from a sulphate solution is explained by the difference in fineness of grain. In the presence of magnesium sulphate, the deposit contains 0.2 to 0.4 percent magnesium. This deposit is no harder than ordinary nickel plate, but is very flexible and well suited to the production of electrotypes. A bath containing magnesium salts ought to be more acid than other baths, to prevent the deposition of oxide. A higher acid content explains the fact that nickel deposited from solutions containing ethyl-sulphuric acid are very hard. Sulphate solutions give more flexible deposits than chloride baths. Deposits from solutions containing sodium salts are especially flexible, probably because of their finer grain. Iron renders the nickel deposit very brittle."—K. Engermann.[40]

"A solution of chloride of nickel is used as electrolyte. By this method it is possible to prevent the contamination of electrolytic nickel with sulphur, as would be the case were a sulphate solution used as the electrolyte."[41]

In spite of the recommendation by various experimenters of baths containing only nickel salts, there is a very general belief that for a successful nickel plating bath the salt of some other metal must be present, to form a double salt.

"Indeed it has been heretofore held as impracticable to nickel-plate with a single salt."—J. Yates.[37] "On the other hand, the simple acid salts of nickel have not hitherto been found to answer for the purpose of electrodeposition, from the fact that such solutions refuse to yield a reguline or cohesive deposit of metallic nickel."—J. Powell.[42]

Brass World[43] published a number of experiments with nickel sulphate solutions, made by an experienced practical plater to settle the question of whether or not single nickel salts can be used for plating. The conclusion is, "It is apparent, therefore, that single nickel salts cannot be used alone for plating."

The writer cannot subscribe to this result, for in 1904 he tried the deposition of nickel from a solution of 140 grams of commercial nickel sulphate per liter. Several trials gave black deposits, but finally a good deposit resulted. The solution was slightly diluted and 4 drops of sulphuric acid added. At the end of 38 hours electrolysis, with a current density of 5 amperes per square decimeter, falling to zero at the end, because of the complete solution of the anode, the deposit was excellent. Another trial of the same bath for 8 hours at 6 amperes per square decimeter gave a deposit of excellent appearance and firmly adherent. The current efficiency, however, was low.

Brochet[3] (page 229) says: "At the cathode the ion $Ni^{\cdot\cdot}$ ought to be discharged, and the metal pass into the molecular state and be deposited. In reality the reaction is much more complex, and the electrolysis of a pure salt of nickel generally gives poor results. With the sulphate there is the production of a slight black deposit, accompanied by an abundant evolution of hydrogen. With the chloride there is a deposit of nickel hydrate mixed with the oxychloride, and a similar evolution of hydrogen. A mixture of the sulphate and chloride of nickel gives much better results. The addition of an alkali-salt: potassium, sodium, ammonium, seems to be necessary to secure a good deposit; but then the series of reactions is entirely different. A complex salt is formed."

"It is a practice commonly adopted to momentarily use a high

E. M. F. until the work is just covered with nickel, and then to reduce the E. M. F.. This is called "striking," and 5 to 6 volts may for a few moments be used for this purpose. The E. M. F. is then quickly reduced to 2 or 3 volts."—Field.[44]

It is well known that there is greater difficulty in obtaining a satisfactory deposit of nickel on some metals than on others. Sackur[45] contends that: "A metal is more difficult to nickel, the farther its potential lies from that of nickel. Zinc, for example, possesses a higher electromotive force than brass, and this, in turn, more than iron. Potassium cyanide solution has a lower E. M. F. of decomposition than nickel chloride, and this again smaller than the sulphate. Good nickeling depends only on the choice of the right E. M. F., not upon the composition of the bath." This is an excellent illustration of the pitfalls of error which lurk within the covers of our electrochemical authorities—errors all the more insidious from the grain of truth in them.

One trouble, which was encountered in the earliest commercial nickel-plating, and it seems to have persisted to the present, in spite of the numerous remedies proposed, is the tendency of the deposit to peel off from the underlying metal.

In 1871 Keith[46] says: "The objection to nickel-plated goods thus far is that the deposit is so brittle that it cannot be bent, nor on many articles stand necessary wear even if not bent, and that it will also scale or peel off." In spite of the cure for this trouble announced by Keith, Peters[45] (page 153) writing in 1900, says: "When deposits of electrolytic nickel exceed a fraction of a millimeter in thickness they usually separate from the cathode in thin brittle leaves."

"The usual methods of electrolytically separating nickel from aqueous solutions of its salts do not permit of the production of deposits of more than one-hundredth of a millimeter in thickness, since with a longer continuance of nickeling the layer formed comes off in thin scales. This disadvantage can be avoided by using a heated electrolyte, as has been long known; but a thick nickel plate thus produced shows a crystalline structure as compared with the rolled nickel of commerce, is very brittle, and is therefore not suited for direct manufacture or technical utilization without being first melted over again."—M. Kugel.[20]

Turning from patentees, who may be regarded as prejudiced witnesses, we find D. H. Browne,[47] saying: "The bug-bear encountered by all who attempt to produce sheets of nickel thicker than that used by nickel platers has been the tendency of nickel to crack and curl off in rolls, like wood shavings."

"Two of the difficulties which are often encountered in electroplating (with nickel) are either the formation of gray pulverulent deposits, or else the deposit does not adhere, but cracks and curls from the cathode. . . . The former difficulty has been found to be due to employing too high current density and too high E. M. F., whereas the latter difficulty is due to the electrolytes being too acid and at too low a temperature, or else to a film of grease or dirt on the cathode."—E. F. Kern.[48]

"Nickel well deposited is extremely hard, so hard that it cannot be burnished, and is somewhat brittle. Thick coatings are especially liable to flake off in use, unless exceptionally well deposited, and even the thinnest films will part from surfaces which are not chemically clean."—McMillan[4] (p. 217).

The cause of this brittleness and peeling of nickel deposits is indicated in the following quotations: "Using a neutral or ammoniacal solution of pure sulphate of nickel there is an abundant disengagement of gas from the anode; soon followed by an increasing production of hydrogen at the cathode, and the deposited nickel becomes detached, curling up like wood shavings."—M. Gresy.[49]

"The deposition of nickel requires a neutral bath. The presence of much free acid causes deposition of hydrogen, and the deposit of nickel in scales. Peeling of the nickel deposit is due to occlusion of hydrogen, which always exists in deposits of nickel and cobalt."—A. Brochet.[50]

"It is commonly considered that the curling up of electrolytic nickel plate is due to the co-deposited hydrogen."—Schoch.[51]

"The difficulty of obtaining thick nickel deposits is due to hydrogen evolved along with the metal and absorbed by it, causing brittleness."—A. Hollard.[52]

Another trouble occasionally referred to is the formation of pits on the surface of the deposit.

"The trouble you experience from dark and pitted deposits is due to occluded hydrogen. This trouble develops when the solution is low in metal and hydrogen gas forms very rapidly upon the surface of the articles being plated. This gas theoretically burns holes in the deposit, causing the pitting noticed."[53]

"The occlusion of hydrogen tends to make the deposit somewhat brittle, and more or less porous, and hydrogen gas clings to the surface of the deposited metal in the form of very fine bubbles, thereby making the surface more or less warty and rough. . . . By maintaining in the bath a small amount of material which will combine with free hydrogen, *e. g.*, chlorine, the occlusion of hydrogen, etc., is prevented. . . . The chlorine may be introduced as a gas, by adding fresh bath saturated with chlorine, or in case of a chloride electrolyte by using a small insoluble anode to which a portion of the current is shunted. Free bromine may be used, but gives inferior results."—T. A. Edison.[54]

Photographs showing such pitting of iron[55] and nickel[56] deposits have been published.

The remedies most frequently proposed for the curling and brittleness of electrolytic deposits of nickel are strict neutrality of the bath, and electrolysis at high temperatures, varying between 30° and 100° C. H. J. Brownell[57] secures a deposit of nickel which will stand drawing, bending, spinning, etc., of the plated metal. "The article to be plated being heated by immersion in water or otherwise to a temperature of nearly 100° C. (212° F.), and then subjected to a hot nickel-plating bath." Foerster,[58] by heating from 50° to 90° C. an absolutely neutral bath containing 140 g. nickel sulphate per liter, obtained deposits 0.5 to 1.0 mm. in thickness. The current density was 2 to 2.5 amperes per $dm.^2$ Other methods of preventing the curling of nickel, depending on the addition of particular substances to the electrolyte, will be mentioned later.

Purity of Nickel Anodes.

Calhane and Gammage,[59] analyzed commercial anodes from two different establishments and found 7.57 and 7.52 percent iron in them, and 92 percent nickel. Using these anodes, the deposit always contained iron, varying in amount between 0.07 and 0.75 percent.

The following is a formula given for the making of nickel anodes:[60] 92 parts nickel, 4 parts tin, 4 parts old files.

O. W. Brown[61] finds copper present in a nickel anode: "The presence of the copper, rather than being a detriment, seems to be advantageous in allowing a high anode current density to be used.

"Commercial nickel anodes contain, in addition to nickel, iron, tin and carbon. These are introduced intentionally to render the anode 'soft,' *i. e.*, so that it will dissolve easily in the solution during plating."[62]

Since such anodes are largely used in this country it is evident that much of the nickel plate produced here contains a small amount of iron. It is to this iron that Bancroft[63] ascribes the ready rusting of nickel-plated objects when exposed to the weather: ". . . All our nickel plate contains iron. I am confirmed in that belief by the fact that the nickel-plating on the Weston instruments, which I assume to be as good as any that would be put on the market, rusts red in the laboratory. I take it that this is due to iron in the nickel plate. . . . If a bicycle is left out over night it will rust." The writer does not regard the above allegations as proved until rust has formed on such nickel plate deposited on copper or some other surface which is in itself entirely free from iron.

Passivity of Nickel Anodes.

It has long been known that rolled nickel anodes do not dissolve satisfactorily in the standard plating solution, nickel ammonium sulphate. This phenomenon was brought to the attention of this Society by O. W. Brown.[64] Brochet[3] (page 228) says: "Nickel is a passive metal, that is to say that to a certain degree and under certain conditions it dissolves incompletely and acts as a noble metal—as an insoluble anode. Sulphuric acid is then formed at the anode, and nickel dissolves in an amount less than that required by Faraday's law." Speaking of nickel anodes, McMillan[4] (page 222) says: "Nickel anodes must be as pure as it is possible to obtain them. They are to be had cast or rolled. Cast anodes being the more readily soluble are more likely to neutralize the acid set free by electrolysis at the anode, and hence the natural tendency of the (ammoniacal) nickel bath to become alkaline asserts itself. Rolled anodes are more likely, by insufficiently neutralizing the acid, to cause the bath to become acid." Bancroft[63] points out that a pure nickel anode may be made to corrode satisfactorily in nickel ammonium sulphate by adding to the solution a small percentage of nickel chloride or ammonium chloride. He recommends the use of anodes of pure nickel and the complete elimination of iron from the nickel bath. Brochet[65] says: "The greater or less passivity of the anode depends on the physical nature of the metal, *i. e.*, the hammering or rolling to which it has been subjected, not on its purity."

On the contrary, Kern[48] says: "Another cause of gassing is the use of pure metal anodes in nickel-ammonium sulphate electrolyte, as the pure metal does not readily dissolve. However, pure nickel anodes may be successfully used in this electrolyte if a small amount of chloride salt is added, the presence of which causes the anode current efficiency to approximate 100 percent." Langbein[5] (pages 247 and 254) objects to the addition of chlorides or nitrates to baths for nickeling iron: "Iron objects nickeled in such a bath come out faultless, but in a short time, even if stored in a dry place, portions of the nickel layer will be observed to peel off, and by closely examining them it will be seen that under the deposit a layer of rust has formed which actually tears the nickel off." E. Weston[66] says: "It has been found that the solution of the double chloride of nickel and ammonium is better adapted for coating iron with nickel than the double sulphate solution, the latter answering better for brass."

In the electrolytic refining of iron the writer found that deposits from a chloride electrolyte rusted very much worse than those obtained from a solution containing only sulphates.

NICKEL PLATING BATHS.

For convenience the baths will be classified as follows:

I. Baths containing single salts of nickel.
II. Baths containing double salts.
III. Miscellaneous baths.
IV. Baths for deposition of malleable nickel.
V. Baths producing thick deposits.
VI. Agents for the production of smooth deposits.
VII. Nickel electrotypes.
VIII. The nickeling of zinc.

I. Baths Containing Single Salts of Nickel.

a. Neutral Baths:

Under this title will be grouped the baths formed by simple solution of the nickel salt without rendering it distinctly acid or alkaline, as well as those baths whose neutrality is specifically stated.

75. Yates' acetate solution.[67] Nickel acetate is dissolved in water to a strength of 8° or 10° Bé. (1.058 to 1.074 sp. g.). It is claimed to have the advantage over other solutions of a larger proportion of metal of not being subject to the irregular decompositions which render the continued operation of other baths so difficult, and to permit of direct nickeling on metals which it has heretofore been impracticable to nickel without a previous coating of copper. Plate steel, cast and wrought iron are mentioned as examples of this. With care, zinc may also be nickeled directly in this bath.

In referring to the fifty different nickel baths tried by Alexander Watt,[68] a number placed in parenthesis after the title of the bath indicates the numbering in his paper.

76. Watt's acetate bath (1). This consisted of 120 grams of neutral nickel acetate per liter. At a current density of 2.4 amperes per square decimeter a uniform but somewhat dark deposit was obtained. At the end of an hour's deposition a steel burnisher was applied, which brightened the surface, showing that the metal was softer than that obtained from the ordinary double sulphate solution.

77. Watt's[68] nickel benzoate solution (46). This solution yields a bright deposit, soft enough to be burnished.

78. Watt's[68] nickel borate solution (48). This yields a white deposit.

79. Nickel chloride solution[68] (22). 15 grams of nickel chloride per liter gave a brisk evolution of hydrogen and a deposit of metal not quite so white nor so fully adherent as the deposit from the double sulphate.

80. Nickel citrate solution[68] (6). This was prepared like most of the other salts of this set of experiments, by digesting moist nickel carbonate with a hot solution of the acid. The first

deposit was not of satisfactory whiteness, but this was improved by increasing the current.

81. Nickel lactate[68] (12). This salt is readily soluble, and gives a deposit of fairly good color.

82. Nickel nitrate[68] (16). Nickel carbonate was dissolved in nitric acid diluted with two volumes of water until a neutral solution was obtained. Neither a deposit of metal nor of hydrogen was obtained with one, two or even three Daniell cells in series. There was a slight evolution of oxygen at the anode.

83. J. Mathieu's propionate solution.[69] He used a solution of nickel propionate of about 5° Bé. (sp. g. 1.0357). No results are stated, nor are any claims made in regard to the superlative excellence of the product.

84. Nickel salicylate[68] (47). This gives a white deposit.

85. Nickel sulphate[68] (18). A solution was made by dissolving 100 grams of the crystals per liter of water. The deposit was of good color, but was not so adherent as deposits from the double sulphate of nickel and ammonia.

86. Nickel sulphate, neutralized by lime or calcium carbonate.[70] To 100 parts of an acid aqueous solution of nickel sulphate he adds 3.75 to 7.5 parts of hydrate of lime to exactly neutralize the acidity of the sulphate. To avoid the danger of an excess of alkali he prefers, however, to neutralize by the carbonate of lime. "This solution produces a brighter metallic deposit than the solution in general use, and without the addition of ammonia in any form."

87. Nickel sulphocyanide[68] (20). Moist nickel carbonate was dissolved in a strong solution of potassium sulphocyanide, and this was electrolyzed with the current from three cells. A dark steel-gray deposit was immediately formed, which did not alter during a half hour's deposition. Gas was evolved at both electrodes.

88. Nickel tartrate[68] (11). The solution prepared by digesting moist nickel carbonate in a strong, hot solution of tartaric acid is a poor conductor, and three cells in series were required to produce a deposit of an indifferent color. It was noticed that the cathode became more fully coated with metal on the back than on the front.

b. Acid Baths:

89. Nickel acetate.[71] The solution contains about 60 grams of nickel acetate per liter, and is maintained strongly acid by acetic acid. "These solutions thus prepared and used do not become depleted in using, and require no addition of nickel to keep up their strength other than that derived from the nickel of the anode."

90. Nickel citrate[68] (26). The solution was prepared by electrolyzing a strong solution of citric acid with a nickel anode. The deposit was very bright, of a good white color, much softer than is usual with nickel, and received a high polish under the steel burnisher.

91. Nickel formate.[72] The solution contains nickel formate with excess of formic acid. Among its claims to merit are: "The solution needs no replenishing with salts of nickel, the nickel being supplied from the anode. No precautions need be taken to see that the solution is free from the presence of potash, soda, alumina, lime or nitric or other acid. The deposit may be of any thickness, and will always be firm, flexible and white."

c. Alkaline Baths:

92. Nickel ammonio-acetate[68] (32). Ammonia was added to a strong solution of nickel acetate until the liquid acquired a deep blue color. The deposit was bright, of a good color and very adherent.

93. Nickel ammonio-carbonate[68] (35). Nickel carbonate was dissolved in strong ammonia, diluted and electrolyzed. The deposit was white, and retained its original brightness after an hour's deposition.

94. Nickel carbonate[68] dissolved in a strong solution of ammonium carbonate gave a rather dark deposit.

95. Nickel ammonio-chloride[68] (30). Strong ammonia was added to a solution of nickel chloride until the solution acquired a deep blue color. The deposit was white and very bright. Very little hydrogen, but much oxygen was evolved.

96. Nickel ammonio-citrate[68] (33). Ammonia was added to a strong solution of nickel citrate. The deposit was white, bright

and very adherent. The anode kept perfectly clean during the electrolytic action.

97. Nickel ammonio-ferricyanide[68] (45). Nickel ferricyanide was dissolved in strong ammonia. The filtered and diluted solution gave a prompt and fairly white deposit on brass.

98. Nickel hydroxide in ammonia[68] (15). This solution gave a yellowish deposit of nickel, without hydrogen. Oxygen was abundantly evolved at the anode, which became coated with a brownish film.

99. Nickel ammonio-nitrate[68] (31). Excess of strong ammonia was added to a solution of nickel nitrate. The nickel deposit was rather dark in color, and after a half hour the anode had a deep brown color.

100. Nickel ammonio-sulphate[68] (19). An experiment was tried to ascertain the effect of small and increasing additions of ammonia to the sulphate solution. The current from three cells was used, and a fresh brass cathode was used after each addition of ammonia. After the first addition of ammonia the deposit appeared much brighter than that obtained from nickel sulphate alone, and this characteristic was maintained until the solution acquired a deep blue color. The anode was almost black, and a flocculent precipitate formed in the solution.

The evolution of oxygen or the formation of nickel oxide on the anode, mentioned in many cases, indicates that those particular baths are not suited to practical use because of poor corrosion of the anode. In only one case, No. 96, is there mention of good anode corrosion in these alkaline baths.

II. Baths Containing Double Salts.

In connection with these baths it will be of interest to review the patents of Adams under which for many years nickel plating was monopolized. His first U. S. Patent, 93,157, of Aug. 3, 1869, claims:

"1. The electrodeposition of nickel by means of a solution of the double sulphate of nickel and ammonia, or a solution of the double chloride of nickel and ammonium, prepared and used in such a manner as to be free from the presence of potash, soda, alumina, lime, or nitric acid, or from any acid or alkaline reaction."

"2. The use, for the anode of a depositing cell, of nickel combined with iron to prevent the copper and arsenic which may be present from being deposited with the nickel or from injuring the solution."

"3. The electroplating of metals with a coating of compact, coherent, tenacious, flexible nickel of sufficient thickness to protect the metal upon which the deposit is made from the corrosive agents with which the article may be brought in contact."

"4. The deposition of electrotype-plates of nickel to be removed from the surface on which the deposit is made and used separately therefrom."

It is easy to see how it was possible to monopolize nickel plating under this unjust patent. Even today manufacturers of anodes have not recovered from its baneful influence, but are still furnishing anodes in accordance with claim No. 2, to the great detriment of the nickel plating industry.

Adams' patent, 100,961, March 22, 1870, is remarkable for its contradictory claims. "This improvement consists in the use of three new solutions from which to deposit nickel by the electric current: First, a solution formed of the double sulphate of nickel and alumina, or the sulphate of nickel dissolved in a solution of soda, potash, or ammonia alum, the three different varieties of commercial alum; Second, a solution formed of the double sulphate of nickel and potash; Third, a solution formed of the double sulphate of nickel and magnesia, *with* or without *excess* of *ammonia*. . . . I prefer to use these solutions at a temperature above 100° F. (38° C.), but do not limit my invention to the use of these solutions at that temperature. I therefore claim:

"1. The electrodeposition of nickel by means of a solution of the double sulphate of nickel and alumina, prepared and used in such a manner as to be free from the presence of ammonia, potash, soda, lime or nitric acid, or from any acid or alkaline reaction."

"2, . . . A solution of the double sulphate of nickel and potash, prepared and used in such a manner as to be free from the presence of ammonia, soda, lime, or nitric acid, or from any acid or alkaline reaction."

"3. . . . A solution of the double sulphate of nickel and magnesia, prepared and used in such a manner as to be free from the presence of potash, soda, alumina, lime or nitric acid, or from any acid or alkaline reaction."

In U. S. Patent 136,634, March 11, 1873, Adams' claim was still further extended. "I now claim . . . The electrodeposition of nickel, or the electroplating with nickel, by means of a solution of either of the soluble salts of nickel, such solution being prepared and being used, substantially, free from the presence of potash, soda, lime, alumina, and nitric acid, or either of them, and free from acid and alkaline reaction, or from either."

a. Neutral Baths:

In this class will be included baths made by merely dissolving normal salts, as well as those solutions which have been carefully neutralized.

The bath most generally used is a solution of nickel ammonium sulphate.

101. Pfanhauser's solution[73] (page 361). 75 grams of nickel ammonium sulphate per liter. Current density, 0.3 ampere per dm.^{2} Temperature 15 to 20° C. Resistivity 24.6 ohms. 3.5 volts for 15 cm. between electrodes. Temperature coefficient 0.0176 for 1° C. Specific gravity 1.047. Current yield 91.5 percent. Deposit per hour 0.0034 mm. Cast anodes of ½ to ¾ the area of cathode should be used. The deposit is hard, good for plating iron or steel. Langbein[5] says the cast anodes rapidly render the bath alkaline, necessitating a frequent correction of the reaction. Brochet[3] (page 237) says: "This bath is poor in metal, even in case of the saturated solutions (98 grams at 18° C.). It is better to replace a part of the double sulphate by the single sulphate." He recommends:

102. Solution of single and double sulphates:[3]

Nickel sulphate	166 grams.
Nickel ammonium sulphate	55 grams.

Specific gravity 1.101, resistivity 23.9, at 18° C., nickel per liter 39 grams. "Baths rich in metal possess the advantage of greater covering power and are less influenced by cold. The addition of ammonium sulphate is sometimes recommended to increase the conductivity of the bath; this should not be done, since it results in the impoverishment of the bath in metal."—Brochet.[3]

103. The double sulphate with ammonium sulphate:[5]

Nickel ammonium sulphate....	50 grams
Ammonium sulphate	50 grams

"E. M. F. at 10 cm. 1.8 to 2 volts. Current density 0.35 ampere. The bath deposits rapidly, and all metals (zinc, lead, tin, and Britannia, after previous coppering) can be nickeled in it. Upon rough castings and iron, a pure white deposit is difficult to obtain. On account of the great content of ammonium sulphate in the bath, the deposit piles up, especially on the lower portions of the objects, which readily become dull, while the upper portions are not sufficiently nickeled."—Langbein.[5]

104. Pfanhauser[73] gives:

Nickel sulphate	50 grams
Ammonium chloride	25 grams

Specific gravity 1.0357 (5° Bé.). Resistivity 17.6 ohms. Temperature coefficent 0.025. E. M. F. for 15 cm. 2.3 volts. Current density 0.5 ampere. Current yield 95.5 percent. Deposit per hour 0.0059 mm. Cast anodes half the area of cathode. Langbein[5] gives 57 grams and 29 grams, respectively, of the same salts, and states that the deposit is soft and white, that heavy deposits cannot be obtained because of the danger of peeling, and that the bath is not suited to the direct nickeling of iron.

105. Bath with magnesium sulphate:[5]

Nickel ammonium sulphate ..	56 grams.
Magnesium sulphate	26 grams.

"E. M. F. 4 volts at 10 cm. Current density 0.2 ampere. Good for plating on iron, and may be used for the direct nickeling of zinc. The deposit is soft, and of a yellowish tinge. The bath does not remain constant, but fails after working three or four months, even cast anodes being but little attacked."—Langbein.[5]

Watt experimented with a solution containing the sulphates of nickel and magnesium. At first the deposit was decidedly yellow in tone, but became whiter after a few hours' use of the solution.

Adams' patent of the double sulphate of magnesium and nickel has already been noticed.

106. To a solution of nickel ammonium sulphate Watt[66] gradually added a concentrated solution of ammonium citrate. A bright deposit of a slightly yellowish tone was obtained, which retained its brightness during deposition for a long time, but finally became dull. The deposit was soft enough to be burnished. There was a brisk evolution of gas at the anode, and a few bubbles of hydrogen clung to the cathode.

107. Langbein[5] gives a somewhat similar bath, as do C. H. Procter[74] and Pfanhauser:[73]

	Langbein	Procter	Pfanhauser
Nickel sulphate	26.0 grams	30 grams	40 grams
Ammonium chloride	17.5 "	30 "	0 "
Potassium citrate	17.5 "	18 "	35* "

* Sodium citrate.

Langbein specifies for copper and copper alloys: Current density 0.45 to 0.5 ampere, E. M. F. at 10 cm. 1.5 to 1.7 volts. For zinc, current density 0.8 to 1 ampere, E. M. F. 2 to 2.5 volts.

Pfanhauser gives a current density of 0.27 ampere, E. M. F. at 15 cm. 3.6 volts. Specific gravity 1.039 (5½° Bé.). Resistivity 51.7 ohms. Temperature coefficient 0.0348. Current yield 90 percent. Deposit per hour 0.00301 mm. Rolled anodes. The bath yields a soft white deposit, and is especially suited for plating pointed objects like knives.

108. An English solution:[16]

Nickel ammonium sulphate	100 grams.
Ammonium acetate	50 grams.

109. Another English solution:[16]

Nickel ammonium acetate	100 grams.
Ammonium chloride	20 grams.
Glycerine	5 grams.

110. Nickel and ammonium chlorides:[5]

Nickel chloride, cryst.	37.5 grams.
Ammonium chloride	37.5 grams.

The bath is neutralized by ammonia. E. M. F. at 10 cm. 1.75 to

2 volts; for zinc, 2.8 to 3 volts. Current density 0.5 ampere. "The bath deposits readily, and is especially liked for nickeling zinc castings."

111. H. P. Dechert's solution:[75]

Nickel chloride, cryst. at least	141 grams.
Calcium chloride solution of 30° Bé. (sp. g. 1.261).....	1 liter.

The advantages claimed for this solution are very low resistance, elimination of hydrogen bubbles from the surface to be plated, thus removing the danger of spotting, a permanent and enduring solution, and a smooth, close and tough deposit of nickel.

112. Watt[68] gradually added to a solution of nickel sulphate a solution of ammonium tartrate, and obtained a very bright and very white deposit of nickel.

b. Acid Baths:

E. Weston[66] in his patent claims: "1. The electrodeposition of nickel by means of solutions of the salts of nickel containing boric acid, either in its free or combined state."

"2. A solution of the single or double salts of nickel to which has been added boric acid, either in its free or combined state." The exact composition of the baths is not stated by Weston. He claims that the addition of boric acid or its compounds prevents the deposition of sub-salts upon the cathode, renders the solution more constant and stable in composition, diminishes the liability to the evolution of hydrogen, permits the use of a more intense current, and improves the character of the deposit by rendering it less brittle and by increasing the tenacity with which it will adhere to a metal surface.

Langbein[5] (page 249) says: "Boric acid, recommended by Weston as an addition to nickeling baths, has a favorable effect upon the pure white reduction of the nickel, especially in nickeling rough castings. . . . Numerous experiments have shown that the deposit of nickel from nickel solutions containing boric acid is neither more adherent nor softer and more flexible than that from a solution containing small quantities of a free organic acid. Just the reverse, the deposit is harder and more brittle in the presence of boric acid.

"Weston recommends the following composition for baths:[5]

"113.	Nickel chloride	26 grams.
	Boric acid	10.5 grams.
"114.	Nickel ammonium sulphate	38 grams.
	Boric acid	19 grams.

"Both solutions are said to be improved by adding caustic potash or caustic soda so long as the precipitate formed dissolved. These compositions, however, cannot be recommended, because the baths work faultlessly for a comparatively short time only."

115. Pfanhauser[73] gives:

Nickel ammonium sulphate	40 grams.
Ammonium chloride	15 grams.
Boric acid	20 grams.

Current density 0.5 ampere. E. M. F. for 15 cm. 2.8 volts. Resistivity 20.85 ohms at 15° to 20° C. Temperature coefficient 0.0156. Current yield 89.5 percent. Deposit per hour 0.00556 mm. Specific gravity 1.0357 (5° Bé.). He, too, speaks of the difficulty of regulating the bath, and recommends cast anodes of half the surface of the cathode.

Maigne and Mathey[16] ascribe to Weston the two baths which follow:

116.	Nickel chloride	50 grams.
	Boric acid	20 grams.
117.	Nickel sulphate	50 grams.
	Boric acid	17 grams.

118. Bath of Julius Weiss:[16]

Nickel sulphate	40 grams.
Ammonium chloride	20 grams.
Citric acid	2 grams.

119. Langbein[5] (p. 253) gives:

Nickel ammonium sulphate	64 grams.
Ammonium sulphate	20 grams.
Citric acid	4.4 grams.

E. M. F. 2 to 2.2 volts at 10 cm. Current density 0.34 ampere. The materials are dissolved in boiling water, and ammonia is added until blue litmus paper is only slightly reddened. Very careful regulation of the current is required to avoid peeling off. The anodes should be cast and rolled in equal numbers. According to experiments by Dr. Langbein it is better to decrease the amount of ammonium sulphate to 2 grams.

This bath is operated so nearly neutral that it closely resembles bath No. 107.

120. J. H. Potts[76] uses:

Nickel acetate	28 grams.
Calcium acetate	16 grams.
Acetic acid, sp. g. 1.047 (35 percent)	8 grams.

Potts claims: "I have succeeded in producing a nickel-plating solution having the advantages of the presence of free acid and of great density, and yet free from the objections which have been heretofore made to acid solutions. . . . To the presence of the acetate of lime I also attribute the fact, which I have discovered in practice, that in the use of my solution no such care and nicety in the regulation of the electric current are necessary as in the use of the ordinary solutions. . . . Another advantage of my solution is the entire freedom of iron work plated in it from liability to corrosion after removal from the the cleansing bath of warm water in which it is necessary to place it after leaving the plating solution, thus obviating a very serious objection heretofore made to the presence of free acid in a nickel-plating solution—an objection which has been found to exist in the use of ordinary solutions." Watt[11] (p. 297) quotes Wahl as follows: "It gives satisfactory results without that care and nicety in respect to the condition of the solution and the regulation of the current which are necessary with the double sulphate solution. The metallic strength of the solution is fully maintained without requiring the addition of fresh salt, the only point to be observed being the necessity of adding from time to time (say once a week) a sufficient quantity of acetic acid to maintain a distinctly acid reaction. It is rather more sensitive to the presence of a large quantity of free acid than to the opposite condition, as in the former condition it is apt to produce a black deposit, while it may run down nearly to neutrality without notably affecting the character of the work. The deposited metal is characteristically bright on bright surfaces, requiring but little buffing to finish. It does not appear, however, to be so well adapted for obtaining deposits of extra thickness as the commonly used double sulphate of nickel and ammonium. On the other hand, its stability in use, the variety of conditions under which it will work satisfactorily and the trifling care and attention it calls for make it a useful solution for nickeling."

121. "W. Baker and J. Unwin[77] dissolve nickel hydrate in tartaric acid and add potassium hydrate or ammonia nearly to neutralization, so that a double salt is formed."[17]

122. Placet and Bonnet's nickel solution, see bath No. 25, this paper.

123. For Nagel's nickel solution see bath No. 7.

124. For Kugel's nickel solution see No. 23.

c. Alkaline Baths:

125. Roseleur's solution:[16]

Nickel ammonium sulphate ..	40 grams.
Ammonium carbonate	30 grams.

126. Desmur's solution:[11]

Nickel ammonium sulphate ..	70 grams.
Sodium bicarbonate	8 grams.

The bath is worked nearly at the boiling point. If, after working for some time, the deposit becomes dark, a small lump of sodium sulphide will remedy it. "Of all the solutions of nickel which I have tried," says M. Desmur, "this has, without doubt, given me the best results both as to quickness of working and whiteness of deposit, which is equal to that of silver. Nickel deposited from this solution can be burnished."

121. Bischof and Thiermann's[78] solution:

Nickel sulphate	86 grams.
Ammonium sulphate	67 grams.
Ammonia, sp. g. 0.905......	110 grams.
Volume	1 liter.

Platinum anode. E. M. F. 2.8 volts. Current density 0.5 ampere.

128. Prior's solution.[79] He adds to nickel chloride solution ammonium chloride, sodium chloride and potassium hydrate until the solution is strongly alkaline.

129. Gutensohn's solution.[80] He claims to deposit nickel, aluminum, copper, lead and zinc from a solution of the phosphate of the desired metal dissolved in a solution of sodium hydrate to which ammonia is added.

130. F. Weil[81] dissolves nickel hydroxide in Seignette's salt and sodium hydrate.

III. Miscellaneous Baths.

Although even traces of nitrates are declared by Adams to be harmful in the nickel bath, several solutions have been used or patented in which a nitrate is the principal or an important ingredient.

131. Boden's solution:[16]

Nickel nitrate	27 grams.
Sodium sulphite	333 grams.
Ammonia	27 grams.

132. George Brucker[82] patents a solution composed of:

100 parts saturated solution of nickel in nitric acid.
3 parts cream of tartar.

133. Watt[68] (17) added ammonium nitrate to a neutral solution of nickel nitrate but obtained only a slight discoloration of the cathode. No hydrogen was liberated, but small bubbles of gas appeared at the anode.

134. Watt[68] (43) also tried the addition of ammonium citrate to the solution of nickel nitrate, but without any favorable action.

The double cyanide solution, used for the deposition of so many of the metals, in the case of nickel is conspicuous by its absence from all save two of the books on electroplating so far referred to in this paper. Watt[11] says, page 298: "This was one of the earliest solutions used for depositing nickel, and is capable of yielding an exceedingly white deposit. Though neither so economical nor so susceptible of yielding stout deposits of nickel as the ordinary double sulphate or double chloride, it may be advantageously employed when only a thin coating of a fine white color is desired. It is stated to be somewhat extensively used in some large nickel-plating works in the United States." Nickel cyanide is dissolved in a strong solution of potassium cyanide and a small excess of the latter is added. "The solution should be as concentrated as possible, almost to the point of saturation."

135. Thomas and Tilley[83] in 1854 patented a nickel bath consisting of a solution in potassium cyanide of the washed precipitate from a solution of nickel in nitric acid.

Watt[68] failed to get a deposit of nickel in the three experiments which follow:

"A solution was prepared by digesting recently precipitated phosphate of nickel in a moderately strong solution of cyanide of potassium. With the current from three cells, no metallic deposit was obtained, but a red salt formed at the cathode. A deposit of a black color appeared on the anode. There was a copious evolution of gas at both electrodes."

"A solution was prepared by adding recently precipitated and moist carbonate of nickel to a strong solution of cyanide of potassium. . . . There was much hydrogen given off, and the solution failing to yield a good film was abandoned."

"To a strong solution of cyanide of potassium moist ferricyanide of nickel was added. . . . No deposit of nickel could be obtained even when the cathode was briskly agitated in the bath. There was a brisk evolution of gas at both electrodes."

It looks like a case of too much free cyanide in the above solutions.

136. Bates[84] black nickel solution:

"Nickel salts"	120 grams
Cyanide of potassium	75 grams
Ammonia	108 grams
Water	1,000 grams

The nickel salts are dissolved in water, the cyanide added with stirring until the precipitate formed is dissolved, then the ammonia added—which should turn the solution to a light blue color. Nickel anodes are used. "The object of my invention is the electrodeposition of a black nickel which shall be as compact, coherent, tenacious, and flexible as the best deposit of white nickel."

Many "black nickel" solutions contain sulpho-cyanides, compounds of arsenic, antimony, or other substances whose presence in other baths, containing no nickel, causes a deposit similar to "black nickel." Until proved by analysis, the writer doubts that "black nickel" is either nickel or one of its compounds. Hence modern "black nickel" solutions are not included in this paper.

137. Adams' sulphite solution:[85]

Nickel sulphate	37.5 grams.
Ammonium sulphite or bisulphite	22.5 grams.

"The resulting products are sulphite of nickel and sulphite of ammonia, and a residuary product of sulphate of ammonia. This solution may also be made from the nitrate, chloride, or acetate of nickel by adding the proper quantity of sulphite or bisulphite of ammonia. It may be used with special advantage where the nickel plate forming the anode in the solution contains zinc. Nearly all commercial nickel contains more or less zinc, the presence of which tends to increase the evolution of hydrogen on the deposited plate. There is less tendency to this evolution of hydrogen with this solution than with those heretofore described in books."

138. Langbein[5] gives a phosphate solution:

Nickel phosphate	19 grams.
Sodium pyrophosphate	80 grams.

E. M. F. at 10 cm. for copper 3.5, for zinc 3.8 volts. Current density for copper 0.5, for zinc 0.55 ampere. "The bath yields a very fine dark nickeling upon iron, brass, and copper, as well as directly, without previous coppering, upon sheet zinc and zinc castings. For the same purpose a nickel solution compounded with a large quantity of ammonia has been recommended. However, experiments with this solution always yielded lighter tones than the above bath."

139. Powell's pyrophosphate solution:[86]

Nickel phosphate	22.5 grams.
Sodium pyrophosphate	26.2 grams.
Nickel citrate	15. grams.
Sodium bisulphite	7.5 grams.
Ammonia, 16 percent	37.5 grams.

"One great advantage arising from the use of my solutions is that the various metals and their alloys are electronegative to a solution containing pyrophosphates or phosphoric acid; hence, no decomposition or local action occurs when they are immersed in the bath. Thus zinc articles, which cannot be plated in a solution of double sulphate or chloride of nickel and ammonia, are beautifully plated with a firm adhesive layer of metal by using my solutions, and the deposit is white in color and very ductile."

140. Nickel fluosilicate:[87]

Nickel fluosilicate	100 grams.
Aluminum fluosilicate	50 grams.
Ammonium fluoride	50 grams.

The deposit is claimed to be smooth, dense, coherent, and adherent. It is advisable to add ammonium fluoride from time to time during use to prevent the separation of silica.

141. A bath with sodium chloride:[3]

Nickel sulphate	50 grams.
Nickel ammonium sulphate	50 grams.
Sodium chloride	10 grams.

Sp. gravity 1.064 (8½ Bé.). Resistivity 23.4 ohms. Nickel per liter 18 grams. "The addition of 10 to 15 grams of boric acid per liter preserves the whiteness of the nickel deposit, which the presence of the chloride tends to make it lose."

Organic salts and compounds have been largely used, either as the basis of the bath, or as an addition for the purpose of improving the permanency of the bath or the nature of the deposit.

142. Watt[68] added sodium chloride to a strong solution of

nickel acetate, and with two cells obtained a good white deposit of nickel on brass.

143. To a strong neutral solution of nickel acetate Watt[68] added potassium acetate. The deposit of nickel was very uniform and white. There was only a moderate evolution of gas at the anode, and none at all on the cathode.

144. To a solution of nickel sulphate Watt[68] added a solution of nickel acetate. The deposit was bright, very white, and brightened under the burnisher without excessive pressure.

For other acetate baths see solutions 75, 76, 89, 92, 108 and 109.

Citric acid and citrates are frequently used in the nickel bath.

145. Pfanhauser[73] gives:

Nickel sulphate	40 grams.
Sodium citrate	35 grams.

E. M. F. at 15 cm. 3.6 volts. Current density 0.27 ampere. Specific gravity 1.0394 or 5½° Bé. Resistivity 51.7. Temperature coefficient 0.0348. Current yield 90 percent. Deposit in one hour 0.00301 mm. Rolled anodes should be used of twice the cathode surface. This bath is equally good for nickeling iron, steel and brass, and is especially good for nickeling pointed objects. The deposit is white and ductile.

146. Langbein[5] gives a similar bath:

Nickel sulphate	48 grams.
Sodium citrate	30 grams.

"E. M. F. at 10 cm. 3.0 volts. Current density 0.33 ampere. This bath is claimed to be especially useful in preparing nickel electrotypes, but Langbein's experiments proved it to possess the disadvantages of all nickel baths prepared with large quantities of organic salts. For the special purpose for which it is recommended no better results were obtained than with any other nickel bath rationally composed for heavy deposits. It is very suitable for nickeling objects with sharp edges and points. The deposit is quite soft, and in grinding such nickeled instruments, peeling off of the nickel happens less frequently than with instruments nickeled in other baths."

147. Watt[68] added citrate of ammonia to a solution of citrate of nickel. Three cells caused a somewhat dull deposit, but on diluting the solution the color and brightness of the deposit were much improved. The deposit was readily brightened by the burnisher. The anode was covered with a greenish coating, which dissolved on standing at rest in the solution. Addition of a slight excess of citric acid kept the anode clean.

148. J. E. Chaster[88] patents a bath consisting of a solution of nickel ammonium citrate. It is to be used about three-fourths saturated. Its particular advantage over the double sulphate is claimed to be its lower E. M. F. of decomposition.

149. Watt[68] also tried the effect on the deposit of continued additions of nickel citrate to a solution of nickel sulphate. Even a small addition of the citrate caused a whiter deposit than that from the sulphate and a larger amount caused the deposit to continue bright, instead of becoming dull after a short deposition as it usually does in a solution of nickel sulphate. The metal felt soft under the burnisher, and a brilliant polish was obtained.

For other citrate baths see solutions 80, 90, 96 and 107.

Jas. Powell[89] patents the addition of benzoic acid or benzoates to any of the salts of nickel, claiming that it renders the solution more stable, causes proper corrosion of the anodes and yields a tough, cohesive and reguline deposit of beautiful silvery-white nickel. As an example of his solution he cites:

150.	Nickel sulphate	34 grams.
	Nickel citrate	15 grams.
	Nickel phosphate	15 grams.
	Benzoic acid	7.5 grams.

The four solutions which follow are also ascribed to Powell:[16]

151.	Nickel sulphate	27 grams.
	Nickel citrate	20 grams.
	Benzoic acid	6.5 grams.

152.	Nickel chloride	14 grams.
	Nickel citrate	14 grams.
	Nickel acetate	14 grams.
	Nickel phosphate	14 grams.
	Benzoic acid	7 grams.

153.	Nickel sulphate	20 grams.
	Nickel citrate	20 grams.
	Nickel benzoate	7 grams.
	Benzoic acid	1.8 grams.
154.	Nickel acetate	20 grams.
	Nickel phosphate	7 grams.
	Nickel citrate	20 grams.
	Sodium phosphate	14 grams.
	Sodium bisulphite	7 grams.
	Ammonia	32.5 grams.

For Watt's benzoate bath see solution No. 77.

155. Placet's bisulphate, biphosphate and biacetate solutions have been given under bath No. 25.

156. Villon's solution:[16]

Nickel ammonium sulphate	50 grams.
Nickel ammonium oxalate	20 grams.
Ammonium phosphate	10 grams.

157. Keith's solution.[90] "For preventing and overcoming this brittleness . . . I add to a solution of nickel . . . one or more of the salts, either single or double, . . . which are formed by the union of the various organic acids, acetic, citric and tartaric, with the alkalies and alkaline earths, ammonia, soda, potassa, magnesia or alumina. . . . The result is a deposit possessing elasticity, toughness and all the hardness, brilliancy and other qualities of pure nickel. . . . These various organic acid salts may be added interchangeably and collectively, though I prefer to use, in case of the double salts of nickel, the organic acid salts which have for their bases the alkali or alkaline earth which is associated with the nickel in its double salt. . . . Of the salts which can be used to accomplish the desired effect I prefer the tartrates. . . . To twenty volumes of a solution of the double sulphate of nickel and ammonia of a gravity of 7° Bé. (sp. g. 1.0507) I add one volume of a solution of an equal gravity of neutral tartrate of ammonia in water. These solutions may for some purposes be made alkaline—for instance, in the electroplating of brass and iron, wherein local action would interpose provided the solutions were left in an acid condition."

158. An English formula:[5]

Nickel sulphate	52.5 grams.
Tartaric acid	28 grams.
Caustic potash	7 grams.

For other tartrate baths see solutions Nos. 80 and 112.

159. Classen's oxalate bath may be found under solution No. 24.

Jules Meurent[91] secures highly adherent deposits of metals or their alloys by adding to an aqueous solution of the chloride of the metal to be deposited "a compound of a metal of the alkalies containing oxygen, and adding thereto a solution of chloride of ammonia and a carbohydrate," and electrolyzing. He specifies the addition of the following: Arabit, arabinose, xylose, rharmose, or isodulcite, saccharin, isosaccharin, metasaccharin, mannite, dulcite, sorbite, triose or glycerose, tetrose or erythrose, pentose, mannose, glucose, galactose, fructose, sorbinose, formose, acrose, methylenetan, glucoazone, isoglucosamine, osone, glucosone, glucosamine, the mannoses, methylerose, mannoheptose, glucoheptose, methylheptose, manoctose, nonose, mennononose, saccharose, lactose, maltose, mycose or trehalose, melibiose, raffinose or melitose, melitriose, melectose, also the following mono-acids, the biacids and the tribasic acids: The acids arabonic, aposorbinique, trioxyglutaric, saccharonic, trioxyadipinic, desoxalic, oxycitronic, dioxypropantricarbonic, as also the aldehydes and the ketones, hexavalents—that is to say, the acids mannitic, gluconic, dextrinic, mannonic, galactonic, etc., the saccharic, mucic, isosaccharic acids, etc. "I add also all the class of gums comprising especially arabine, gum arabic, the gums of the country obtained from plum trees, cherry trees, apricot trees, etc., wood-gum, vegetable mucilage, anisie bassorin, pectic mathers. I add also the classes of collagenous and chandrogenous matters containing ossein, glutine or gelatine, and all kinds of glues, as also chondrin and chitine."

160. Meurent's nickel solution:

Nickel sulphate	50 grams.
Ammonium chloride	25 grams.
Citric acid	5 grams.
Gum arabic	50 grams.

"If the bath is too acid, it is necessary to neutralize it. Seventy-five grams of sugar or 100 grams of glucose may replace the gum arabic."

IV. Malleable Nickel.

E. Weston,[66] in his patent mentioned on page 132, claims to obtain from the solution below "A new article of manufacture—a deposit of nickel which is so tough, malleable and ductile that it can be worked in much the same way as brass or copper are worked by the operations of rolling, punching, drilling, spinning, drawing," etc.

161. Weston's solution consists of five parts of chloride of nickel and two parts of borate of nickel. The amount of water is not stated in the portion of the patent available.

162. Villon's solution of malleable nickel:[16]

Nickel ammonium sulphate .	60	grams.
Nickel ammonium oxalate..	20	grams.
Ammonium phosphate	10	grams.
Palladium oxalate	0.1	gram.

163. Kern's[92] fluoborate solution contained 8 percent metallic nickel as nickel fluoborate. In 300 hours at 1.2 amperes per square decimeter the deposit weighed 290 grams and was 5/16 inch thick. "It was bright, smooth, malleable, solid and adherent."

Two solutions previously given are claimed to yield malleable deposits: No. 23, Kugel's, and No. 139, Powell's. Deposits from the following solutions are said to be soft enough to burnish: Nos. 76, 77, 90, 106, 122, 126, 144, 147, and 149.

V. Baths Producing Thick Deposits.

Brochet,[3] Langbein,[5] Maigne and Mathey,[16] and Peters[17] all give the following:

163. Formula used in Belgium:

Nickel sulphate	50	grams.
Ammonium tartrate, neutral	36	grams.
Tannin	0.25	gram.

E. M. F. 3.5 volts; current density 0.3 ampere.

"The bath is said to yield a very white, soft and homogeneous deposit of any desired thickness, without roughness or danger of peeling off."

164. Nickel ethyl sulphate.[93] "By the use of an electrolyte which contains nickel ethyl sulphate, or the ethyl sulphates of the alkalies or alkaline earths, deposits of any desired thickness can be produced if the bath be constantly agitated by mechanical means or by the introduction of hydrogen. Agitation by blowing in air is not permissible on account of oxidation of the ethyl sulphates. Experiments with such ethyl sulphate combinations by Dr. G. Langbein & Co. resulted in formulas for prepared nickel salts, from which thick deposits of nickel capable of being polished can in a few minutes be obtained in the cold way. The salts are known in commerce as Mars, Lipsia, Germania and Neptune. In an electrolyte of given composition, which has to be kept slightly acid with acetic acid, nickeling may for weeks be carried on at the ordinary temperature without any peeling off of the deposit, and in this respect this bath surpasses all other known baths. In the course of six weeks Dr. Langbein has produced upon guttapercha matrices galvanoplastic nickel deposits 6 millimeters in thickness."—Langbein.[5]

165. A. Hollard's solution.[94]

Boric acid	65 grams.
Hydrofluoric acid (43 to 46 percent)	142 grams.
Nickel carbonate	excess.
Water	1,000 grams.

The boric acid is dissolved in 125 c.c. of boiling water, cooled, put in a rubber jar and the hydrofluoric acid added. The nickel carbonate is slowly stirred in until it remains undissolved, and then stirred for 24 hours by a motor to completely neutralize the acid. It is then filtered. At first the deposit is curly, but after three or four days of continuous operation it works satisfactorily. One may deposit nickel as thick as desired, and the deposit may be used for electrotypes on wax, guttapercha, etc. Nickel can be deposited directly on cast iron and on aluminum.

The writer can confirm Hollard's statement of the suitability of the nickel fluoborate electrolyte for thick deposits. About two years ago the writer began experiments with fluoborate solutions of several metals, obtaining deposits of considerable thickness. Last fall, as the laboratory nickel solution was not working satisfactorily, about three gallons of the fluoborate solution were added to the 30-gallon nickel tank as a corrective. The solution then gave light deposits of excellent quality, but heavy deposits, run for a week or more, were badly pitted by gas bubbles which clung to the cathode. Although he has never collected and analyzed the gas, the writer is inclined to consider the trouble due to air absorbed while the solution stood idle in

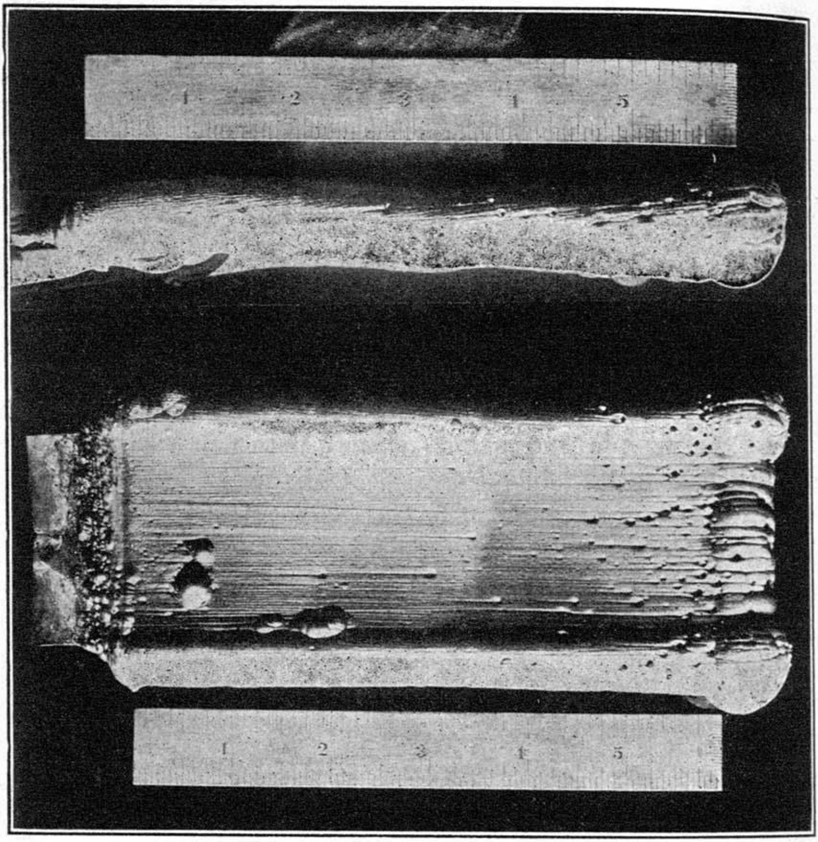

FIG. 1. ELECTROLYTIC NICKEL.

the summer. After several weeks of occasional use the pitting had diminished considerably, and an attempt was made to secure a really thick deposit of nickel.

Since the regular anodes, over a foot long, were left in the tank, there was naturally an excessive deposit on the bottom of the cathode. The deposit weighs 1,500 grams, and the cathode has a maximum thickness of 30 mm. The edge is 17 to 22 mm. in thickness. The bath operated at room temperature without stirring, and no additions were made to the solution during the 85 days of deposition. The current density averaged about 0.8 ampere per square decimeter. The deposit was brilliant and very satisfactory except for the pits caused by the gas bubbles. Although the cathode was lifted from the solution every few days for examination, there was no trouble from peeling. The deposit is very hard and somewhat brittle. In comparison with those deposits of copper, iron and lead of equal thickness which have come under the observation of the writer, the smoothness and freedom from protuberances of this deposit is remarkable. It is evidently not necessary that the entire bath consist of nickel fluoborate in order to obtain thick deposits.

Of the baths previously described, No. 22, No. 91 and No. 146 are claimed to give thick deposits at ordinary temperatures.

The heating of the electrolyte to prevent curling and peeling of the deposit has already been mentioned, and doubtless the thick deposits claimed for bath No. 22 are due to the elevated temperature specified.

VI. *Agents for the Production of Smooth Deposits.*

"A small addition of gelatine or transparent white glue will give an exceedingly bright lustre to the nickel deposit, providing the deposit is not too heavy."—C. H. Procter.[95]

Bruce adds carbon disulphide to the nickel bath to prevent the deposit from becoming dull when it reaches a certain thickness. "This is not advisable."—Langbein[5] (p. 261).

Classen[96] obtains brilliant mirror-like electrolytic deposits of the metals by adding to the plating baths glucosides, phlorglucosides, or extract of althæa, or Panama licorice extract.

J. A. Nussbaum[97] obtains smooth, dense deposits of metals by adding to aqueous solutions of their ordinary salts small quantities of colloids, which wander toward the cathode, *e. g.*, seed mucilages (linseed), mucilage from roots or bulbs (salep), vegetable gums, albumin, glutin, chondrin, mucin, etc.

"I found that by the addition of potassium cyanide to an alkaline electrolyte of nickel the deposit of nickel formed was smoother than that obtained by using other solutions. The addition of ammonium carbonate in place of ammonia produced smoother deposits when from 1 to 2 percent of cyanide was present."—E. F. Kern.[98]

"Other conditions being the same, we shall get the smallest crystals the greater the potential difference between the metal and the solution. This is the recognized explanation for the excellent character of deposits from cyanide solution."—Bancroft.[99]

Q. Marino dissolves nickel ammonium sulphate in glycerine at 60° to 80° C. instead of in water. Foerster and Langbein[5] (p. 250) find that the deposits do not possess the good qualities claimed by the patent. "The owners of the Marino patents have apparently themselves recognized the disadvantages of the glycerine electrolyte, and have applied for a patent, according to which 15 to 20 percent of glycerine is to be added to solutions of metallic salts in water. The glycerine is claimed to act as a depolarizer, and allow of the production of lustrous nickel deposits of great homogeneity. By experiments made in this direction it was found impossible to produce a better technical effect with such an addition of glycerine than without it, in properly prepared baths."—Langbein[5] (p. 250).

VII. Nickel Electrotypes.

Of the baths mentioned, Nos. 23, 91, 146, 164 and 165 are claimed to be suitable for the production of electrotypes, etc., in nickel.

VIII. The Nickeling of Zinc.

Owing to the corrosion of zinc by many of the common nickel baths much difficulty has been experienced in plating nickel directly upon zinc. Recourse has frequently been had to a preliminary coating of copper or brass from a cyanide solution.

"Some manufacturers nickel the cleansed sheet wthout previous coppering or brassing, and claim special advantages for such direct nickeling. Sheet-zinc directly nickeled does not show the warm, full tone of sheets previously coppered or brassed. The nickel deposit upon brassed sheets shows a decidedly whiter tone than on copper sheets, and brassing would deserve the preference if this process did not require extraordinarily great care in the proper treatment of the bath, the nickel deposit readily peeling off. This peeling-off of the deposit may be prevented by avoiding too large an excess of cyanide, and by regulating the current so that no pale yellow or greenish brass is deposited." —Langbein[5] (p. 298).

The following baths are said to be suitable for the direct nickeling of zinc:

Nos. 107, 109, 138 and 139.

Electrolytic Determination of Nickel.

The methods and conditions described under Nos. 52, 53, 54, 55, 56, 57, 59, 60 and 61 for cobalt, may also be used for nickel.

No. 58, given by Classen[27] (p. 162) is stated by Perkin[28] to be less satisfactory for nickel than for cobalt, and to give rather low results.

166. Ammonium hydrate and ammonium borate.[28] Dissolve the nickel salt in 30 c.c. of water and add 70 c.c. of a solution containing 50 grams of ammonium borate dissolved in 700 c.c. of water and 300 c.c. of ammonia (sp. g. 0.88). Current 0.5 to 1 ampere at 30° C. If a slight anode deposit forms, a few cubic centimeters of strong ammonia will remove it. Time 3 to 4 hours. The method is very accurate, but the deposit is not so fine in appearance as in other methods.

There remains for consideration a few alloys of nickel with iron, zinc and other metals, but these have been purposely omitted. Although these alloys have been deposited from their various baths, they have not as yet reached any commercial importance, and it was not deemed advisable to incorporate them in this article, already bulky beyond expectation.

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The Discussion following the Symposium on Electrodeposition of Metals, at the Twenty-third General Meeting of the American Electrochemical Society, at Atlantic City, N. J., April 5, 1913, President W. Lash Miller in the Chair.

DISCUSSION ON THE ELECTRODEPOSITION OF METALS

DR. W. LASH MILLER: We are glad to have with us a number of the members of the American Electro-platers' Society, and we shall now have the pleasure of hearing Mr. Charles H. Proctor, of Arlington, N. J., the founder and first president of that society.

MR. CHAS. H. PROCTOR: Mr. President and Members of the American Electrochemical Society. As one of your individual members and a representative of the American Electro-platers' Society, I can assure you it gives me great pleasure to meet with you in this your first Symposium on electroplating. I believe this will be a red letter day in the history of the electrodeposition of metals, because from this day hence we can rely upon the electrochemist to participate with us in bringing the art to a higher level, and a day when men of theory can join hands with the practical man who has toiled for years and, with dogged indifference to his surroundings, has brought the art of electroplating to its present standard in the commercial world.

It has not been due to his education, because very few of the men who have made a name for themselves, or have through their limited chemical knowledge become the heads of large plating establishments, have received a college or university education, and many of them not even a high school education; but with persistence they have overcome difficulties and have accomplished results which without that persistence could never have been accomplished.

The several papers to be presented at this Symposium dealing with electrodeposition of the various commercial metals, which through the courtesy of Prof. Richards, your honored secretary, were sent to every member of our Society, show that the work of the various committees has been accomplished in a very thorough manner, and I am sure these papers will prove very valuable as works of reference to every electroplater who has had the privilege of receiving them.

In going over hundreds of complex formulæ contained therein it will be somewhat difficult for a novice to decide what formula to adopt for a successful deposit of the metal to be applied to a given surface. It proves from this mass of information that the time is ripe to accept as standard, formulæ that can be relied upon at all times to fill the demands required of them, and to discard the voluminous mass that has proved that they were produced more from a theoretical standpoint rather than to produce commercial results, which are absolutely necessary in these days of competition in commercial products.

In the past thirty years wonderful developments have been accomplished in electroplating, so far as the electrical and mechanical features of the art are concerned, and during that period very little has been brought forth that has proved to be of any great advantage in the chemical composition of the plating bath.

Patents have been granted indiscriminately, and the men who have the supervision of this work in the Patent Office have no conception of the art or of its requirements; all that was possible for them to do was to refer to known formulæ, and any addition to these formulæ, whether in the form of metallic salt or an organic substance, has been passed upon as an improvement or distinct advantage, and the patent has been granted. Ninety percent of such patents have never had any commercial value. They have been laboratory experiments which should never have gone beyond that unless they had been tried out practically on a commercial scale.

With the co-operation of the members of the American Electrochemical Society interested in this branch of work, and the members of the American Electro-platers' Society, much can be accomplished in simplifying the composition of the plating baths and producing a standard commercial formula containing as few ingredients as possible, because in practice the bath that contains the least ingredients has proved must easier to control than baths with a complex composition.

The members of the American Electro-platers' Society appreciate the work that has been accomplished by individual members of your Society in the electrodeposition of metals, and realize that with the co-operation of such members a wonderful advance can be made in the future.

I have no doubt that there are but few of the gentlemen present at this Symposium, outside of the members of the American Electro-platers' Society, who have any conception of the knowledge required at the present time to successfully supervise and produce profitable results from a large plating department. The plater must not only have a certain amount of practical chemical knowledge, but he must also understand the nature of all the common metals, how to prepare the surfaces for successful deposition; this includes the method of polishing in its various stages, to the finished product, the plating of the rare and commercial metals, the production of chemical and pigment colors in decorative, antique and period effects, so that artistic designs in metals produced according to the various periods from Pompeian to the Flemish Renaissance, the Elizabethan period, the schools of Louis XIV, XV, XVI, and the Colonial and Napoleonic periods down to the conglomeration of mixed periods, can be finished and colored true to the periods in vogue or to the fanciful ideas of the modern consumer.

All metals must be protected from atmospheric influence except in one or two instances, so the modern plater in charge must understand the application of these protective coatings and their nature.

In a large manufacturing concern in the East, which produces articles of metal in everyday use as well as period effects in metals, the plater in charge must produce on the average one new finish or copy a finish of some other manufacturer every day of the year. This will give you some idea of what is expected of the modern electroplater.

Now, gentlemen, the successful electroplater of the future should emanate from your universities. He should receive his chemical, electrical and mechanical education there. In fact, when he graduates from your university he should be not only a theoretical but practical electrochemist and electroplater. This will save much controversy in the future as to who is superior in electroplating, the man who had graduated as an electrochemist with laboratory practice only, or the man who has gained his knowledge by practical experience in producing commercial results.

I know of several large concerns where electrochemists are employed, and indirectly they have supervision of the plating departments. This diversity of opinion creates considerable feeling with the practical man.

The university man makes an effort to prove his value to his employers, and this is accomplished ofttimes to the disadvantage of the practical man in charge of the plating department, which creates a friction and ofttimes distrust. This problem can be readily solved in the future by training young men who anticipate following the art of electrodeposition of metals as a vocation. Let their laboratory and chemical knowledge be supplemented with practical instruction in the deposition of metals upon a commercial scale; have a plating department in charge of the most experienced and practical man you can obtain, and when your graduates go forth from your university they will be equipped with essential knowledge to take charge of a plating establishment and produce commercial results that are essential in this age of competition.

THE SECRETARY then read the following letter from the acting president of the American Electro-platers' Society:

> The members wish to express their thanks for advance papers on electroplating that are to be read at your Spring meeting.
>
> We regard this as a very special honor and feel greatly indebted to the American Electrochemical Society. We know of no work that has been done that equals that accomplished by these papers. Their value to the electro-plating industry can never be estimated, and the interest that they will command will do much for the plater himself.
>
> We wish you a very successful meeting and assure you that we feel proud to be recognized by so learned a body of men.
>
> Thanking you for the personal interest that you took in our behalf we beg to remain,
>
> Yours fraternally,
>
> THE NATIONAL ELECTRO-PLATERS ASSOCIATION,
> CHAS. A. STIEHLE, *Acting President.*

DR. W. LASH MILLER: We all appreciate these kind words from the acting president of the American Electro-platers' Society, and also the address which we have heard from the founder and first president of that Society. The way we can do the most good in this matter is to take advantage of the good will displayed by these gentlemen in attending our meeting, and to co-operate with them as far as lies within our power.

Mr. Bennett presented the paper on "Electrodeposition of Copper."

Dr. W. Lash Miller: It is for the discussion of these papers that we are gathered here at this meeting, and I hope that our members, and particularly our visitors, will say exactly what they think about any of the receipts or any of the conclusions contained in the papers which are to be presented during the day.

Mr. Lawrence Addicks: The second half of this paper brings out how many different things have been used as "addition agents" in different cases, and the recognition of drug effects in electrolytes has explained many puzzling difficulties. Dr. Weston has told me of how many cases of diseased nickel plating in the early days were due to platers bailing the solutions into barrels while tank leaks were being repaired. The barrels were usually sized with glue, which put evil spirits into the electrolyte.

In the copper refining plant at present under my supervision we have found that a straight acidified copper sulphate electrolyte produces a deposit which soon becomes covered with fine needles, which grow as the deposit thickens, and act as the nuclei for the tree formations which finally limit the life of the cathode. By trial and accident, combined with close observation on the part of those immediately in charge of the electrolysis, it was found that the addition of mineral oil yielded some substance which turned these needles and made compact nodules of them, or, if enough oil were used, suppressed them entirely. At the same time, however, the structure of the deposit deteriorated into what the men call "cocoa matting" or "rotten" copper. The addition of glue corrects this and gives a firm, hard deposit, so that the proper balance of these two agents, oil and glue, gives excellent deposits, and we can work under much more severe conditions than formerly. Glue, on the other hand, has a marked effect on the working voltage, and its excessive use may increase the potential 30 or 40 percent. It is generally admitted that gelatin diminishes the size of the crystal, and apparently we supply electrochemically the power generally applied mechanically in working the metal. Sufficient gelatin will harden the deposit so that it will ring when struck.

Regarding chlorides, I think it is the custom in all the refineries to add small quantities of salt or hydrochloric acid. We carry 0.004 percent of chlorine in the electrolyte. I confess I don't know why. It may precipitate any silver that succeeds in dissolving, or it may form an oxychloride with antimony, or it may improve the deposit. I have never tried omitting it, as the cost is negligible and its use almost a tradition. Early in my acquaintance with the refining of copper I was told stories by tankhouse foremen of the terrible things that had happened when copper had been deprived of chlorine, and as nurses' tales have an influence in after life, I put salt in the electrolyte just as I do on my beefsteak.

One other point regarding addition agents: It depends a great deal on whether we are (I) refining the metal, (II) electrotyping or plating, or (III) making copper tubes, etc.

In refining we care only for fair smoothness and structure. In electrotypes we want great smoothness and hardness. In tubes, sheets, wire, etc., we want smoothness, but, above all, ductility. These three processes call for radically different treatment.

DR. W. D. BANCROFT: At the St. Louis meeting, held about ten years ago, I outlined a tentative theory of electroplating, but we did not get much discussion, because one man after another said, "Of course, everybody knows cases to which this theory does not apply," but no one gave me any specific instances at that time or since. I am hoping better things from this meeting today, and in order to facilitate discussion, or give a basis for it, I have had printed some cards which give six self-evident truths in regard to electroplating, no one of which will probably be accepted by more than one or two persons, and I do hope we can get a specific discussion, with specific cases, showing wherein these axioms are considered to be wrong, and afterward I will try to show the mistake on the other fellow's part. The axioms are as follows:

AXIOMS OF ELECTROPLATING.

1. Bad deposits are due to excessive admixture of some compound or to excessively large crystals.

2. Excessive admixture of any compound can be eliminated by changing the conditions so that the compound cannot precipitate.

3. Increasing the current density, increasing the potential difference at the cathode, or lowering the temperature, decreases the size of the crystals.

4. The crystal size is decreased when there are present, at the cathode surface, substances which are adsorbed by the deposited metal.

5. If a given solution will give a good deposit at any current density, it will give a good deposit at any higher current density, provided the conditions at the cathode surface are kept constant.

6. Treeing is facilitated by a high potential drop through the solution and by conditions favorable to the formation of large crystals.

MR. CHARLES H. PROCTOR: In connection with Axiom No. 3 we found in actual practice that the lowering of the temperature, especially of the silver solutions, brought about an increase in the size of the crystals. I believe one of our members here at the present time has a sample of a piece of copper plated with silver in a solution at a low temperature.

MR. GEO. B. HOGABOOM: Speaking about these axioms puts me in mind of a little story I heard in Toronto of a policeman who found a horse dead on Cholmondeley Street. He went to the station house to make a report, and tried to write the name of the street, but finally gave it up and asked the sergeant how to spell the name of Cholmondeley Street. The sergeant said he did not know. They thought over it for some time, and at last the policeman put on his hat and coat and moved toward the door as if he was about to go out. The sergeant asked: "Where are you going?" The policeman replied: "I am going to drag that horse into King Street." (Laughter.) That is the way with these axioms; while they are very good, I am afraid that the plater does not understand them. We will have to drag them some place else so that he can understand them.

Mr. Bennett says that he obtained a better deposit from an alkaline solution than from an acid solution. While the texture of the deposit from an alkaline solution may be better than the texture of a deposit from an acid solution, yet for electroplating the acid solution is better. All ormulo gold work has been plated in an acid solution, as the finish could not be put on over a cyanide deposit. The lead or the spelter has first been given a coating of cyanide copper, and has then been finished in the acid copper solution. Wherever heavy deposits are required they are put in the acid bath. We have a gentleman with us from Philadelphia who deposits copper an inch and an inch and a half in thickness with the acid copper solution, and it would be impossible for him under any consideration whatever to obtain these deposits from a cyanide solution. If you gold plate over a cyanide copper deposit, you do not get the color, you do not get the wearing qualities, as you would if the acid copper solution were used.

On page 237 Mr. Bennett says: "Copper plating is widely used as a basis for nickel plating on iron, steel and such metals. The object here is to obtain a thin, smooth coating over the surface of the metal of such a nature that the iron will not be dissolved by and contaminate the nickel solution." I respectfully call Mr. Bennett's attention to the fact that all nickel anodes contain anywhere from 4 to 10 percent of iron, and that iron in a nickel solution is very, very common, exceedingly common; and as for iron work contaminating the nickel bath, from an electroplater's standpoint that is not a fact. I have had considerable experience in nickel plating tool work. One of the hardest things to nickel plate, I believe, is a hammer head, and I did several thousand of them. The makers insisted on these being copper plated before nickeling, not to prevent the solution from becoming contaminated with iron and steel—they did not care anything about the solution—but because they thought that would prevent them from rusting. This is the only theory I ever heard put forth to justify a preliminary electroplating with cyanide copper. I do not, however, believe in that theory, because when we did the hammer work we found if the copper deposit was not clear and perfect that after nickel plating the deposit would peel. So we stopped it, and plated directly upon the steel, with nickel, and seldom had a piece to strip.

Our solutions had been running for about eighteen years, without removing the iron, or doing anything to it but adding nickel salts from time to time. It do not know how large a percentage of iron was in the solution; the iron did not affect the deposit. After we stopped the preliminary copper plating we never had a complaint of a hammer head, and you know what severe usage a hammer receives.

Another thing is that copper in a nickel solution will do a great deal more harm than iron in a nickel solution. If you had a small percentage of copper in the nickel solution you would get "black nickel." I call it "black nickel," but I think Dr. Watts says he does not think it is black nickel; he will not say definitely until he makes an analysis and discovers exactly what it is. Whatever the deposit may prove to be, if you take a double nickel sulphate solution and add to it bisulphite of sodium and sulpho-cyanide of potassium, and no other metal, you get a very heavy black plate which will stand buffing. The work can be and is run for three hours; this deposit is used on automobile parts and on typewriter parts, and is called "black nickel." The voltage to use on such work is 0.5, but if it is increased to 1 volt, black and white streaks will appear, so it would seem it must be some form of nickel.

Still another point: You gentlemen who have experimented in these matters, and you gentlemen who have prepared these papers, have worked with chemically pure chemicals, C. P. chemicals, to a great extent. If a plater gets C. P. chemicals, he is one of the most fortunate of platers. I never saw a plater who always could get C. P. chemicals. I have seen platers discharged because they insisted upon having distilled water. Just as soon as you go into a body of platers and say, "I have to have C. P. this, or C. P. that, or C. P. the other thing, or I cannot get any deposit," every fellow says, "That fellow does not know how to plate; he is only trying to find an excuse."

In regard to these addition agents which are added, we have had some interesting discussions in the meetings of the American Electro-platers' Society over these points. We found with these, and with all the chemicals that were used, that results were not nearly as good as they should have been, theoretically. One of our members was employed at a large plant, and they were adding dextrine to the acid copper solution, thinking they would get a good deposit, and they had all kinds of trouble, and could not make out what was the matter. Upon analysis the dextrine was found to contain 55 percent glue—that is what the electroplater is going up against all the time.

The addition agent that was found to give the most satisfactory results is common alum. Sulphate of alumina, I believe, was added by Cowper-Coles; he patented it, I believe. Mr. Proctor made some experiments with that, but because the solution is patented (and the plater cannot use any solution that is patented) he added common alum, and it gave very good results; no matter how much you added to the solution, a good, smooth deposit was obtained.

Mr. F. A. Lidbury: I was very much interested in Mr. Hogaboom's illustration pleading for a terminological ground upon which we can all meet in common. I would suggest, however, that the ground ought to be chosen in a mutual manner, and he would assist such a choice if he would send his policeman to drag into King Street the ounces per gallon and the degrees Baumé.

Mr. Geo. B. Hogaboom: It seems to me, as representing the platers, that Barclay and Hainsworth in their work on electroplating have taken the proper course by placing alongside of grams and liters the ounces and gallons. Some of these things published upon electroplating, some of these papers, are entirely incomprehensible to the plater. They do not understand them.

I might say, in answer to Mr. Lidbury, some of these papers state that the current density must be so many amperes per square decimeter, and that the anode and cathode must be just so far apart, and that the cathode density and anode density should be different; and in these very illuminating axioms which have been circulated we have statements regarding the potential. For example: "Treeing is facilitated by a high potential drop through the solution and by conditions favorable to the formation of large crystals." If you asked an ordinary plater what potential drop meant he would not know what you were talking about.

To bring the matter back to the practical conditions under which the plater has to work: We will take a nickel solution, say, of 1,500 or 1,800 gallons. In that solution you will require somewhere around 2,000 pounds of nickel anodes, large-sized nickel anodes. There are generally three anode rods and two cathode rods. The connections on the tank are placed permanently. Imagine the job a fellow would have to move the anode in a solution like that, to get it equal to the cathode surface.

Imagine the job a fellow would have so that he would get exactly the proper distance between the anode and cathode. We will suppose that a man was plating chandeliers or electroliers. They have the base and the column and the little caps. The base may have a height of eight inches, and the column an inch and a half in diameter; they all have to be plated in the same bath. How can you regulate the distance between the anode and cathode in that case? If any of you gentlemen went into a job plating shop you would find that they would have fifty jobs in one tank, consisting of bicycle parts, parts of sewing machines, and innumerable other things; and how would you regulate the distance between the anode and cathode in cases like that? The bath is there—a very large bath—and you cannot plate only the small parts or the large parts; you must fill the bath up with the work on hand.

As to the square decimeters, if cathode surface should have so many square decimeters, etc., I would like one of the gentlemen present to compute how many square decimeters there are on a gross of table forks. This is talking from a practical point of view; I cannot tell you anything theoretically, but what the actual conditions are in the metal plating business.

Now, about measuring—take the work I am employed in, deposit work. We have a whiskey bottle—most of you are familiar with that—and we decorate it. We will run through four dozen whiskey bottles, and in that four dozen bottles there will be probably five different designs. Each one of these must have a certain thickness of deposit so that it can be engraved. Probably there are only four or five that will require the same weight of deposit. In the case of a "bar" bottle, where a cheaper grade of work is required, that is, just a few lines here and there, not over 12 pennyweight of silver will be put on the bottle—manufacturers don't figure in grams—while in the same tank there may be another bottle that is to be covered over entirely, and that will require six ounces of silver. We have to put these in side by side, the whole 36 or 48 bottles into one tank, and they come out all exactly at the same time and with the correct weight of silver deposited. This may give some idea of the conditions a plater is up against.

MR. LAWRENCE ADDICKS: I want to voice of word of protest about the use of pure salts. I find the pure food laws under which they must be shipped are very stringent, and it is almost impossible to produce them. I was interested by the reference to one solution which was said to have lasted eighteen years. No one knows how many times new anodes were added to the solution in the eighteen years. The bath should be cleansed periodically and not allowed to become foul, and then the blame for unsatisfactory work would not be laid at the door of relatively pure salts.

PROF. JOS. W. RICHARDS: I suggest that in that solution which lasted eighteen years the impurities were being continuously deposited, the iron continuously deposited with the nickel.

MR. GEO. B. HOGABOOM: I carried on an experiment a short time ago. I sent out 40 pieces of aluminum to as many platers all over the country, and had them deposited with nickel, and had them state the age of all these different solutions, and we just roughly tried to find out how much iron was in each of the deposits, and it was found that the older the solutions the larger the percentage of iron there was in the deposits.

DR. EDW. F. KERN: As to that electrolyte which has been in constant use for eighteen years, I believe that new chemicals were added to it from time to time, so that the solution would not be so impure as the electroplater might think. When the articles which had been plated were removed from the bath a certain amount of the electrolyte adhered to them, which was washed off and the washings thrown away. The electroplater is continually measuring the strength of his solutions by the use of an hydrometer, determining its concentration in degrees Baumé. In order to maintain his bath at a proper working strength he adds water to bring up the volume, and salts in such amounts that the concentration of the solution is brought to the proper degrees Baumé. This is what may have gone on during the eighteen years referred to, so that in this way the electrolyte was really maintained at a certain commercial purity during that time. The fact is, the electroplater is continually holding his electrolyte to a certain standard of purity by the use of the hydrometer, whereas the electrochemist maintains his electrolyte at a certain percentage composition and depends upon chemical analyses as his guide.

Mr. Lawrence Addicks: All I am pleading for is fair play. Let the men who furnish the salts supply their share of the impurities as well as the city water works and the man who furnishes the anodes. I do not want any more.

Mr. P. S. Brown: I take the same attitude that the previous speaker took in this matter.

In plating iron, prior to nickel plating, it is quite customary and has been quite customary to plate with copper. Some firms have gone so far as to deposit the copper very heavily. They use a strong cyanide solution, and put on a heavy coating of copper, and then acid copper. I think that history will show that the reason why the copper plating is done prior to the nickel plating is almost always because of the cleansing effect of these solutions. The average copper solution, if it has been in use for some time, contains a very large percentage of carbonate of soda, and also a large percentage of cyanide of potassium. The effect of this alkaline solution, even when cold, is a cleansing one. When you bear in mind that in some plants they use these solutions warm, you will find that the cleansing effect is appreciable. The average plant which strikes up in a copper solution merely strikes the poor and thin deposits of nickel. I have made tests, and never found there was any advantage in the copper weight by weight; in other words, if you can get 5 grams of copper per square inch, and add to it 10 grams of nickel, you have the equivalent of 10 grams of copper and 5 of nickel, or of 15 grams of nickel alone, on actual corrosion tests, in the air, in salt water, and acid water. The whole value of the process of copper plating before nickel plating is in the additional cleansing action and therefore better adherence and better deposits.

Mr. C. W. Bennett: At what voltage does Mr. Hogaboom run his baths?

Mr. Geo. B. Hogaboom: One volt.

Mr. C. W. Bennett: You run it at one volt under all conditions, practically?

Mr. Geo. B. Hogaboom: Practically one volt.

MR. C. W. BENNETT: As I pointed out last year before this Society, there are a number of factors interrelated which control the size of the crystals of a deposited metal. First, the rotation of the cathode is equivalent to cold-working the metal; second, working at high temperatures is equivalent to annealing the metal, that is, causes the crystals to grow larger than if the metal was deposited at a lower temperature; lastly, current density or rate of precipitation is a very important factor. With a high current density, and therefore a rapid rate of deposition, the metal is always obtained in a finer crystalline state because the rate of crystallization is very rapid. Conversely, with a low current density the crystals are large because the rate of crystallization is slow.

The electroplater controls the progress of his process by controlling the voltage. Let us inquire what will happen in a cyanide solution during electrolysis with constant voltage at different temperatures. The conductance of the solution decreases with a decrease in temperature, so that at a constant voltage less current will flow through the solution at the lower temperature. This means, therefore, that under the same conditions the current density, and therefore the rate of precipitation at low temperature at constant voltage, are lower than at higher temperatures. Therefore the crystals must be larger because the rate of deposition has a greater effect on the crystal size than the effect occasioned by the decrease in temperature, operating in the other direction. I have no doubt that if Mr. Hogaboom will take the trouble to measure the current and keep this constant, instead of the voltage, the crystal size of the deposited silver will be smaller at the lower temperature. We have checked this up from the standpoint of tensile strength in the case of copper. Copper deposited at low temperatures has a higher tensile strength than that deposited at higher temperatures, showing that the crystals are smaller.

With regard to the statement that the deposit is better when made from acid solutions, I cannot question this from the plater's standpoint. From the standpoint of theory, however, as is stated fully in the paper, a finer textured deposit, that is, a deposit made up of finer crystals, will be obtained from the alkaline solutions, under the same conditions of temperature, current density, etc.

Commercially, however, the conditions are quite different. The current density in acid solutions is very much greater than that in alkaline solutions, so that here again is introduced the effect of increased current density. The deposit from alkaline solutions may not be so pure as the deposit from acid solutions, which would, of course, introduce practical difficulties. The conclusion, nevertheless, remains that alkaline solutions under the same conditions will give finer crystalline deposits than acid solutions. From the standpoint of cost, of course, it will be impossible for the plater to use alkaline solutions altogether on account of the fact that the current density is low, and the work would have to remain in the bath for a long time.

The criticism which Mr. Hogaboom makes of the statement that iron contaminates the nickel bath is a perfectly logical one to be made by the practical plater of today on account of the fact that nickel anodes containing iron are used in practice. This use of nickel-iron anodes I will not admit as good practice. It has been found that iron in deposited nickel is a very important agent in causing it to peel (unpublished notes). The coating of the metal with copper, of course, prevents a reversal of the current and the solution of the metal, as is noted by Fontaine (Electrolyse, 2d ed., p. 78). If the plater were using practically pure anodes and practically pure solutions, the iron which might dissolve and be reprecipitated would prevent the adhering of the deposit. We have found in the laboratory that the best deposits are obtained by the use of electrolytic anodes with nickel ammonium sulphate as an electrolyte. A small amount of chloride is added, either as ammonium chloride or nickel chloride, to insure the quantitative solution of the anode. Under these conditions the deposit contains practically no iron, does not crack or peel off, and does not rust. At least, samples I had made some time ago have not rusted yet. Presumably, therefore, the pure metal gives a more resistant and a better grade deposit. If this fact is remembered by the platers here, and if they will attempt to use purer materials, we certainly should get a better grade of nickel deposited. Under theoretically ideal conditions, therefore, the contamination of the nickel bath by iron would be an important factor. The reason stated by Mr. Brown for plating iron objects with copper is not a theoretical one, but is merely a practical one.

Coating iron with copper to insure a clean surface seems to be a rather expensive substitute for the ordinary methods of cleaning. Why should not the plater, therefore, clean the material with greater care, so that the copper plating could be omitted?

MR. GEO. B. HOGABOOM: I ask if Mr. Bennett tried to melt the electrolytic nickel to cast it into anodes?

MR. C. W. BENNETT: We have not attempted to cast anodes, but we have melted electrolytic nickel and cast it into small test bars about half an inch in diameter, say, for corrosion tests. Electrolytic nickel can be purchased on the market containing 0.14 percent iron, average composition. When the metal is cast it will probably contain a little more, due to contamination from the containing vessel.

MR. GEO. B. HOGABOOM: A very large manufacturer of nickel anodes in this country bought several hundred pounds of electrolytic nickel and put it into the furnace and tried to melt it. It was impossible to do it unless an electric furnace was used. They lost a great deal of money through their experiments. We made some experiments; we wished to get a pure nickel containing no iron to alloy with gold, as a small percentage of iron in gold will make it crack. We talked it over, made some compositions with electrolytic nickel, and tried to melt them down without having an electric furnace; it was almost impossible.

DR. W. D. BANCROFT: I should say that this interesting experience we have just heard about furnishes an admirable illustration of the necessity of carrying on experiments on a laboratory scale before trying them commercially.

PROF. JOS. W. RICHARDS: I do not know whether it is a suggestion worth while or not, but I thought that if the manufacturers of electrolytic nickel could be induced to deposit their electrolytic nickel in the shape of anodes it would avoid all the cost and impurities due to remelting.

MR. C. A. HANSEN: Electrolytic nickel can be satisfactorily melted in the arc type of electric furnace. We have melted it in 1,000-pound batches at a cost not exceeding $20 per ton. We deoxidized with small doses of aluminum or silicon, cast it into 4-inch and 6-inch ingots some 3 feet long, forged it into bars, and used the bars. If the silicon or aluminum go higher than ½ percent, the metal pulverizes under the hammer.

Mr. Bennett presented the paper on "Electrodeposition of Brass and Bronze."

MR. GEO. B. HOGABOOM: What does Mr. Bennett mean by bronze? That is, would he expect an electrodeposited bronze to analyze up to regular bronze that you can cast?

MR. C. W. BENNETT: From a chemical standpoint bronze is an alloy of copper and tin. The two constituents may be present in varying proportions, and electrolytic bronze, therefore, would be any deposit of copper containing any amount of tin. In regard to the statement that no real bronze was being plated commercially it may be said that, with thanks to Mr. Hogaboom, who furnished me with addresses, something like 75 letters were sent to that number of platers' concerns requesting that they give the character and amount of plating they were carrying on with the solutions used. A number of formulæ for "bronze" solutions, so-called, were received, but these solutions invariably contained zinc instead of tin.

MR. GEO. B. HOGABOOM: In the Reading Hardware Company they run a bronze solution containing tin, and have done so for twenty years. George Irvin is the plater. You will find a description of that process in a review of the proceedings of the American Electro-platers' Society.

MR. C. W. BENNETT: I am very glad to hear of this, and will communicate with Mr. Irvin as soon as I return to Ithaca.*

MR. CHAS. H. PROCTOR: The electroplater in producing bronze tones naturally has always followed the process of making an alloy of copper and zinc. He has found that this solution is a good deal easier to handle than one with tin. Some time ago I was talking with a plater in Lancaster, Pa., and he told me that at the present time in the production of bronze deposit they are using nickel with the copper, and get very good results. It seems to me that nickel would naturally produce a very good bronze

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* The bath used by Mr. Irvin contains copper and nickel. This information was very kindly furnished me by Mr. Hogaboom himself upon my return to Ithaca, so that it was unnecessary to communicate with Mr. Irvin. His process of bronze plating is published in the "Quarterly Review," National Electro-platers' Association, copyrighted, 2, Sept., Oct. and Nov., p. 27 (1911).—(C. W. B.)

tone. At the present time, the color of the deposit is sometimes regulated by the addition of arsenic; by using arsenic we get a more nickel-like structure, considerably darker than nickel. In depositing bronze upon hardware, we use a bath consisting of copper and zinc salts in a certain proportion, and then regulate the color by arsenic.

It seems to me that there could be a good deal of experimenting done with bronze solutions that would probably in the end produce very satisfactory deposits, and while, as practical men, we do not always have the time to go into this sort of thing, we do hope that you men who take such an interest in the electrolytic deposition of metals will solve these problems for us.

DR. EDW. F. KERN: This discussion seems to bring out the fact that it is color which the practical electroplater produces and sells, and not an alloy deposit; whereas from the scientific side, the electrochemist wants an alloy deposit, which has a characteristic color.

MR. LAWRENCE ADDICKS: It seems it is more or less the idea, as the electroplater puts it, that he should be able to sell zinc, bought at 6 cents, for tin at 50 cents.

MR. CHAS. H. PROCTOR: That is the commercial side of plating.

The Secretary presented Dr. Watts' paper on "Electrodeposition of Cobalt and Nickel."

MR. GEO. B. HOGABOOM: Speaking of the electrodeposition of cobalt and nickel, it may be interesting to bring out the fact that in experimenting with the enameling of agate ware, etc., it was found that if cobalt could be purchased cheaply enough, it would be much preferable to nickel as a coating under the enamel. At present very rich nickel solutions are used with a very high current, which "burns" the nickel deposit, making it come out black. I do not know what the current density is at which they operate the bath, but if you happen to touch the work against the anode, it will put a hole in the work, and crack it, the process is under such high pressure. The black deposit that is obtained is the base for the enamel coating and produces what is known as nickeled steel agate ware. Experiments proved that the enamel would take better upon a cobalt deposit than upon a nickel deposit.

MR. LAWRENCE ADDICKS: The situation in regard to cobalt, commercially, is very interesting. I understand that the International Nickel Company has withdrawn from handling it, and the market has gone to pieces. There is plenty of it. Some of the new copper fields in Central Africa carry a great deal of cobalt. There is considerable of it in Europe at the present time. The question which presents itself to us at the present time is how to get rid of the cobalt, and not how to save it. If anything can be done to make cobalt worth while, if it can be used commercially, there is almost an unlimited quantity of it that can be obtained. I do not know what price can be got. Cobalt is generally marketed as one of the three oxides, but could be readily produced as metal.

MR. H. T. KALMUS: I should like to enlarge on the statement of the last speaker by saying that the Canadian Government has set itself the task of finding an outlet for the deposits of cobalt which are on hand in that country. The metal itself, I believe, can be made into castings for something like $1.00 a pound, which is not excessive. When I say that, I mean in moderate quantities, and if a market could be assured for large quantities, it might be considerably reduced. There is an accumulation of cobalt at the smelters in Ontario, which at the price mentioned would have a value of something between $10,000,000 and $15,000,000. You must remember that that is an accumulation which has been brought about in the working of the silver ores. If the platers have uses for cobalt, we should be glad to hear from them. The Canadian Government is spending over $10,000 a year in experimenting with cobalt to find uses for it, and the results have been very gratifying. Publications in detail will appear during the coming year.

MR. CHAS. H. PROCTOR: The reason we cannot use it is the price. Get the price down to that of nickel, and we can use it. Maybe it will give us a cheap nickel anode and enable us to bring our product down to a lower price.

MR. LAWRENCE ADDICKS: What we need is some differentiation of the properties of nickel and cobalt. They are usually considered to be practically identical. If nickel can be purchased more cheaply than cobalt, cobalt is ruled out.

MR. GEO. B. HOGABOOM: I will state some of my experiences with cobalt and nickel deposition. I bought some sulphate of cobalt and paid $1.75 a pound for it and experimented with it in combination with nickel. I deposited some cobalt upon a piece of polished brass, and on another piece I plated from a solution of double sulphate of nickel, 8 ounces, sulphate of cobalt, 2 ounces, and chloride of ammonium, one-half ounce; this gave an elegant, bright deposit. I ran the deposit for two hours, straight, and it did not discolor. The objects which were plated were exposed to the elements all winter, and it was found that the cobalt changed its color and turned somewhat pinkish, while the cobalt-nickel did not change. Another thing about the cobalt-nickel deposit was that we could bend it, or twist it, without any danger of the deposit peeling. Samples were exhibited at the meeting of the American Electro-platers' Society. Whether that solution could be maintained so as to hold the same proportion of metal, is something I do not know.

MR. F. A. LIDBURY: Were any analyses made of the nickel-cobalt deposit to show if any appreciable amount of cobalt is deposited from the mixed solution? We know very little about the conditions of deposition of these two metals from solutions containing both, and it occurs to me that possibly from such a solution only nickel might have been deposited.

MR. GEO. B. HOGABOOM: The result was much different; it was almost silvery white. The South Bend Watch Company wants a very light deposit on their watch parts that would not tarnish. I suggested the cobalt-nickel bath to the plater, who tried it; he said it was the whitest deposit they ever obtained, but it was not satisfactory to the manufacturers; they wanted something more of a silvery color.

MR. H. T. KALMUS: I deposited some cobalt-nickel alloys running as high as 20 percent in cobalt, and they are tougher than either the cobalt plate or the nickel plate deposited under corresponding conditions.

DR. EDW. F. KERN: As a student I attempted to separate nickel and cobalt by electrolysis, and tried a number of different solutions, but in no case was I able to prevent the cobalt being deposited with the nickel. The ratio of cobalt to the nickel in the deposits was about the same in all cases as that of the two metals in the electrolyte. So it seems to me that if you wish to form an alloy deposit of nickel and cobalt it would only be necessary to use an anode of the composition you desire the metal to be deposited on the cathode, and also use an electrolyte which contains the nickel and cobalt salts in the same molecular proportion as the two metals in the desired deposit.

MR. H. T. KALMUS: I wish to point out one or two matters which I think are becoming misunderstood. In the first place, cobalt can never compete with nickel as to price. When I said that cobalt, ultimately, with large orders, would more nearly approach nickel in price, I had in mind the ultimate possibility of working ores at present too lean in silver to pay, but which might be worked if their cobalt content had a market. I doubt if you can buy 10 pounds of 99.5 percent cobalt anywhere at any price just now; you can buy plenty of cobalt oxide. Over one-third of the output of the Canadian mines is utilized in the production of Co_3O_4, largely for the manufacture of blue coloring substances; the other two-thirds of the output is on hand. The total output is not comparable with that of nickel, and cobalt can probably never compete with nickel, pound for pound. We must find uses for cobalt, if we are to use it at all, such that cobalt will do things which nickel will not do; there is no use in trying to substitute cobalt for nickel, for I do not think you will be able to buy cobalt for much less than a dollar a pound for some time to come. Someone suggested that the Canadian Government might supply working samples for the electroplaters. I cannot represent the Canadian Government, but I am in charge of a department at Queen's University, Kingston, Ontario, which is experimenting for the Mines Branch of the Dominion Government. As a result I have on hand somewhere between 50 and 100 pounds of fairly pure metallic cobalt, and I would be glad to see that any plater who is interested in undertaking experiments on the use of cobalt is provided with a reasonable sample. On the other hand, I would be very glad if any of the platers, or anyone else, who knows of work that has been done with cobalt, that is at all practicable, would advise me in reference to it. I hear occasionally of experiments, but find almost nothing in the literature which will give me any clew to the possible commercial uses of cobalt, so that no doubt we are doing things which have already been done and which have been filed away.

MR. C. W. BENNETT (*Communicated*): As to the question of electrodeposition of nickel from baths containing pure nickel salts, we have found some peculiar phenomena which we hope to report on later. Roughly speaking, the efficiency of deposition is proportional to the amount of ammonia at the cathode, up to a limiting value of course. The efficiency, on nickel ammonium sulphate solution, starts low and increases up to the maximum value as the alkalinity of the cathode compartment goes up. The efficiency reaches the maximum after a certain amount of ammonia is formed, and then begins to fall off. The deposition can be begun at any desired efficiency from the low value to the maximum by the addition of different quantities of ammonium hydroxide to the solution. This phenomenon of alkalinity at the cathode, when the efficiency is good, and when the deposit is best, seems to point to the fact that any iron which might be introduced at the anode compartment will be deposited as hydroxide before it reaches the surface of the cathode. It is very probable, therefore, that during the formation of a good deposit of nickel there is very little iron at the cathode, although we may be adding it at the anode continuously, so that, although the bath in the center may contain large amounts of iron, there may be a film over the surface of the cathode which is comparatively free from this metal, so that the addition of iron around the cathode, by solution of iron objects, for instance, may be of more or less importance.

The Secretary presented Mr. Frary's paper on the "Electrodeposition of Gold and Silver."

MR. C. A. STIEHLE (*Communicated*): I was very much interested in reading over the compilation of formulas collected by Mr. Francis C. Frary on the electrodeposition of gold, and found very few that are of any commercial use. In my thirty-five years of experience in gold plating I have used some of those given in the paper, and will try to give the results of my experience.

The baths made with ferrocyanide are too unstable to be used in a commercial way, as they will not dissolve any gold from the anode, and therefore after using a short time become exhausted, and, as new gold cannot be added, have to be discarded, the gold recovered, and new baths made. About the only use that can be made of them is for gilding enameled work, as the enamel does not chip so easily in them as in the regular cyanide baths; but even for this purpose the cyanide bath, if properly proportioned and worked, is better.

The cyanide baths with the addition of other salts, such as sodium phosphate, sodium sulphate and caustic potash, work fairly well for a short time; then the work will become spotted or of a "foxy" color, and as a rule they cannot again be made workable.

A 10 percent gold chloride solution can also be used as a plating bath, but the metal deposited is spongy and has not a good color.

I have found that a good and practical gold bath, which always gives the same results, can be used indefinitely, and gives a deposit of any thickness from a flash to 1/32 of an inch (0.8 mm.), and good gold color, must contain nothing but the gold and cyanide. Either the potassium or sodium cyanide can be used, as the gold anode will dissolve in either one.

The gold may be put into the plating bath by electrolysis (by the porous cup method), and I have found that this is the very best method, although it takes more time than the following method; it always gives first-class results.

But I find it quickest and easiest to make the solution from fulminate of gold; this always gives good results. In dissolving the gold for fulminate, use about 3 oz. (90 cc.) of aqua regia to 15 dwts. (23 g.) of gold, and as soon as the gold is dissolved (there is no benefit in waiting until the chloride becomes syrupy) add about 2 quarts (1,900 cc.) of water, then 4 to 5 oz. (120 to 150 cc.) strong ammonia, which will precipitate the gold, filter and wash once with hot water, put into a vessel containing water in which the proper amount of cyanide has been dissolved, heated to 160° to 180° F. (70° to 80° C.), and in a few minutes the fulminate will be dissolved and the bath ready for use. This bath may be used with as small an amount as 3 dwts. gold and ½ oz. of cyanide to the gallon (1.25 g. of gold and 3.75 g. of cyanide to the liter), when it will give a very light deposit, merely a flash, but a good gold color, in from 8 to 15 seconds, with 2 volts; or with as much as 25 dwts. of gold and 3 oz. of cyanide to the gallon (10 g. of gold and 22.5 g. of cyanide to the liter), with which I have deposited gold 1/32 of an inch (0.8 mm.) in thickness with a voltage of 0.5 to 0.8 in thirty-six hours. For a good color, such as is known as a Roman color, the bath should contain about 15 dwts. gold and 2 oz. of cyanide to the gallon (6 g. of gold and 15 g. of cyanide to the liter), the work to remain in the bath from three to five minutes at a pressure of 2 volts. There must never be too much free cyanide in the bath, as then the color of the deposit will be pale, and, where only light deposits are put on, the deposit may even, after disconnecting from the negative rod, be redissolved, and so much of the base metal to be plated may also dissolve before it is covered with the gold that the bath becomes contaminated thereby, which will result in poor color. There should be just enough free cyanide to dissolve enough gold from the anode to replace that which is taken from the solution. The appearance of the anode should always be clear and crystalline; if it becomes dark or black more cyanide must be added.

The anodes should always be fine gold and of the same surface area as the cathode, so that the gold in the solution can always be kept constant. I find that in plating with gold baths most platers think only a small anode surface is necessary.

This solution can be used indefinitely (with occasional filtering to remove organic matter) if it be not allowed to become contaminated with base metal. The solution I am now using I made three years ago, using it every day about eight to nine hours, and it gives as good results as when new. I deposit from 5 to 8 dwts. (8 to 12 g.) of gold out of it every day. These baths must all be worked at 160° to 180° F. (70° to 80° C.). For the carat gold solutions, such as 12 kt., 14 kt., red or green gold, I have found the best way to make them is to allow the anode, made of the proper carat and color, to dissolve into the bath electrolytically, as you then get the carat and color of the anode, which, unless you are a pretty good chemist, cannot be done by introducing gold, silver, copper and cadmium as salts that dissolve in the cyanide solution; and it is a quicker way, as a bath can be made ready for use in from two to three hours. In these baths the gold content should be from 5 to 15 dwts. of gold and 5 to 8 oz. of cyanide to the gallon (2 to 6 g. of gold and 37.5 to 60 g. of cyanide to the liter), and the voltage should be from 4 to 8 volts; these baths can be used at a temperature of from 80° to 180° F. (30° to 80° C.).

MR. GEO. B. HOGABOOM: This day marks an epoch in the history of electroplating in this country, and the gentlemen who have compiled this collection of formulas should have the thanks of the American Electro-platers' Society for the very great service they have performed to the practical electroplater.

One of the greatest needs of the electroplating industry today is co-operation between the practical man and the electrochemist. One of the ways I think this can be accomplished is by having the universities that have courses in electrochemistry co-operate directly with the plater. This could be done by having some of these universities employ a practical man and put him in charge of the electroplating laboratory, under the supervision of the instructors. I know of young men who would be willing to enter the employment of some institution of learning for the sake of the education they would receive, provided they could get enough money just to live on for the time being. A man need not be engaged for an unlimited length of time, but be engaged for four or five years, until he had finished his course, and then another young man could step into his place. In that way you would educate the plater and gain the practical man's knowledge.

Another thing which should be arranged is some way by which the practical man could get in touch with the members of this Society. He can meet with platers and practical men and exchange ideas and experiences in regard to the everyday affairs of the plater, but if he only had the co-operation of the chemist to help him over some of his problems, look at the good which could be accomplished, for these things would be published and become public property.

The mere precipitation of metal from an electrolyte which contains the metal is not, in the true sense of the word, as we would understand it, electroplating. To electroplate an object means more than to simply just coat it with the metal. You can coat aluminum with a metal, but the aluminum will not be electroplated. To be electroplated the surface must be thoroughly cleansed, it must be put into an active state so that the deposit will thoroughly adhere, the deposit must be smooth, it must be of a small, crystalline structure, in the case of silver it must be so that it is tractable to the burnisher, and it must be left in such shape that it can be easily polished on the wheel. It must also easily lend itself to any of the many decorations that may be called for, and for which not every deposited surface is suitable.

We will take the solutions one after another briefly, beginning with the nickel solution. There are about three classes of work which require nickel plating that differ from one another. First grey iron castings, such as stove work. Look at a stove casting and you will usually see highly polished nickel on the high lights and exceedingly white color in the deeper part, the background. The solution for such work must be able to deposit the metal heavily into every space on the article which is to be plated; a heavy deposit is required, and one that is perfectly white. In nickeling polished brass a different condition arises. This work must be plated so that there will be no white deposit whatever, so that after an hour's run the metal can be taken out of the solution so bright that it needs only to be wiped off to give it a brilliant color. A solution that will successfully deposit on iron work *can* be used to give the bright deposit on brass, but it is not the best. Finally for barrel plating, where a large number of pieces are put into a mechanical contrivance that rotates during electrolysis, and must all come out bright, an entirely different solution from either of the former two is required. It requires a solution that contains a large percentage of chlorine, so that it can throw the metal in, one that has a high specific gravity, and that can be operated under a higher pressure than any other solution. Thus there are three classes of nickel solution, and instead of saying in a general way that nickel can be deposited from a double-sulphate solution, or single-sulphate solution, with this or that added, a thorough investigation should be made to find just what solution is the best for each class of work.

Next, the gold solutions. Gold deposited on any surface reflects the color upon which it has been deposited. If you want a real yellow color, you can take a solution of cyanide of potassium and fulminate of gold containing, say, four pennyweights of gold to the gallon, and just enough free cyanide to give it action and operate it under a pressure of 1.5 volts. Plate with that on silver, you will get what is known as an 18-carat color; plate with it on brass you will get still another color, on copper still another. Plate with it on nickel and you get an exceedingly pale color. If the same solution be used for "inside work," that is, for plating the inside of a cream pitcher or sugar bowl, you will have a very poor color, "foxy," as it is called. A deposit that would look a nice orange color on inside work would look "brassy" anywhere else.

To obtain a "rose finish" you require a solution heavy in metal, very little free cyanide, and running under a higher pressure and even temperature. The shade must be uniform; the finish produced a year ago is brought up and matched with the finish produced today. You must operate the solution so that if you have 500 pieces finished, you can put the 500 pieces in a line and no one could pick out a single piece of a shade or color different from the rest.

To obtain green gold, one may use different proportions of gold and silver with either sodium arsenite or carbonate of lead, to produce the darker shades. Or the green gold anode can be cast and the gold "run in" with a porous cup. There are differences of opinion among platers as to the use of arsenic and lead, one prefers lead, the other arsenic. It is claimed that the atmosphere attacks the "arsenic" color more readily than the "lead" color.

Another gold solution referred to in the papers presented is the "sea water" or as it is more often called the "salt water" gold solution. This is made with the fulminate of gold, ferrocyanide of potassium and some sodium salts. A special apparatus is necessary and while no current from an outside source is necessary, it can be operated with it. This solution is used on the cheaper grade of novelty jewelry and can be operated very cheaply. One plater claims to have plated nine pounds of collar buttons with five pennyweights of gold.

The "dip" gold solution is also used for cheaper work. The articles are first "bright" dipped and then swilled in a boiling hot "dip" solution. The color appears very rapidly and the deposit is exceedingly light. At one time we "plated" some mesh bag frames four inches wide, a double chain, six inches in length, with a belt hook attached, for thirty-five cents a gross and made money. We used gelatin dissolved in hot water for a lacquer. This could not be accomplished at such a low price by electrodeposition, and have as uniform a color. It might be said that a gross of articles were dipped at once.

The plater in a factory where different classes of work are turned out is supposed to know every one of these solutions, and to be able to operate them successfully, day in and day out. They do not give you twenty-four hours to analyze a solution. They bring in a batch of work and say—we want that at such and such a time. If your solution does not work, you must make it work, and there is no opportunity for analysis. You must go ahead and do things.

Thirdly, the silver plating solutions, which are among the most simple to operate. Experience has shown that nothing but silver and cyanide should be added to the bath, but the solution must contain a sufficient amount of metal. A solution should contain approximately from 2.5 to 3 ounces of silver per gallon (18.5 to 22.5 g. of silver per liter) and should be operated under a pressure of one volt.

Now, when I speak of one volt pressure, of course, I know that from the point of view of the electrochemist I should say what current density is required. In the refining of metals, as in copper refining, where you can measure the cathode surface and the anode surface perfectly, and you know the density of the solution continually, and the temperature, it is all well and easy enough to say that the bath should be operated at a given current density for so many square decimeters of surface. In electroplating where the cathode surface changes continually and the anode surface remains practically the same, there should be some way of knowing whether you are getting the proper deposit or not. While it would be very nice to know how to figure out the proper current density to use, nevertheless, in practice it is almost an impossibility; and therefore the plater talks volts, and the volt is the most important unit to the plater. He very, very seldom talks amperes. He knows that by regulating his anode surface so that he will get a pressure of a certain number of volts he is going to get a deposit, homogeneous and smooth.

The weight of the deposit is, of course, another important matter, and how much weight can be deposited in a given length of time depends on the solution. Now this solution may have been worked day in and day out all through the week; it can only be fixed up at the end of the week on Saturday afternoon or Sunday, so that very probably it does not contain as much metal or as much cyanide on Friday as it did on Monday. If the plater was capable of analyzing the solution and finding out how much metal and free cyanide there was in it, he could bring the solution to the proper composition, but he cannot; there is no laboratory in any plating room, outside of a few very large manufactories. Every square foot of space is occupied and space costs money, so they cannot give a suitable place in which to put a balance and other necessary apparatus, and there is no time during the day to analyze solutions; the work must be got out.

Meetings like today can and will do much toward bringing about a better understanding of the electro-plating industry. If the manufacturer, the electro-chemist, the practical plater can be brought together more, each would receive benefits that would be of an infinite value. But first, start with the practical side that is beyond the experimental stage, and then work out new theories from what has been accomplished. Don't try to theorize the practical plater; rather make the electro-chemist a practical plater.

Dr. W. D. Bancroft: I have enjoyed Mr. Hogaboom's address very much, but he has not told us one or two things which, in my particular case, were the ones that I should really have liked to have heard. In the case of nickel plating he has told us that one must use different types of solution for plating the tops of stoves, for plating brass, or for use in the plating of steel. That is perfectly true, but it would help me a great deal more if he told what is undoubtedly perfectly obvious to him, that is, just why the deposit from one bath is not satisfactory in the other cases.

One solution was used for gilding the outside of a cream pitcher and another solution for the inside. There are more cross reflections on the inside of the pitcher, but I should like to be told more regarding the actual difference in the color of the gold and why in the case of these deposits the gold is just the right color you want on the outside and on the inside. I am willing to admit the fact, but when Mr. Hogaboom says that a solution "will not work," I would like to ask *why* it will not work. That is the thing on which I want help.

With all due respect, I would say one word about this difficulty of the chemist and the laboratory, of which Mr. Hogaboom gave us a very pathetic picture. It seems to me that the thing to do is to show the manufacturer that he cannot afford to go along in the present way, and that it will pay him to have a laboratory and to have his solutions analyzed. If it will not pay him, that is another matter; but as a chemist I think it would.

MR. GEO. B. HOGABOOM: For years all the plating has been done by men who have had no laboratory. If any plater should go to his employer and ask him to go to the expense of putting in a laboratory, the employer would laugh at him. The employer would say "We have had our work done satisfactorily for years, and we have had this proposition of a laboratory put up to us before, and we don't think there is much in it." I will give an illustration—there is a firm in Brooklyn, a well-known firm that does a great deal of silver plating work. The man in charge of the plating department asked for a voltmeter. They said to him: "We have been doing silver plating for twenty-five years, and we have never had a voltmeter in the place. What do we need a voltmeter for? Our work has always been satisfactory."

I will give you one more instance. Suppose I were to tell you that one of the largest manufacturers of electrical instruments in this country did not run his plating room upon a chemical basis? He would not think of employing anybody but a thoroughly educated electrical engineer in his electrical laboratory. Still I have known of his putting in a man as head plater who did not know the first principles of chemistry. I have known of that man buying 100 pounds of carbonate of soda and throwing the whole into a sulphate of nickel solution to make it more alkaline. This manufacturer will employ only electrical engineers for the electrical end, but in the plating room he employs men who do not know anything at all about chemistry.

As far as the two colors are concerned, gold inside and outside, the reflection of light upon gold has a great deal to do with the color. If you deposit gold inside a cream jug, the light is all reflected in, and it will be an orange color. If you plate with the same solution on the outside where the light is diffused, the color of the underlying metal will show through, for gold deposited from a solution is translucent, and a different color will result. Thus if you first coat the outside with copper, then gold plate it, you can match the inside very easily, but if you plate the outside directly on the silver you will not and cannot get the same color.

A very highly polished piece of brass work does not require as heavy a deposit of nickel as a piece of grey iron. A half-hour deposit is sufficient and the work will only need a light coloring with a buff. On grey iron the surface is dull and consequently the deposit of nickel will be dull and the brilliancy of the deposit can only be obtained by polishing with a rag or a felt wheel, using "lime" for the abrasive. There is some work that has to be done very cheaply and a large amount of it must be turned out so that it will pay. A three-hole gas hot-plate, such as is ordinarily used, must be taken as it comes from the foundry, polished, nickeled and colored for about 23 cents; this must include the legs and the white nickeling of the grates.

MR. P. S. BROWN: I sincerely hope that this discussion will lead toward a better co-operation and better feeling between the electrochemist and the plater, but I do not agree with Mr. Hogaboom that the solution of the difficulties is to submit samples of the materials for analysis, because the chemist's time is worth money. What the electroplater must do is to convince the manufacturer that the chemist is needed now and then, and let the manufacturer pay for the services of the chemist; even if he does not put in the equipment, let him send the samples out to the chemist and have the work done, because I can see if you once encourage the foremen electroplaters to submit samples, every chemist in the United States will be swamped within six months.

No doubt there are many problems that we would like to solve, but we must go at their solution in a rational way.

As to this case of voltage and amperage, I believe that is a matter of information; in other words, the chemist and the electroplater need standardizing as much as the machine shop. I have had some experience in standardizing electroplating departments, and in some cases have been able to put all the work on a piece-work basis. The average plater would think that was impossible; he would think that if a man wanted to shirk his work, or soldier, all he need do is to take out the racks a little quicker. This difficulty was overcome by insisting that every piece of plated ware that goes out of the department must meet a specific test for the quantity of nickel or silver or copper per square inch of plated surface; so many pieces are tested every day from every lot of work, a square inch of the nickel being removed and analyzed by a simple method which allows a great many of these tests to be made in a day. On such strong individual testing lies the ability to systematise the department. Assume that you want eight loads a day of a certain material, and you want the eight loads absolutely standard in quality and the same from one day to the other the year round. In such a case it is possible to make out an individual card for every part that goes through. That card gives the rack on which the part shall be placed, tells how many pieces to put on the rack, how many racks are to be put in the tank, and it then tells how many amperes must go through these racks and how long. If it says 300 amperes for thirty minutes, they must stay in thirty minutes and get the 300 amperes. If by chance the man who is in charge of the solution fails in his job, lets the solution get away from his control, the work may be spoiled under the conditions of current prescribed, because in efficient work you work close to the maximum possible rate of deposition. If the solution is low in metal, a current that normally might require three volts would perhaps need 4.5 volts, and at the end of twenty-five minutes the work might be burned on the edges. That would be the fault of the solution expert, because he should be able to tell by a comparison of the actual voltage with that on the card whether or not his solution is in proper working order.

In this method of working, the proper voltage is entered on the cards merely as a control of the condition of the solution. It is probably less applicable in silver and gold plating than it is in the plating of ordinary metals, but there are undoubtedly establishments today that are using the same method in silver plating.

PROF. JOS. W. RICHARDS: I think Mr. Bancroft has asked too much of Mr. Hogaboom when he asked him to tell him *why*. The way I view it is that the plater with practical experience will have to provide the facts which are lacking to the scientific man, and after the scientific man has these facts *he* must tell the practical man *why* they are so.

In regard to Mr. Hogaboom's suggestion that electroplating establishments might be established at the universities, I wish to venture a different opinion. I do not think the university is the place to teach men the practical details of the trade, but a place for a man to study and get the principles. I do not think that anything could be better for a student who desires to be a plater than to spent a year in the plating works before going to the university, and then afterwards following up the knowledge which the university has given him by the practical application of this knowledge to actual work.

The Secretary presented Dr. Mathers' paper on "Electrodeposition of Lead."

DR. W. D. BANCROFT: The question of "addition agents" is brought prominently before us by this paper. In some cases the effect can easily be explained, as where colloids are carried to the cathode, and gelatine, etc., is used to prevent crystallization. There are other substances, however, such as oils, which when added to the solution have a very marked effect. From the point of view laid down in the "Axioms of Electroplating," which I distributed, it follows that these substances, in order to act as they do, must be adsorbed by the metal. For fear some person might turn around and say, "You are simply inventing that hypothesis in order to rescue your theory," one has to get some other way of showing the adsorption, apart from the electrochemical side.

Such independent evidence is suggested by the work which has been done in the last eight or ten years on the flotation of ores, where you treat a zinc sulphide ore with oil in an acid solution. I wished to show my students an experiment illustrating this, and therefore shook finely-divided copper and a little quartz sand with kerosene oil and water. The copper went to the top, and the sand remained at the bottom. On tipping the bottle [*demonstration*] you will find in a moment or two that the oil carries the metal up again. The same principle is involved in the bronzing liquids. They contain aluminum powder or copper powder, for instance, with amyl acetate, in case you want an expensive one, or kerosene and resin, in case you are economizing; but the essential thing is that they hold the metal up, which proves that the metals adsorb these liquids. I have no doubt but that Dr. Mathers would find, if he shook up his powdered metals with different oils, that oil of cloves, which is the best one to use in electrolysis, would prove to be the best for suspending the metal. I believe that the flotation of ores, the behavior of bronzing liquids and this electrodeposition of the metals in the presence of these oils all depend upon the same general principle; all that is necessary in these cases is to use an oil or other substance, which is carried to the cathode and which is adsorbed by the metal, and it will then prevent the growth of large crystals.

MR. N. S. KEITH: In connection with the use of addition substances I recall that quite early in the 70's, in a nickel-plating establishment, I discovered that one of the platers was in the habit of chewing tobacco and squirting the tobacco juice into the solution. When I took him to task he said he found it gave good results. There was certainly organic matter put into the solution with a vengeance.

This seems to be an opportune time to correct the statements which have been made on page 170 of Mr. Mathers' paper, not on his own authority, but quoted from former publications, as stated. The original publication (Eng. Min. J. **26**, 26, 1878) was based upon my United States patent, October 15, 1878, No. 209,056. This was followed by my United States Patent, May 20, 1879, No. 215,463.

This latter patent claimed among others, an electrolyte composed of lead sulphate dissolved in a solution of sodium acetate. This latter electrolyte had been found much superior to the former one in the fact that the acid solution could not in practice be kept of constant composition, because more lead was dissolved from the anode than was deposited on the cathode, thus neutralizing the free acid. Then followed the formation and deposition on the anode of lead peroxide; subsalts dissolved in the electrolyte, with increased resistance and polarization in the cell circuit. If acid were added to preserve the integrity of the electrolyte, an accumulation of dissolved lead salt necessitated other manipulations for the recovery of the lead therein. The case is different with the electrolyte consisting of lead sulphate dissolved in the sodium acetate solution. The crystals of lead are much coarser and more coherent than those produced in an acid solution. They remain untarnished in the electrolyte for a long time. Several pounds of these crystals in a large bottle filled with some of the electrolyte, which were exhibited at the electrical exhibition of the Franklin Institute in Philadelphia in 1884, were bright and uncorroded more than a year thereafter.

During the time of the exhibition, namely, September, 1884, I read before the Philadelphia meeting of the American Institute of Mining Engineers a paper describing the process and the apparatus therefor then established at Rome, New York. That lengthy paper seems to have been overlooked, purposely or otherwise, by those who have been interested enough to print alleged descriptions of the process and their comments and deductions thereon. Those who are sufficiently interested may find the paper in the Transactions of the American Institute of Mining Engineers for the year 1884. See also "Electrolytic Separation of Metals," by Gore, 1890, pp. 244-5-6-7, for purity of the refined lead.

I have with me two discs made by compressing some of these crystals in 1883. It will be observed that these discs are metallic, and only superficially corroded, as any piece of lead might be which has been exposed to the action of the atmosphere of many climes for thirty years.

The process and the apparatus, etc., were fully described in the paper published in the Proceedings of the Mining Engineers in 1884; it went out of use mainly because it was so early in the electrolytic art, I think, that they could not induce the leading refiners to adopt it. They used the zinc process of separation, and have in great measure continued it, though some are using the Betts electrolytic process and using it very successfully. I think, however, that the acetate solution can be used under the methods now pursued with equal efficiency at least; it is free for all who wish to test it.

DR. W. LASH MILLER: It is with great pleasure that we hear these remarks from Dr. Keith, who, as is well known, is one of the pioneers in the electrolytic industry.

MR. CHAS. H. PROCTOR: The only use we electroplaters have for the deposition of lead is in the production of what is commercially termed Royal Copper—this is the beautiful pigeon-red color resembling enamel noted upon cases of electrical measuring instruments such as made by the Weston Electrical Instrument Company and as a finish upon art metal goods. In using lead solution for the purpose we use nothing more than the common solution of acetate of lead and caustic soda. The idea of getting this film of lead on the copper surface is to prevent oxidization previous to the immersion in the molten solution. We produce this oxidization by immersing in potassium nitrate, and protect the copper surface from the moisture and atmospheric influence previous to the immersion by coating it with lead. The only other instance I know of where lead is used is for the production of what we term "Metallo-chromes," or iridescent colors by reverse current. I do not think that our members can enter into any discussion on the electrodeposition of lead.

Dr. Kern presented his paper on the "Electrodeposition of Tin."

MR. A. S. CUSHMAN: I have been using an electrolytic method for determining tin in canned foodstuffs. I adopted this method as a very rapid and convenient way of determining very small amounts of tin in the presence of an excess of organic matter. You are probably aware that under the food inspection decisions of our Government any tinned goods are liable to condemnation that contain more than 300 milligrams of tin salts per kilogram of the packed food.

I have had charge of an investigation in which a very large number of cans, representing all the ordinary foodstuffs packed in tin, were put up under test conditions. This necessitated the determination of tin salts in a great many hundreds of samples of different sorts of foods. The old-fashioned method for the determination of tin in a material of this kind called for the complete destruction of the organic matter by the introduction of nitrosulphuric acid. This was an expensive process, destructive to laboratory flues and hoods, etc., and consumed a great deal of time.

By means of the electrolytic method we can now turn out 30 tin determinations a day. The method has already been published, so I need not describe it at this time. (Journal of Industrial and Engineering Chemistry, **5**, No. 3, 1913.)

You may be interested in hearing of one or two of the points that have been developed by these investigations. In the first place, it would seem probable that those fruits and vegetables which are most acid would be most highly contaminated with tin salts; that is not invariably found to be the fact. Tomatoes are quite an acid vegetable, as everyone knows, and yet tomatoes come very well within the limit of 300 milligrams per kilogram, even after two years' enclosure in the can. Tomatoes rarely run over 100 milligrams per kilogram, whereas squash, which is a neutral vegetable, will practically detin a can inside of a year. The reason for the fact that most acid fruits do not always take off the most tin seems to lie in the fact that there are other organic bodies that have a much higher solvent or corroding power on tin than the dilute organic acids have. For instance, shrimps and some other shell fish are very destructive to the tin containers in which they are packed. This is believed to be due to the action of certain nitrogenous or amido bodies contained in or developed by the fish.

Perhaps the most interesting point developed in these researches is the following: For years it has been the practice among canners to specify different weights of tin coating on the sheet from which the cans are made, and they have the choice of three separate grades of tin. These grades are sold under the designations "charcoal" plate, "coke" plate and "canners' special," the charcoal carrying the heaviest weight of tin, the canners' special second, and the coke the lightest.

Among the very great number of test cans to which I have referred we had a number of cans made of these three different grades of tinplate, and in almost every case where the results were scrutinized it was seen that there was no advantage to be gained by selecting the heavy tin coating for packing food. This is one of the very rare examples of a case where the cheapest way of doing a thing is as good as the most expensive.

17

A paper presented at the Twenty-fifth General Meeting of the American Electrochemical Society, in New York City, April 18, 1914.

ADDITION AGENTS IN THE DEPOSITION OF ZINC FROM ZINC SULPHATE SOLUTION.

By O. P. Watts and A. C. Shape.

This paper presents the effect of the separate addition of over two score different organic substances to a zinc plating solution.

The electrolyte was made by adding an excess of zinc to dilute sulphuric acid. The solution had an acid reaction and contained 25 percent of $ZnSO_4.7H_2O$. The amount of organic substance added was one gram per liter. Except when otherwise stated, the solutions were electrolyzed for two hours at about 22° C., with a zinc anode and an iron cathode, at a current density of about 10 amperes per square foot (1.1 amperes per sq. dm.). For comparison, the well-known Meaker galvanizing solution was electrolyzed under similar conditions.

The majority of the substances added had an injurious rather than a beneficial effect upon the deposit. The most common defect was the production of vertical grooves or striations, shown in various degrees by cathodes 25, 13 and 32 of the photograph. Cathode 1, from the Meaker solution, is typical of the best deposits. Cathode 47, a 16-hour deposit with eikonogen as addition agent, shows the mossy tufts which frequently appear on zinc deposits. Cathode 48 shows the effect of amidol in the same time, and resembles a thickly-planted apple orchard.

The results, arranged in tabular form, follow:

No.	Addition Agent	Current Density Amperes		Deposit
		Per Sq.Dm.	Per Sq. Ft.	
1	Meaker solution.	1.23	11.2	Excellent, non-crystalline, adherent.
2	$ZnSO_4$—no add'n	1.20	10.9	Poor, striated.
3	Acetanilide	1.17	10.6	Verv poor, badly striated.
4	Acetphenetidin .	1.26	11.5	Very poor, striated, dark.
5	Amidol	1.20	10.9	Poor, pitted.
6	Benzoic acid....	1.27	11.5	Good, non-crystalline, adherent.
7	Betanaphthol ...	1.27	11.5	Excellent.
8	Caffeine	1.20	10.9	Fair, crystalline.
9	Creosote	1.38	12.5	Fair, crystalline, slightly striated.
10	Dextrine	1.20	10.9	Poor, striated, granular.
11	Eikonogen	1.23	11.2	Very good, smooth, but dark.
12	Eucalyptol	1.20	10.9	Bad, striated, very dark.
13	Formin	1.20	10.9	Poor, striated.
14	Gallic acid	1.17	10.6	Very poor, striated.
15	Gelatine	1.32	12.0	Poor, crystalline, dark.
16	Glucose	1.17	10.6	Poor, striated.
17	Gum arabic	1.20	10.9	Fair, slightly striated.
18	Gum copal	1.27	11.5	Very poor, badly pitted.
19	Gum dammar ..	1,20	10.9	Very poor, striated, pitted, non-adh'nt.
20	Gum guaiac	1.14	10.4	Bad, striated, non-adherent.
21	Gum sandarac ..	1,20	10.9	Very poor, striated, pitted.
22	Gum tragacanth.	1.17	10.6	Very poor, striated, pitted, non-adh'nt.
23	Hydroquinone ..	1.23	11.2	Poor, striated, pitted.
24	Isinglass, Brazil.	1.27	11.5	Bad, striated, crystalline, dark.
25	Licorice	1.27	11.5	Very bad, striated, very dark.
26	Oil of cedar....	1.23	11.2	Bad, striated, dark, non-adherent.
27	Oil of cloves....	1.27	11.5	Bad, striated, dark.
28	Oxalic acid	1.17	10.6	Poor, striated.
29	Peptone	1.23	11.2	Bad, dark, non-adherent.
30	Phenol	1.29	11.8	Fair, slightly striated and pitted.
31	Pyrocatechin ...	1.23	11.2	Very poor, striated.
32	Pyrogallol	1.23	11.2	Fair, slightly striated.
33	Salicin	1.20	10.9	Very poor, striated, pitted.
34	Salicylic acid....	1.27	11.5	Very poor, striated.
35	Salol	1.20	10.9	Very poor, badly striated.
36	Saponin	1.20	10.9	Very poor, striated.
37	Resorcine	1.13	10.3	Poor, striated, pitted.
38	Tannic acid	1.27	11.5	Very poor, gray, striated, granular, pitted.
39	Tartaric acid ...	1.20	10.9	Poor, striated.
40	Terpin hydrate..	1.30	11.8	Fair, crystalline.
41	Turkey-red oil..	1.20	10.9	Poor, crystalline.
42	Turpentine	1.20	10.9	Bad, striated, non-adherent.

Addition agents which are insoluble in water were dissolved in alcohol before adding them to the electrolyte.

Those addition agents which gave the best results, *viz.*, gum arabic, benzoic acid, betanaphthol, caffeine, eikonogen, formin, pyrogallol and terpin hydrate, were tested repeatedly for different

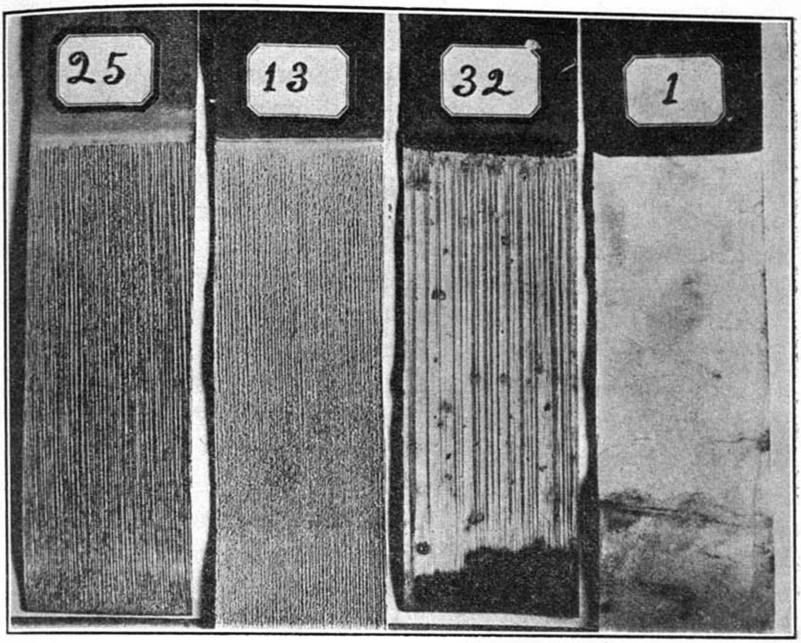

FIG. 1.

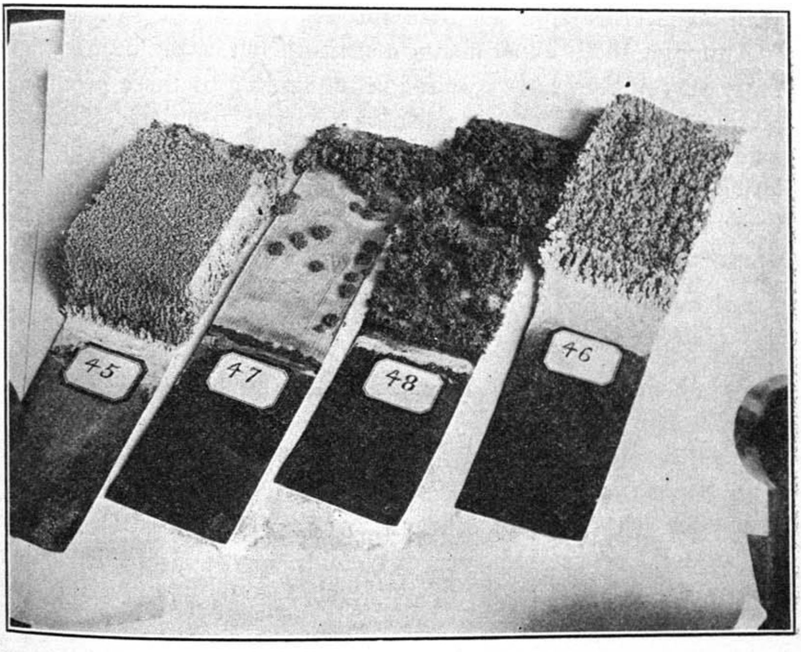

FIG. 2.

lengths of time. These tests resulted in the selection of betanaphthol, eikonogen and pyrogallol as the best addition agents.

Solutions containing these three reagents were electrolyzed for seven days at 0.5 ampere (10.5 amperes per square foot (1.16 amperes per sq. dm.)) in series with the Meaker solution. Although most experimenters have reported that addition agents are used up during electrolysis, and so require replenishing from time to time, it is claimed that the Meaker solution is self-sustaining and requires no additions to it during use.

After a number of hours' electrolysis of the above solutions, all except the betanaphthol became rough and unsatisfactory. It was only after several days that this deposit also became rough and spongy. Cathode 45 is the 7-day deposit from the Meaker solution, and cathode 46 that from the betanaphthol solution.

Whether or not failure of the electrolytes was due to exhaustion of the addition agents, and can be prevented by adding a fresh supply of these from time to time, was not determined in these experiments. There is, of course, also the possibility that some of the addition agents which failed under the conditions described may prove effective at a higher temperature or with some other zinc salt than the sulphate as electrolyte.

Although these experiments constitute but a preliminary and hasty survey, they have resulted in the finding of three promising addition agents for the deposition of zinc from a solution of zinc sulphate, *viz.*, eikonogen, pyrogallol and betanaphthol. The latter is best, and, so far as the writers have observed, has not heretofore been suggested as an addition agent for the deposition of any metal.

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University of Wisconsin.

DISCUSSION.

J. N. Pring (*Communicated*): An investigation extending over some years, which has been carried out by Mr. U. C. Tainton and myself,[1] on the influence of colloids on the electrodeposition

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[1] C. f. Brit. Pat. 7235 of 1911. U. S. Pat. 1,059,233. Trans. Chem. Soc. London, **105**, 710 (1914).

of zinc, has shown that deposits similar to those reproduced in the paper of Messrs. Watts and Shape can be obtained under the following conditions: An electrolyte is taken of zinc sulphate together with from 10 to 20 grams of free sulphuric acid per 100 cc., and a small quantity of a colloid such as gum arabic. A current density at the cathode of between 20 and 50 amp. per square dcm. is employed. When using lead anodes, this current can be obtained with 4.5 to 5.0 volts in the above electrolyte. The current efficiency varies from 90 to 96 percent. With these conditions, considerable quantities of most impurities have no great deleterious effect on the deposition of the zinc. Moreover, iron, which is the most troublesome impurity in ordinary practice, remains for the most part in the electrolyte during electrolysis, on account of passivity or retardation phenomena. These conditions have been found to be the most favorable for conducting the extraction of zinc from solutions made from ores and for the purpose of electro-galvanizing, as deposits of very high luster are obtained with suitable colloids.

It would be of great interest if Messrs. Watts and Shape mentioned the current efficiency obtained in their electrolyses and also if measurements have been made with commercial solutions.

O. P. WATTS: Unfortunately, no determinations of current efficiency were made in our experiments, but the absence of noticeable evolution of gas at the cathode would indicate an efficiency of 95 percent or above.

I wish to congratulate Dr. Pring on two notable achievements: The deposition of zinc on stationary cathodes at 465 amperes per square foot, smooth and solid enough for galvanizing, and the attainment of current efficiencies of 90 to 95 percent from solutions containing 20 percent of free sulphuric acid, a degree of acidity which even copper refiners do not venture to use. Dr. Pring's experiments disclose new and undreamed-of possibilities in the electrometallurgy of zinc, and emphasize the importance of trying experiments which, in the light of our present imperfect knowledge of the laws of nature and the properties of matter, would seem sure to fail.

H. E. Holbrook,[2] using faintly acid zinc solutions, probably

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[2] B. S. Thesis, University of Wisconsin, 1912.

richer in iron than Dr. Pring's, found the same tendency for the iron to stay in solution. At 13 amperes per square foot, with stationary cathodes and soluble anodes, he electrolyzed for 30 minutes a solution containing 20 grams of zinc sulphate and 50 grams of ferrous sulphate per liter, and obtained a deposit containing 6.21 percent of iron. In a similar experiment the electrolyte contained 30 grams of each sulphate per liter, and the deposit was only 1.25 percent iron. Whatever may be the cause of this unexpected phenomenon, I do not see how passivity can explain the failure of the iron to plate out, once it has dissolved in the electrolyte.

A paper presented at the Twenty-fifth General Meeting of the American Electrochemical Society, in New York City, April 18, 1914.

18

THE EFFECT OF ADDITION AGENTS IN THE ELECTRODEPOSITION OF IRON.

By O. P. WATTS and M. H. LI.

The results set forth in this paper formed part of a thesis written by the junior author for the degree of Chemical Engineer at the University of Wisconsin, and are here presented as an addition to the rapidly growing literature dealing with the effects of small additions of foreign substances to solutions for the electrodeposition of metals.

Previous experience in refining iron had shown the senior author that, while an electrolyte containing only chlorides gave a much smoother deposit than one consisting of the sulphates of iron and ammonia, the iron produced rusted so badly after removal from the electrolyte that a pure chloride electrolyte was not considered practical.

It was found, however, that the admixture of some chloride with the sulphate electrolyte improved the smoothness of the deposit without causing excessive rusting of the iron produced.

When a solution of ferrous sulphate alone was used as an electrolyte its rapid oxidation caused the formation of excessive and harmful amounts of precipitate. The addition of 60 grams of ammonium sulphate per liter of solution considerably diminished this precipitate and resulted in the production of better cathodes than in its absence.

The electrolyte chosen as a basis for the addition of various substances consisted of 150 grams crystallized ferrous sulphate ($FeSO_4.7H_2O$) and 75 grams ferrous chloride ($FeCl_2.4H_2O$) per liter, and had a specific gravity of 1.125 at 20° C.

Fluosilicates and fluoborates have proved very successful for the deposition of lead and nickel, and a test of these electrolytes was therefore made for the deposition of iron. The solutions were prepared by dissolving iron in the respective acids and then neutralizing by ammonia.

A. Ferrous ammonium fluosilicate was electrolyzed with an anode of mild steel for 170 hours at 10 amperes per square foot (1.1 per sq. dm.) at room temperature (26° C.). The deposit was dark gray, streaky and very nodular. The electrolytic cell was half full of a white precipitate.

B. Ferrous ammonium fluoborate was electrolyzed similarly for 150 hours, with similar results as to deposit and electrolyte. These electrolytes were very inferior to ferrous ammonium sulphate.

The next set of experiments consisted in a comparison of the effect of additions of the sulphates of ammonium, aluminum, magnesium and sodium to the above mentioned basic electrolyte (ferrous sulphate and chloride). The results are indicated in Table I.

TABLE I.

Time of electrolysis 90 hours, current density 1 ampere per sq. dm.

	Addition Agent	Result
C.	50 g. $(NH_4)_2SO_4$ per liter.	Deposit white, but pitted. Little precipitate in electrolyte.
D.	50 g. Na_2SO_4	Poor, gray and pitted deposit. Much precipitate.
E.	50 g. $MgSO_4$	Deposit gray, nodular and rusts badly. Much precipitate.
F.	50 g. $Al_2(SO_4)_3$	Deposit gray, streaked, and peeling off at top. Solution half filled with flucculent precipitate.

To prevent the formation of precipitates, 30 cc. of dilute sulphuric acid (1 volume of acid to 4 volumes of water) was added to each liter of electrolyte and the amounts of the sulphates increased to 120 grams. The results appear in Table II.

TABLE II.

Time, 140 hours, at 1 ampere per sq. dm.

	Addition Agent	Result
G.	120 g. $(NH_4)_2SO_4$ 30 cc. dil. H_2SO_4	Deposit bright, but nodular. Solution clear and yellowish.
H.	120 g. Na_2SO_4 30 cc. dil H_2SO_4	Deposit gray and very nodular. Gas evolved at cathode. Solution clear.
I.	120 g. $MgSO_4$ 30 cc. dil. H_2SO_4	Deposit dark gray with large nodules. Gas at cathode. Little precipitate.
J.	120 g. $Al_2(SO_4)_3$ 30 cc. dil. H_2SO_4	Deposit smooth and white at first, but finally gray and nodular. It rusted badly. Solution half filled with precipitate.

Since none of the other sulphates compared favorably with ammonium sulphate as an addition agent, the last named was used in all electrolytes for testing what further improvement could be made by organic substances.

TABLE III.

Electrolyte: 150 g. $FeSO_4.7H_2O$
75 g. $FeCl_2.4H_2O$
120 g. $(NH_4)_2SO_4$
per liter.

Current density 1 ampere per sq. dm. Amount of addition agent is in grams per liter, and if not soluble in water was added as an alcoholic solution.

No.	Addition Agent	Time in Hours	Deposit
1.	0.5 g. acetanilide	170	Good, bright, but slightly pitted.
2.	0.5 g. acetphenetedin	170	Fair, good color, but much pitted.
3.	0.5 g. amidol	240	Fair, good color, but pitted.
4.	10 g. ammonium acetate 20 cc. dil sulphuric acid	120	Bad, black and worthless.
5.	23.4 g. ammonium citrate	120	Bad, dark and streaked.
6.	10 g. ammonium oxalate 20 cc. dil. sulphuric acid	120	Excellent, bright and smooth.
7.	20 g. ammonium oxalate	170	Very good, but inferior to No. 6.
8.	40 g. ammonium oxalate	40	Poor, brittle and peeling, contaminated by yellow precipitate.
9.	10 g. ammonium oxalate	290	Excellent.
10.	12.3 g. ammonium tartrate	50	Poor, slightly nodular and peeling off.
11.	0.5 g. benzoic acid	100	Bad, nodular and greenish. Gas at cathode.
12.	1 g. *beta*-naphthol	170	Poor; deposit of good color, but badly pitted.
13.	0.5 g. boric acid	200	Poor; deposit of good color, but badly pitted.
14.	2 drops bromoform	170	Poor, deposit white but badly pitted.
15.	2 drops creosote, white	170	Poor, of good color, but pitted.
16.	1 g. dextrine	170	Very good, white and smooth.
17.	0.5 g. eikonogen	220	Poor, of good color, but badly pitted.
18.	3 drops eucalyptol	170	Fair, brilliant, but nodular.
19.	4 drops formaldehyde (40 percent)	240	Excellent, bright and smooth.
20.	4 drops formin	250	Excellent, bright, smooth and compact.
21.	0.5 g. gallic acid	170	Fair, streaky.
22.	0.5 g. gelatine	100	Bad, corrugated, pitted and nodular.
23.	1 g. glucose	170	Good, slightly nodular.
24.	0.5 g. gum arabic	240	Poor, vertical streaks and grooves.
25.	0.5 g. gum copal	120	Poor, good color, but badly pitted.
26.	0.5 g. gum dammar	170	Poor, good color, but pitted.
27.	0.5 g. gum sandarac	170	Fair, brilliant, but pitted.
28.	1 g. gum tragacanth	100	Fair, brilliant, peels off.
29.	0.5 g. licorice	200	Poor, much pitted.

No.	Addition Agent	Time in Hours	Deposit
30.	...extract logwood	200	Poor, good color, but pitted.
31.	2 drops lysol	200	Bad, gray with very large pits.
32.	3 drops oil of cedar.	140	Poor, of good color, but pitted.
33.	8 cc. oil of cloves	150	Fair, of excellent color, but pitted.
34.	0.5 g. peptone	170	Bad, mossy.
35.	4 drops phenol	190	Excellent.
36.	2 drops pyridine	120	Poor, of fair color, but pitted.
37.	1 g. pyrocatechin	170	Excellent.
38.	1 g. pyrogallol	120	Bad, dark colored, rusts badly.
39.	0.6 g. pyrogallol	100	Poor, brilliant, but nodular.
40.	1 g. resorcine	170	Very good, white and smooth.
41.	0.5 g. resorcine	240	Very good, white, but slightly nodular.
42.	0.5 g. salicin	170	Poor, gray and pitted.
43.	1 g. salicylic acid	120	Bad, gray and rough, rusts badly.
44.	0.5 g. saponin	100	Bad, spongy and badly rusted.
45.	0.5 g. tannic acid	100	Poor, badly pitted.
46.	0.5 g. terpin hydrate	170	Fair, of good color, but many small pits.
47.	3 drops turkey red oil	170	Bad, dark and badly pitted.
48.	2 drops turpentine	170	Poor, light gray and badly pitted.

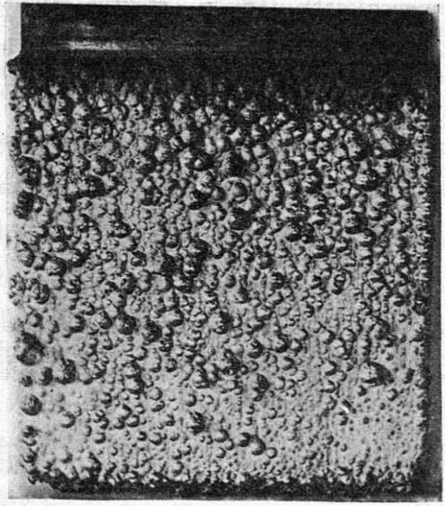

FIG. 1.

An objectionable tendency of electrolytic deposits is that they grow rough with increasing thickness, so that there is a limit, depending on the purpose for which the deposit is to be used, beyond which deposition cannot profitably be continued. Figure 1 shows a cathode of electrolytic iron a foot square and an inch or more thick, a very good deposit. Cathodes of copper or lead of equal thickness are fully as rough and nodular. This might be called the natural state of electro-deposited metal. It is the function of the successful addition agent to remedy this roughness. A, 10 and I in Fig. 2 show the nodular structure produced by several addition agents, the original electrolyte giving deposits free from nodules until the cathode attains at least three times the thickness of those shown.

For convenience the addition agents used have been classified according to certain well-marked physical characteristics of the cathodes. In each class the order indicates the relative quality of the cathodes in respect to that characteristic, *e. g.*, under pitted deposits each is more pitted than the one following, while those italicised show this action to an exceptional degree.

Nodular Deposits: *11*, *1*, 18, 41. Pitting caused by the clinging of bubbles of gas to the cathodes is a trouble to which thick cathodes of iron, nickel and zinc are subject. Copper and silver, whose discharge potentials in acid solutions are below that of hydrogen, are not subject to this trouble, so far as the writers have observed. 33, 47 and 31 in Fig. 2 show different degrees of pitting by gas bubbles. Although many of the addition agents are reported to cause pitting, there is a probability that experiments covering a longer period would have eliminated the pitting in several cases, for this has been found to grow less the longer electrolysis is continued, and seemingly it does not always keep step with exhaustion of the addition agent.

Pitted deposits: *31*, *C*, *25*, *47*, *48*, 17, 13, 42, 34, 46, 12, 21, 33, 27, 36, 3, 1, 29, 26, 30, 32, 15, 22.

Vertical grooves or striations is another trouble occasionally met with. Cathodes *24* and 5 were so afflicted.

"Brighteners" for silver and brass solutions have long been known among platers. Several addition agents produced bright deposits of iron, but these were extremely hard and brittle, and usually cracked and curled off from the starting sheet.

Bright deposits: *28*, *18*, *27*, 40, 8.

Several addition agents caused a badly rusted deposit, in the worst cases consisting entirely of iron rust.

Rusted deposits: *44*, *11*, 1, E, H, 43, 38, F, D, 5, J.

The color of the electrolyte at the end of the test was closely

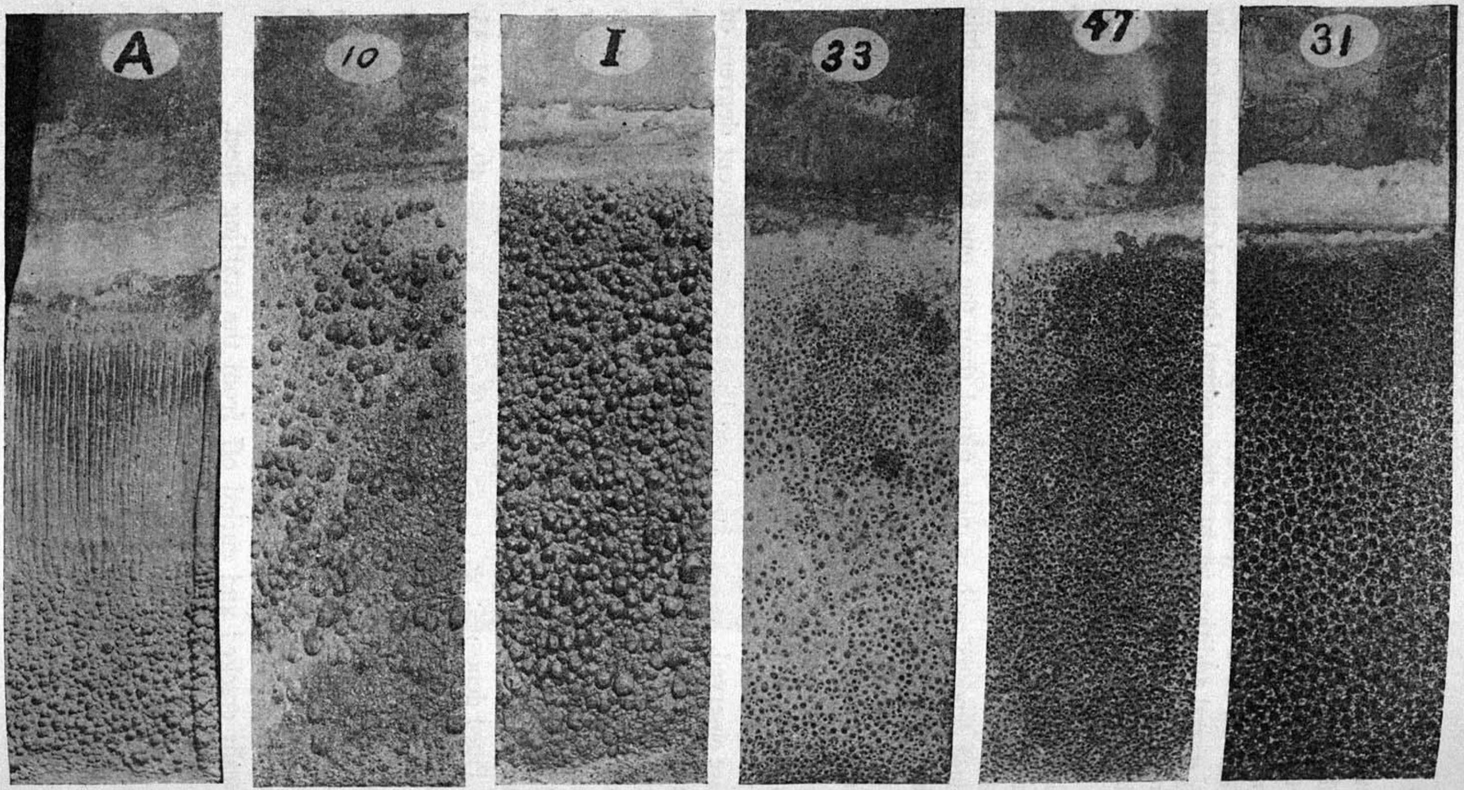

FIG. 2.

related to the quality of metal produced. A yellowish-green electrolyte almost invariably gave clean metal of a fine color, even though it might be too badly pitted to allow of the practical use of that particular electrolyte. A dark electrolyte fouled by much green precipitate usually yielded very bad looking mteal.

Yellowish-green electrolyte with little precipitate: 6, 7, 13, 15, 18, 19, 23, 25, 26, 27, 29, 30, 32, 33, 35, 36, 40, 45, 47, 48.

Ditto, with much precipitate: 2, 17.

Greenish electrolyte with little precipitate: 1, 3, 10, 12, 22, 31, 34, 40, 43, 46.

Ditto, with much precipitate: 20.

Bluish or dark green: 4, 5, 11, 14, 16, 21, 24, 28.

In order to test the best addition agents more thoroughly they were run continuously at 10 amperes per square foot for 21 to 30 days in series with a cell containing the electrolyte without any organic addition agent. The results are given in Table IV.

TABLE IV.

No.	Addition Agent	Days	Deposit
49.	None	30	Excellent, silvery, $\frac{7}{16}$-inch thick, slightly nodular.
50.	6 g. ammonium oxalate	30	Excellent, silvery and smooth. The best cathode of all.
51.	0.6 g. formin or hexamethylenetetramine	30	Excellent, bright and compact Slightly inferior to No. 50.
52.	0.5 g. resorcine	30	Very good, bright and solid, but slightly nodular near bottom.
53.	0.5 g. dextrine	30	Fair, excellent for first three weeks, then vertical grooves developed.
54.	4 drops formalin	21	Excellent, slightly nodular on the lower part.
55.	0.5 g. glucose	21	Fair, nodular near bottom.
56.	2 drops phenol	21	Excellent, white and solid, but with a few nodules near the bottom.
57.	0.2 g. tragacanth	21	Very good, slightly grooved, and thick on the edges.

The quality of metal in all of these deposits was excellent, and the only choice lay in smoothness and freedom from nodular structure.

Arranged in order of excellence, they are: *50, 51,* 56, 54, 49. The first two were distinctly superior to No. 49, which contained no addition agent. The others so closely resembled No. 49 that it is doubtful if these addition agents caused any improvement.

These experiments show that two organic addition agents, ammonium oxalate and formin, are capable of improving upon the remarkably smooth and satisfactory deposit given by the original electrolyte.

Laboratory of Applied Electrochemistry,
University of Wisconsin.

19

A paper presented at the Twenty-seventh General Meeting of the American Electrochemical Society, in Philadelphia, at a Joint Session with the American Electroplaters' Society, April 24, 1915, President F. A. Lidbury in the Chair.

CLEANING AND PLATING IN THE SAME SOLUTION.

By Oliver P. Watts.

For a number of years past the electric current has been extensively used for removing grease and dirt from metals after polishing, and as a preliminary to electro-plating. From this use of the electric current for the successive operations of cleaning and plating metals, it was but a short step, in thought at least, to combine the two operations, and perform the cleaning and plating simultaneously in a single solution. Since its inception seven or eight years ago, this process has been steadily increasing in favor among platers, until today it is very widely practiced. Although the combined cleaning and plating solution is sometimes employed to produce the final deposit, its most frequent use is for giving to iron and steel a preliminary coating of copper before nickeling.

For this latter purpose it possesses great advantages over the use of two separate solutions. Not only is there a saving of the time and labor required to transfer the articles from one solution to the other, but any failure to remove the grease is detected while the object is still in the cleaning solution, by the failure of the copper to completely cover the iron.

Since the copper deposit needed for this purpose is very thin, the low current efficiency of the combined cleaning and plating solution is no drawback to its use. When, however, a heavy deposit of metal is desired, it is a different matter. Effective action by an electric cleaner requires an extremely rapid evolution of gas on the object which is being cleaned. But a plating solution in which much gas is evolved at the cathode has of necessity a low current efficiency of metal deposition. On the other hand, the fact that a portion of the current is used in depositing metal makes the cleaning less effective than it would be in the regular electric cleaner. There is therefore a possibility, at least, that the saving in handling consequent upon the use of the combined cleaner and plater may be more than counterbalanced by the loss in time and increased power cost when heavy deposits of metal are desired. A complete solution of this question can only be obtained in commercial establishments, but it is hoped that the author's laboratory experiments, and the limited conclusions which can be drawn from them may prove of interest, and may lead to investigations of this subject by practical platers.

E. G. Lovering,[1] using a combined cleaning and plating solution, claims that he obtains in 20 minutes a deposit of brass 0.002 to 0.003 inch thick, which would require two hours in the regular brass bath. He gives the following as the composition of his solution:

	per liter
½ lb. H. V. W.'s XXX lye	60 g.
2 oz. copper carbonate	15 g.
2 oz. zinc carbonate	15 g.
4 oz. ammonium carbonate	30 g.
4 oz. potassium cyanide	30 g.
1 gallon water	1000 cc.

For a copper solution he uses the same without the zinc carbonate, and claims to obtain a deposit 0.009 inch thick in fifteen minutes, doing in one tank an amount of work which formerly required three tanks. The solutions are used at boiling temperatures.

For comparison with Lovering's solution two ready-prepared compounds were purchased. One of them, for cleaning and depositing copper, will be referred to as *X*, the other, for cleaning and depositing brass, will be known as *Y*.

Copper.

Cleaner "*X*," consisting of a fine white powder, evidently a mixture of caustic soda with other materials, was dissolved in water to form a solution containing 175 g. of solids in 1 liter of water. Although this solution is sold as a cold cleaner and plater, in order to do it justice in comparison with Lovering's solution it was also used hot. Copper electrodes of equal size were used except where the current densities quoted show anode and cathode to have been of unequal areas. Current efficiencies

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[1] Metal Industry, 1913, p. 173.

were determined by comparing the weight of copper deposited with that obtained from an Oettel copper coulometer connected in series with the plating solution. Since copper has a valence of one in cyanide solutions, at 100 percent efficiency the weight of copper deposited should be twice that deposited in the coulometer. All current efficiencies for copper have been calculated on this basis.

The results of experiments with cleaner *X* are given in Tables I and II.

TABLE I.

No.	Temperature		Cathode			Time, Min.	Deposit	Anode
	C.	F.	Current Density		Efficiency			
			Amp. per Sq. dm.	Amp. per Sq. ft.				
1	24.5	76	4.	37.3	11.4	60	Fine	Black
2	24.5	76	1.8	16.7	20.6	30	Fine	Black
3	50.	122	2.1	19.5	39.1	30	Good	Black

There was a vigorous evolution of gas at the cathode, but none at the anode, which was soon covered with a black coating, probably cupric oxide. The cathodes consisted of sheet brass coated with grease from the polishing wheels, and received deposits which were perfect in continuity and adherence. A comparison of experiments 1 and 2 shows a considerable increase in efficiency as the result of diminishing the current density, and experiment 3 gives a still greater efficiency as the result of heating the solution. The polarization was 1.3 volts.

TABLE II.

No.	Temp.		Cathode			Anode			
	C.	F.	Current Density		Efficiency	Current Density		Efficiency	Anode
			sq. dm.	sq. ft.		sq. dm.	sq. ft.		
4	71	160	7.9	73.5	17.3	5.1	47.4	—3.5	Black
5	70	158	7.9	73.5	16.6	5.1	47.4	—2.4	Black
6	70	158	7.5	70.0	13.8	4.6	43.0	—0.5	Black
7	70	158	1.9	17.7	35.5	1.1	10.2	...	Black
8	70	158	7.0	65.0	14.7	4.6	43.0	4.7	Nearly clean
9	70	158	7.0	65.0	13.3	4.6	43.0	2.7	Clean and bright

Table II shows the effect of the addition of a small amount of potassium cyanide in the hope of dissolving the black film on the anode. The time of deposition was 30 minutes.

The only effect of the addition of cyanide was an improvement in the color and brightness of the deposit. The negative sign before anode efficiencies indicates a gain instead of a loss in weight. In No. 8 an addition of 25 grams per liter of Rochelle salt was made in the hope of inducing corrosion of the anode, and in No. 9 this was increased to 35 grams, with the gratifying result that the black film no longer formed on the anode, although the efficiency of corrosion was still far from satisfactory. It is evident that in order to secure good anode corrosion it will be necessary to lower the current density, add more tartrate, or possibly do both. The previous polarization of 1.3 was unchanged by this addition of the Rochelle salt.

Lovering's solution was next tried. In making this, the zinc carbonate of the formula quoted was replaced by copper carbonate, giving a total of 30 grams per liter of the latter. It was then found necessary to use 70 grams of sodium cyanide instead of 30 grams of potassium cyanide to dissolve the copper carbonate. Tests of this solution are given in Table III.

TABLE III.

No.	Temperature		Current Density		Efficiency Percent
	C.	F.	Amperes per Sq. dm.	Amperes per Sq. ft.	
10	25	77	3.9	36.3	22.1
11	25	77	1.8	16.7	47.6
12	99	210	3.5	32.5	99.4

At room temperature this solution showed a much higher efficiency of deposition than cleaner *X*, but the anode was entirely black. To improve anode corrosion 20 grams of tartaric acid and 20 c.c. of strong ammonia were added. At the same time it was found necessary to add a small amount of sodium cyanide to completely discharge the blue color of the solution. The result of these changes in the electrolyte and the use of half the former current density is shown in No. 11. In spite of doubling the current density in No. 12, which should lower the efficiency, other conditions remaining unchanged, elevation of the temperature to gentle boiling has caused a rise in efficiency to practically 100 percent. Under the conditions of No. 12 this solution would not act as an effective cleaner unless a large amount of sodium cyanide were added.

Since the combined cleaner and plater may be considered as only an ordinary cyanide copper solution to which lye has been added, it was considered interesting to compare Lovering's solution with another bath of the same composition except that the lye was left out. A solution was made up of the following composition:

Ammonium carbonate	40 grams
Copper carbonate	36 grams
Sodium cyanide	36 grams
Water	1000 cc.

Tests of this solution (*L*) in comparison with the same to which 50 grams per liter of caustic soda was added (*LA*) are given for 30 minutes of deposition in Table IV.

TABLE IV.

No.	Temperature		Cathode			Anode		
	C.	F.	Current Density		Efficiency	Current Density		Efficiency
			Sq. dm.	Sq. ft.		Sq. dm.	Sq. ft.	
13 *L*	99	210	4.2	39.0	97.4	...	...	...
14 *LA*	99	210	3.8	35.3	96.7	...	...	...
15 *L*	80	176	2.6	24.2	88.6	...	...	...
16 *LA*	80	176	2.9	26.9	85.2	...	...	...
17 *L*	30	86	3.6	33.5	30.6	2.8	26.0	26.7
18 *L*	82	180	3.8	36.3	86.2	3.0	27.9	80.9
19 *LA*	82	180	2.8	26.0	84.9	2.7	25.4	15.7
20 *L*	25	77	2.2	20.4	49.4	3.0	27.9	51.7
21 *L*	25	77	2.5	23.1	34.0	3.0	27.9	34.0

A comparison of 13 and 14 shows that the addition of caustic soda has no effect upon the efficiency of deposition, but the formation of films on the anodes showed the need of more cyanide, and 5 grams per liter of sodium cyanide was added to each solution. This addition is partly responsible for the lower efficiencies of 15 and 16, the other factor in lowering the efficiency being the fall in temperature. On the other hand the lowering of the current density must have tended in the opposite direction. A comparison of 17 and 18 shows the remarkable effect of temperature upon the current efficiency at each electrode. It has previously been pointed out that elevation of temperature permits the use of unprecedented current densities in nickel plating also.[2] The cause of this greatly stimulating effect of heat upon electrodeposition appears to lie in an increase in the rate of diffusion of dissolved substances with rise of temperature, and the increased circulation of the liquid as a whole, caused by convection currents. To test the effect of artificial circulation upon current efficiency two cells containing the same solution were connected in series so that the same current traversed both, and a stirrer rotated at 1,000 r. p. m. was placed in one cell. The results are shown in 20 and 21, the former containing the stirrer. Since stirring prevents the film of solution in contact with the cathode from becoming depleted in metal it was to be expected that the efficiency of deposition would be increased by stirring. Whenever the current efficiency in a stationary solution is greatly below 100 percent, stirring ought to increase the efficiency, except when the electrolyte contains some corrosive substance such as ferric chloride or an acid, which vigorously attacks the cathode. A comparison of anode and cathode efficiencies for solution *L* shows a very satisfactory state of affairs, as the anode supplies metal at the same rate at which it is deposited. In *LA*, however, the anode was entirely black and corroded so poorly that for long continued use it would be necessary to supply metal by the addition of copper carbonate or cyanide.

It has been stated by Brown and Mathers[3] that the current efficiency of Weil's solution, consisting of copper sulphate, Rochelle salt and caustic soda, is 100 percent at both electrodes for current densities not exceeding 1 ampere per square decimeter. This suggested to the writer the addition of a tartrate for the purpose of increasing the anode corrosion.

To study the effect of a tartrate upon anode corrosion solution *LA* was digested with excess of copper carbonate to re-

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[2] Brass World, 1915, p. 34.

[3] J. Phys. Chem., 10, 51.

move the free cyanide and divided into two portions, to one of which (*LAT*), 60 grams per liter of sodium potassium tartrate was added. Tests of these solutions appear in Table V.

TABLE V.

No.	Temperature		Cathode			Anode		
	C.	F.	Current Density		Efficiency	Current Density		Efficiency
			Sq. dm.	Sq. ft.		Sq. dm.	Sq. ft.	
22 *LA*	71	160	6.6	61.2	33.9	5.1	47.4	3.6
23 *LAT*	71	160	6.0	55.8	35.9	6.1	56.7	55.7
24 *LA*	71	160	6.6	61.2	47.3	5.1	47.1	6.7
25 *LAT*	71	160	6.0	55.8	67.3	6.1	56.7	62.2
26 *LA*	71	160	7.7	71.6	26.8	5.1	47.1	9.4
27 *LAT*	71	160	6.6	61.2	55.1	6.1	56.7	57.1
28 *LA*	99	210	7.7	71.6	79.0	5.1	47.1	39.0
29 *LAT*	100	212	6.6	61.2	97.5	6.1	56.7	100.5
30 *W*	70	158	6.8	63.2	28.4	4.0	37.2	0.3
31 *WCy*	71	160	6.2	57.7	52.1	4.2	39.0	39.7

These tests were made with the two solutions, one without, and one with the addition of the tartrate, connected in series. Nos. 22 and 23 indicated a lack of free cyanide, and 2 grams per liter of sodium cyanide was added to each for tests 24 and 25. For tests 26 to 29, inclusive, the amount of free cyanide was increased to 6 grams per liter. The first addition of free cyanide to *LA* caused an increase in the efficiency of deposition, as well as in anode corrosion; a still further increase in cyanide gave the lessened efficiency at the cathode which had been expected for the first addition. In all tests of *LA* a black coating, probably cupric oxide, formed on the anode, and the corrosion of the anode was absolutely unsatisfactory. The behavior of the anode in *LAT* was in striking contrast to this. As seen in the table its corrosion was closely proportional to deposition at the cathode, and it remained bright and free from any film of oxide or cyanide.

The effect of heating these solutions to boiling was no less striking in 28 and 29 than previously in 12, 13 and 14. In 29 the amount of tartrate had been increased to 110 grams per liter.

To learn more definitely the parts played by the cyanide and the tartrate in producing the very satisfactory operation of solution *LAT*, Weil's bath, was made up as follows:[4]

Copper sulphate	60 grams
Sodium hydrate (lye)	50 grams
Sodium potassium tartrate	160 grams
Water	1000 cc.

To one portion of this (*WCy*) 30 grams per liter of sodium cyanide was added, just enough to discharge the deep-blue color of the original solution. These two solutions, 30 and 31, were then electrolized in series. The nature of the deposited copper, as well as the current efficiency, indicated that more cyanide was needed in *WCy*, while 30 shows that the tartrate without cyanide does not make a satisfactory solution, for combined cleaning and plating, for it is necessary to use a very high current density in order to cut down the cathode efficiency sufficiently for effective cleaning, and this reduces the anode efficiency nearly to zero.

Two experiments to determine the thickness of metal deposited in a half-hour from the boiling solution *LAT*, at 9 amperes per square decimeter or 84 amperes per square foot, gave 0.0042 in. at a current efficiency of 88.8 percent. At this rate of deposition 1 hour and 4 minutes would have been required for a deposit 0.009 in. thick, such as Lovering obtained in 15 minutes, and a current density of 360 amperes per square foot would have been needed to give this deposit in 15 minutes at the current efficiency of these experiments.

These solutions yielded bright, fine-looking deposits, which gave no indication of stripping from the greasy sheet metal on which the copper was deposited. This must not be taken as an indorsement of the use of these solutions for plating objects with crevices or deep cavities, as no such articles were available for testing.

Cleaner *X* is only suitable for preliminary plating which is to be followed by the deposition of a heavier coating from another solution.

Lovering's solution is capable of doing effective cleaning on flat metal, and will when boiling deposit copper more rapidly than the cold copper sulphate bath, as it permits the use of

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[4] J. Phys. Chem., 10, 51.

higher current densities than the latter. In this connection it should be noted that at 50 percent efficiency for the cyanide bath the deposit of copper equals that by the same current at 100 percent efficiency for the copper sulphate solution.

For effective cleaning it is possible that the current efficiency ought not to be allowed to exceed 50 percent and a high current density must be used.

The hotter the solution the more effective the cleaning, and the higher the current density which may be used without producing a bad deposit.

The proportions of the total current devoted to cleaning and to plating may be controlled by adjustment of the temperature, the amount of copper in the bath, the current density, and the amount of free cyanide present. An increase in the first two, and a diminution of the last two increases the percent of the total current which is devoted to the deposition of metal, and *vice versa.*

The addition of 60 to 75 grams per liter (8 to 10 ounces per gallon) of Rochelle salt or other tartrate to Lovering's bath greatly improves the operation of the solutions.

Brass.

A first attempt to clean metal and deposit brass was made with cleaner "*Y*," already referred to. A solution containing 175 grams of the powder per liter evolved much gas, and gave only a very thin deposit looking like pure copper at 71° C. and a current density of 6 amperes per square decimeter. As this is supposed to be used cold, it was also tried at 20° C. with current densities of 3 and of 6 amperes per square decimeter. A very thin deposit of red brass was obtained. The solution cleaned the metal, but did not give a satisfactory deposit of brass.

Lovering's brass solution was made up according to the formula previously given, except that more potassium cyanide was needed to secure solution. As the color of the brass deposited from this was not satisfactory, additions of copper and zinc carbonates and sodium cyanide were made, until finally a good color was obtained between 70° and 90° C. The deposits adhered firmly upon sheet metal covered with grease from the polishing wheels, but thick deposits, equivalent to 15 minutes at 8 amperes per square decimeter, were hard and rather brittle, cracking when the sheet was bent at right angles. No attempt was made to determine current efficiencies. One interesting observation was that the addition of 50 grams per liter of lye to a hot brass plating solution which was depositing brass of an excellent color, caused the color of the deposit to change to that of pure zinc.

The few experiments tried with the brass solution show that brass may be deposited from a combined cleaning and plating solution in a manner similar to copper, but on account of the difficulty of satisfactorily controlling the color of the deposit, the whole matter has been made the subject of a more complete investigation, which is now being carried on in the electrochemical laboratories of the University.

Nickel.

Since the combined cleaning and plating solution for copper is most extensively used as a preliminary to nickeling iron and steel, it was thought that a solution for the simultaneous cleaning and nickeling of iron might be of value to the plating industry. The experiments so far tried for the purpose have failed.

What is needed is an alkaline nickel solution which at or near the boiling point will give a smooth deposit of nickel at a current density of 30 to 50 amperes per square foot, at a current efficiency between 30 and 50 percent.

Naturally cyanide solutions were first tried. A boiling solution containing 70 grams per liter of nickel sulphate in the least amount of potassium cyanide that would dissolve the precipitate gave a bright and adherent deposit of nickel on greasy metal, but the efficiency of deposition proved to be only 0.05 percent. The addition of caustic potash did not improve matters, nor did the substitution of nickel carbonate for the sulphate. The cyanide solution was abandoned, and an attempt was made to hold the nickel in solution by other means. Tartrates prevented the precipitation of nickel by alkalies in cold solutions, but when heated the nickel was precipitated. Experiments are still in progress upon this interesting, but seemingly difficult problem.

The most important result of these experiments is the great improvement in anode corrosion caused by the addition of a tartrate to the copper solution. Other deductions of less importance are to be found at the close of the section on copper.

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DISCUSSION.

C. G. SCHLUEDERBERG: In Dr. Watts' paper particular stress is laid on the value of having the solutions hot. In one place, page 149, he says: "The hotter the solution the more effective the cleaning, and the higher the current density which may be used without producing a bad deposit." In talking the other day, with J. O. Jones, Chief Chemist for the Westinghouse Electric and Manufacturing Company, he suggested a possible use of the immersion type electric heater for the purpose of heating these solutions. It seems to me such a heater could be very well applied to this purpose. Most of you probably know that immersion type electric heaters are now used for many and various purposes. They are even used on circuits for making steam in boilers, although that is very expensive unless you have a low rate for current. There is no question but what satisfactory electric heating apparatus could be supplied for the service discussed in this paper.

C. H. PROCTOR: An occurrence that occurred in my plating department twenty-five years ago will prove that the ideas that Dr. Watts has put forth are correct, but not new.

I think it was in the year 1889 or 1890, while I was employed by the Ansonia Brass and Copper Company at Ansonia, Conn. We were cleaning out some copper tanks. There is a certain amount of sediment which gets in the tanks in use and once or twice a year we cleaned out this sediment. One of my employees was emptying one of the copper tanks and was using a pail to do it. By mistake he took several pails of the copper solution and emptied this in the cleaning solution made of caustic and carbonate of soda. I did not notice this, and nothing was said to me in regard to the addition of the copper solution. When we finally started up I noticed that in cleaning zinc castings we obtained a reddish coating similar to copper. On making inquiries, I found that some copper solution had been added accidentally to the cleaning solution. I immediately connected up the iron tank with a positive lead, and started to deposit out the copper upon sheets of steel. I noticed at that time that the rusty and greasy surface of the steel was cleansed and I obtained a very good coating of copper, which would prove that Dr. Watts' idea is correct but not new. I used the solution for a certain length of time in this manner, but could not see any economic advantage, so discarded its use.

To hold copper in a cyanide solution you must have free cyanide. In heating the solution to 212° F. (100° C.) and removing the grease and organic matter the cyanide decomposes quite rapidly and must be renewed quite often, which proved that the proposition was too costly for use, and I finally discarded the idea of using a combined cleaner and plater. Probably for small articles it may be an advantage. If you could deposit copper from carbonate of sodium or caustic hydrate, we should not have any use for cyanides. Three years ago I was in a plating department in Chicago and later in Cleveland, and cleaning and plating was being utilized there, so it is not a new process.

GEORGE B. HOGABOOM: Dr. Watts said he did not get successful brass deposition. Since the paper was published, I have had a little experience. We have a mechanical plater, with a 350-gallon electric cleaner, and have a foreigner who can not talk English, operating it. He went to the storeroom, as is his practice every morning, to get a certain amount of causticised ash, and instead got forty-five pounds of zinc carbonate and put it into the cleaner. To see what would happen I put in two pounds of cyanide of sodium; the cyanide present dissolved enough copper from the plating racks, which held the work, to combine with the zinc to give a beautiful brass deposit.

S. D. BENOLIEL: Some of the speakers have referred to this method as being impractical. This is certainly true because the method has but very limited applications. In cleaning work before plating, there are a large variety of metals to be cleaned, such as iron, zinc, German silver, brass, etc. Again, the nature of the material to be removed plays an important part. These articles vary to a great extent, and may be composed of such materials as mineral oils, lubricating compounds, vaseline buffing compositions, which may be made up with paraffin, stearic acid, etc., all of which goes to make the problem more or less complicated.

FRANCIS C. FRARY: I would suggest that you use instead of the cyanide, to hold the copper in solution, some form of invert sugar, cheap glucose, or even cahe molasses (preferably first warmed up a little with some acid) because it is well known that these invert sugars will hold copper in alkaline solution as well as the expensive tartaric acid compound. If the process is worth using for any purpose, you might be able to make a saving by this substitution.

GEORGE B. HOGABOOM: In reply to Dr. Frary's statement, I would say that we are making certain solutions containing glucose, corn syrup, 58 percent, 42° Baume, manufactured by the Corn Products Company. In removing the work from the solution containing a substance such as you speak of, and putting it into cold water, the work discolors very rapidly, and it is necessary to pass it through a bath of cyanide to clarify the deposit.

FRANCIS C. FRARY: Did you try the cheapest grade of dextrose sugar instead of glucose?

GEORGE B. HOGABOOM: We used it in zinc plating. If there is any appreciable amount in the solution, it discolors the work and requires cyanide to clarify it.

MR. WATTS (*Communicated*): Concerning the reputed failure of the combined cleaning and plating solution from the economic standpoint, due to excessive consumption of cyanide by the hot solution, I can give no evidence, as my experiments were of too brief duration to determine this point. Although, as previously stated, cleaning is most effective in boiling solutions, excellent results have been obtained at temperatures as low as 60° C. At this lower temperature and with the less vigorous agitation which accompanies it, it is possible that the destruction of cyanide may be sufficiently lessened to permit of the economical use of the combined cleaning and plating bath.

Mr. Benoliel's contention that the method is of very limited application because of the great variety of metals to be cleaned and the many different kinds of grease to be removed in practical plating is incorrect. No other method of cleaning in use today is capable of such general application to all kinds of metals for the removal of every variety of grease as is the combined cleaning and plating solution.

A paper presented at the Twenty-ninth General Meeting of the American Electrochemical Society, in Washington, D. C., April 27-29, 1916.

20

RAPID NICKEL PLATING.

By Oliver P. Watts.

During the greater part of the half century that nickel plating has been practiced, platers were content to follow in the footsteps of their forefathers and deposit nickel at the snail's pace of three to five amperes per square foot. A few years ago "rapid nickel salts," claimed to permit of nickeling at two to three times the usual rate, were imported from Europe. These proved to be only mixtures capable of yielding more concentrated solutions than that enemy of progress, the "double sulphate," which for so long has masqueraded as the plater's friend. The American plater soon learned how to make up his own rapid solution, and as a result nickeling at ten to twenty amperes per square foot is very common today.

The most recent step in rapid nickeling, if nickel's twin-brother and rival, cobalt, may be included in this category, is the remarkable work of Kalmus and Barrows[1] in plating with cobalt at 150 amperes per square foot, turning out commercial plating of high grade in three minutes.

These achievements with cobalt suggested the desirability of obtaining similar effects with the cheaper nickel solution. In so far as the wonderful results of cobalt solution XIIIB depend upon its extreme concentration (312 grams of anhydrous cobalt sulphate, equivalent to 585 grams of the crystallized salt, per liter, or 7½ pounds per gallon) it should be possible to duplicate them with nickel, since its salts are equally soluble. It is in the matter of anode corrosion and in its absorption of hydrogen[2] that nickel is inferior to cobalt as a metal for electro-plating.

The nickel anode becomes "passive" on the slightest provocation, and instead of all of the current dissolving nickel as is desired,

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[1] Trans. Am. Electrochemical Society (1915) 27, 75.

[2] *Idem.* (1915), 27, 121.

a portion of it is spent in producing acid at the anode. Besides cutting down the efficiency of deposition, this acid causes hydrogen to be evolved in considerable quantity on the cathode, where some of it is absorbed by the deposit. Absorption of hydrogen by nickel renders it hard and brittle, and is likely to cause it to curl away from the metal on which it is deposited. The addition of a small amount of some chloride to the sulphate solution usually used for nickel plating is a well-known remedy for this passivity of the anode.

Previous experience with hot nickel solutions indicated their use for overcoming the difficulties just mentioned, since in a hot solution anode corrosion is greatly improved and absorption of hydrogen is lessened.

A 25-gallon (95 liter) hot nickel bath was used at 125 to 150 amperes per square foot (14 to 16 per sq. dm.), with great satisfaction, producing in five minutes a heavier deposit than is obtained in an hour from the usual "rapid" bath at ten amperes per square foot. In spite of the extreme current density the deposits were superior in quality and adherence to ordinary nickel plate. Since the electrical instruments and current supply were inadequate for working this bath to its full capacity, a portion was removed to an enameled pail where it could be tested on small cathodes.

This solution contains nickel sulphate (single salt), nickel chloride, and boric acid in the following proportions:

	Grams / Liter	Oz. Gallon
$NiSO_4.7H_2O$	240	32
$NiCl_2.6H_2O$	20	3
H_3BO_3	20	3

At the outset the anodes were the same that have been used in the plating laboratory for a number of years, *viz.*, strips of electrolytic nickel. Later cast anodes of the same material were employed. Results of some of these tests are presented in tabular form.

Exp.	Temperature C°	F°	Time Min.	Amperes per Sq. Dm.	Sq. Ft.	Ampere-Hours per Sq. Ft.	Deposit
No. 10	67	153	5	31.7	295	24.5	Fine.
No. 48	71	160	5	47.6	422	28	Good.
No. 54	92	198	1	95.3	890	14.8	Fine.
No. 4	25	77	3	5.3	49	3	Fine.
No. 5	25	77	6	14	130	6.5	Mat, polishes well.

In no case was the deposit "burned." In No. 5 there was a vigorous evolution of gas, indicating a low current efficiency of deposition. Deposits from the hot solution were mat, but polished easily.

It is a matter of general observation that electrolytic deposits become rougher with increasing thickness; when comparing different plating baths it is therefore desirable to know the thickness of the deposits as well as their physical qualities. For the same current efficiency, the thickness of nickel deposited will be proportional to the ampere-hours per unit of surface. By a comparison of the ampere-hours per square foot in the accompanying tables, the relative thickness of different deposits may be estimated. At 100 percent efficiency one ampere-hour per square decimeter deposits 0.0123 mm., and 10 ampere-hours per square foot deposits 0.00052 inches, or 0.001 inch in thickness requires 19.2 ampere-hours. One hour at ten amperes per square foot, or ten ampere-hours, is considered good nickeling, and a common cobalt deposit by Barrows was 150 amperes per square foot for three minutes, or 7.5 ampere-hours. Judged by these standards the results shown in the tables are heavy deposits.

In order to secure samples from hot and cold solutions for direct comparison polished aluminum cathodes were used, from which the nickel was easily stripped.

DEPOSITS ON ALUMINUM.

	Temperature		Time	Amperes per		Ampere-Hours per	
Exp.	C°	F°	Min.	Sq. Dm.	Sq. Ft.	Sq. Ft.	Deposit
No. 12	74	165	20	18.9	176	60.3	Fine, mat.
No. 14	35	95	12	11.7	109	22.6	Rolled up, brittle.
No. 15	38	100	22	8.2	76	27.9	Mat, tore in buffing.
No. 49	71	160	5	24.2	225	18.7	Fine.
No. 50	78	172	10	30.7	285	47.6	Fine.
No. 53	98	208	25	15.2	141	60	0.002 inch (0.05 mm.) thick. Five successive deposits.

Plating on aluminum brought out the difference between deposits from cold and from hot solutions. An excellent deposit was obtained from the hot solution in every case, which bore polishing without peeling from the aluminum, and when stripped from the latter proved of excellent physical quality. Most of the deposits from the cold solution rolled up and partly separated from the cathode while in the plating bath, and in the few cases where this did not happen the deposit was torn during polishing. No. 53 consisted of five successive deposits for five minutes, each coating being polished and immersed in the electric cleaner for ten seconds before re-plating. It is 0.0025 inch (0.06 mm.) thick, and is harder than the usual deposit from a hot solution.

Current efficiency tests were made by reading the current on a Weston model No. 280 ammeter, and determining the weight of metal deposited in five or six minutes. Since a difference of three seconds changes the weight of a five minute deposit by one percent, the results are subject to an error of at least this magnitude. Current efficiencies above 90 percent are obtained in the hot solution at 20 amperes per square decimeter (190 amp. sq. ft.). It is evident from the tests that heating the solution and lowering the current density raises the current efficiency.

CURRENT EFFICIENCY TESTS.

	Temperature		Time	Amperes per		Ampere-Hours per Sq. Ft.	Cathode Eff. Percent
Exp.	C°	F°	Min.	Sq. Dm.	Sq. Ft.		
No. 11	45	113	6	31.1	289	28.9	89.6
No. 13	29–40	84–104	6	31.1	289	28.9	19.4
No. 16	60–70	140–158	13	8.6	80	17.3	100.9
No. 46	25–28	77–82	5	19.4	180	15	31.7
No. 48	91–84	196–183	5	9.5	88	7.4	98
No. 51	77–73	171–163	6	26.4	245	24.5	100.5
No. 52	76–84	167–183	6	51.3	477	47.7	99.2

Polarization at the end of No. 52 was only 0.16 volt. Measurements of polarization at 70°C. (158°F.) gave 0.15 volt at current densities varying between 13 and 26 amperes per square decimeter (121-242 amp. sq. ft.). It is therefore probable that hot nickel solutions can be operated at high current densities with less anode surface than is at present used for current densities of 10 amperes per square foot.

In experiments with a solution containing 75 grams per liter (10 oz. per gallon) of the "double sulphate" two and a half times the current was required to cause burning at 70°C. (158°F.) that produced this effect in a cold solution, the weight of metal deposited being the same in the two cases. This indicates that concentration of metal is a greater factor in permitting the extremely high current densities used in these hot solutions than is the temperature. The beneficial effect of heating a nickel solution consists in the improved quality of the deposit, and in better anode corrosion. To avoid convection currents the flame by which the solution was heated was removed at the beginning of each test. At the higher current densities there is noticeable heating of the solution by the current.

A nickel solution that is extensively used consists of the single sulphate, boric acid, and common salt. In order to learn if the substitution of common salt for the nickel chloride of the laboratory plating bath would cause any marked difference in its operation the following solution was tested:

	Grams / Liter	Oz. / Gallon
Single sulphate	240	32
Sodium chloride	30	4
Boric acid	22	3

TESTS OF BATH WITH SODIUM CHLORIDE.

Exp.	Temperature C°	Temperature F°	Time Min.	Amperes per Sq. Dm.	Amperes per Sq. Ft.	Ampere-Hours per Sq. Ft.	Cathode Eff. Percent	Deposit
No. 42	32	90	5	19	177	14.7	25.6	Good.
No. 43	71	160	5	19.6	184	15.3	82.3	Burned one edge.
No. 44	76	169	5	20.8	193	16.1	82.8	Burned one edge.
No. 86c	84	183	3	20.2	187	9.3	...	Fine.
No. 68d	78	172	4	25.3	234	15.6	...	Burned.

Although this solution gave fine results, it is inferior to the bath containing nickel chloride, in not permitting the use of so high a current density.

To make up the bath with nickel chloride proceed as follows: Dissolve the nickel salts in the proper amount of hot water, add nickel carbonate in small amounts at a time and heat until all acid is neutralized; either filter or allow to settle and decant the clear solution, and finally add the boric acid.

In so far as anode corrosion is concerned, any soluble chloride might be substituted for the nickel chloride, but not without some effect on the character of the deposit. Magnesium chloride or sodium chloride seems to be preferred for this purpose. In case either of these is used, neutralizing might well be done by the carbonate of the same metal. Ammonium salts and the "double sulphate" of nickel are to be avoided, since they are likely to cause crystallization from the solution when cold.

To obtain the best results from a hot solution the current density must be high; cables and tank rods must therefore be of ample capacity. Control of a hot solution by regulation of the amount of anode surface will probably be easier than in a cold bath. The heating coil should be of heavy lead (or hard lead) pipe, with a settling space of five or six inches below the lowest coil; lead will also serve as a lining for the tank. If an electric cleaner is operated from the plating dynamo, either the heating coil should be electrically insulated, or all rheostats should be connected on the cathode side of the line. Should gas pitting occur on first using the solution in the morning, it may be avoided by heating the bath to boiling for a few minutes before beginning plating. Seventy degrees centigrade (158°F.) is a good temperature at which to operate a hot nickel bath.

Owing to the peculiar properties of electrolytic nickel, the advantages of a hot over a cold solution are greater in nickel plating than in the deposition of any other metal.

ADVANTAGES OF A HOT OVER A COLD NICKEL SOLUTION.

1. Heating from 25° to 70° C. (79° to 158° F.) lessens the resistance of the solution one-half.

2. The current density may be increased two and a half to three fold.

3. The current efficiency, if less than 100 percent in the cold solution, is raised.

4. Anode corrosion is greatly improved, and higher current densities may be used at the anode as well as at the cathode.

5. The deposit is superior to ordinary nickel plate in toughness and freedom from peeling.

6. In the solution tested, plating may be done at 200 to 300 amperes per square foot (22 to 33 per sq. dm.), at which rate the same amount of metal is deposited in five minutes as requires one and a half hours in the "rapid solutions" now in use at ten amperes per square foot.

Laboratory of Applied Electrochemistry,
University of Wisconsin.

DISCUSSION.

C. G. FINK: A year ago, at Atlantic City, Dr. Kalmus presented a paper on cobalt plating and the results he obtained, in particular with solution No. 13-B, were so remarkable, and the tests of the plating were so good, that many concerns have adopted cobalt in preference to nickel. Now Dr. Watts comes forward and saves the day for nickel.

PRESIDENT ADDICKS: I might repeat the remarks I made a few minutes ago on the other paper. It seems to me impossible to use in practice the rates of deposition recommended in the paper, and I would not think they would be commercial unless the power is almost an insignificant item. I suppose the plating plants have industrial power costing several cents a kilowatt-hour.

G. B. HOGABOOM: They are using this solution in a large plant in Wichita, Kansas, doing some work on lamp bodies, which are rotated very fast, about 1,000 r. p. m., and the deposit is very good. The cost is small considering the amount of work that can be turned out, but the disadvantage is that what is known as white nickel deposit, such as you see on stoves, cannot be obtained in hot solutions, the white in the deep parts has a tendency to turn yellow, which counts against it for such work.

J. C. WOODRUFF: The cost of current is small in the cost of plating. The baths are large, the amount of metal tied up in the anodes is considerable, and the cost of preparation of the surface and handling of the parts makes up a great deal of the total cost of the finished article.

G. A. ROUSH: The saving of time in turning articles out in a few minutes instead of an hour or an hour and a half, largely counterbalances the extra cost of power.

After the Atlantic City meeting last year, manufacturers in our neighborhood who do nickel plating asked me what I could tell them about the Kalmus proposition of cobalt plating, what I thought of its permanence, and the possibilities of its replacing nickel. I told them that I did not think it would replace nickel to any great extent, but that I thought the greatest factor would be the search for methods which would speed up the nickel plating and make the nickel bath do the work they had expected cobalt to do.

J. W. Richards: Your remark, Mr. Chairman, about the impossibility of such high current densities in practice does not apply to the ordinary plating bath, because it is a large bath with a comparatively small number of amperes going through it, as compared with a metal refining bath, which is absolutely full of anodes and cathodes. Furthermore, if it is desired to work at a temperature, of, say, 70° F. (21° C.), the current is useful in keeping the bath at that temperature, and if the bath became overheated a simple device could be used for reducing its temperature, as by circulating the solution outside and thus cooling the bath if it had a tendency to get too hot.

It is my impression that since the appearance of Dr. Kalmus's paper in our Transactions last year it has had a most important effect on the nickel plating industry, in speeding up the work. Mr. Hogaboom knows about that so much better than I do, that I would like to ask him if there has not been more or less of a revolution in the nickel-plating industry in the last year in that respect?

G. B. Hogaboom: It is as Dr. Richards states; nickel plating is being speeded up, and is probably due directly to the deposits which can be obtained from the cobalt solution. However, cobalt solutions are not giving the satisfaction, generally, that is imagined; there are some drawbacks to it. You cannot get the white deposit. The deposit stains very rapidly, and does not have that pure whiteness that nickel has. If it is used on work that is to be heated like electric flat-irons it tarnishes very rapidly, and you cannot remove the tarnish. That works against it, and the price of cobalt is pretty high just now, $1.50 per pound.

Joseph W. Richards: Has the fast nickel plating been satisfactory?

G. B. Hogaboom: It has not been entirely satisfactory, because the solution becomes alkaline so rapidly that it gives the dull deposit. That is the disadvantage of hot nickel solutions. Just as soon as you get a solution alkaline, the deposit becomes dull; and if you keep it on the acid side, then the deposit is usually brittle, and will not adhere.

A. G. GIBBS: If there is any great gain in fast nickel plating the alkali could be removed as formed, by a little diaphragm cell placed in the circulating system. This operates commercially in another process.

O. P. WATTS (*Communicated*): In discussing the cost of power for rapid plating one important point appears to have been overlooked. Six volts is the standard pressure for plating dynamos, and in cold nickel solutions as now operated at 2 to 3.5 volts, 67 to 41 percent of the energy is wasted in the rheostat. So long as the plater gains the extra voltage needed for rapid plating by diminishing the resistance of the rheostat or entirely short-circuiting it, the additional power consumed in his plating tank is not costing him a cent; he is only utilizing energy which was formerly wasted. In most cases it will probably not be desirable to plate more rapidly than 70 to 100 amperes per square foot, for which 5½ to 6 volts should suffice. It was the purpose of this paper to acquaint platers with the possibilities of a hot, strong nickel solution for rapid plating; the particular temperature, concentration of solution and current density for the best results in practical plating can only be determined by experience.

It should be possible to maintain the necessary slight acidity by regulation of the anode surface, and of the amount of chloride in the solution. So far, with electrolytic anodes, my difficulty has been to prevent the bath from becoming too acid. This was overcome by putting in more anodes and by increasing the amount of nickel chloride.

When using a solution so acid that no nickel could be obtained from it at 20° C., heating to 70° C. caused a good deposit. The rise in temperature might be expected to cause an increase in the rate of corrosion of the deposited nickel, due to greater activity of the acid. Will some one explain the anomaly?

A paper presented at the Fifty-ninth General Meeting of the Electrochemical Society, held at Birmingham, Ala., April 25, 1931, President Kahlenberg in the Chair.

21

PROGRESS OF THE HOT NICKEL SOLUTION.[1]

By Oliver P. Watts.[2]

Abstract.

A report is made of the volume and operating conditions of many of the hot nickel plating solutions now in use in the United States and Canada. Since there was an incubation period of five years between the announcement of the advantages of heating the nickel plating solution and its commercial adoption, the reported growth to 158,000 gallons (598,000 liters) has occurred in ten years. Opinions of platers on the respective merits of the hot and cold nickel solutions are included.

In Volume XXIX of the Transactions of this Society (p. 403) the writer presented the results of experiments with a heated nickel solution of higher metal concentration than was then in use, and recommended it for rapid nickel plating. Two months ago C. H. Eldridge, secretary of the Electrodeposition Division, requested a report on the progress made by the hot nickel solution in the intervening fifteen years. Because of the limited time, this paper is a sketch rather than a picture of the present use of the hot nickel solution.

To secure the necessary information a letter was sent to the secretary of each of the twenty-five branches of that other A. E. S., the American Electro-Platers' Society, and thirty inquiries were sent to companies that were thought to be using a hot nickel solution. The results are summarized in Table I.

The following comments were made by the platers upon the use of the hot nickel solution:

A. "We consider the hot nickel bath superior to the cold nickel bath in every particular except color of deposit, if the goods are to receive no finishing treatment such as buffing or burnishing. We find hot nickel baths simpler to control and operate than cold nickel baths. The de-

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[1] Manuscript received February 14, 1931.

[2] University of Wisconsin, Madison, Wis.

posits are wonderfully malleable, adherent and efficient as a protective coating for steel or iron. In one of our baths which is operated at 90° F. (32° C.) and 30 amp./sq. ft. (3.2 amp./sq. dm.) we plated 1,534,810 pieces of various shapes and sizes during 1930. Rejects due to non-adherent deposits numbered exactly twenty-one, and these were spoiled by the operator's switching on an excess of current when the first few pieces were placed in the bath. Our average nickel deposit is 0.002 inch (0.05 mm.) in thickness. Hot nickel solutions have enabled us to accomplish splendid results after repeated efforts with cold nickel solutions had proved useless."

B. "Trying to run much beyond 12 amp./sq. ft. (1.3 amp./sq. dm.), we found bad pitting on the ends of our work due to too high current density."

D. "On high carbon steel and brass castings the hot solution has been found to be far better than a solution operated at room temperature in reducing rejections due to the nickel deposit rising."

G. "In my opinion a hot nickel solution is the only solution for getting a quick and heavy deposit. The cold solution is a back number."

J. "The hot solution deposits faster, gives a better plate, and a better finished article after buffing, especially when a high luster is desired. It is much better than the cold solution for depositing under chromium, especially on articles that are electrically heated in use."

N. "The hot nickel solution is, in our opinion, so much better than the cold solution that any comparison would leave the latter out of the picture. Among the points of superiority may be mentioned the speed with which the deposit is obtained, freedom from pits in the deposit, and the ease with which the solution is kept in good condition.

"Our troubles are so few and far between that we hesitate to mention them. It does happen at rare intervals that a few pits will show on the work. As soon as they are noticed sodium perborate is added, and the solution immediately tested to find the cause, which is usually a lowered pH. During the last six months a trace of pitting appeared just once, and it was stopped when only a few pieces of work were damaged.

"I have never plated chromium over cold-plated nickel, but the opinion among platers here seems to be that hot nickel is far more successful than cold. In fact, I have been unable to find more than one plater who is now using cold nickel under chromium, and he is in a small plant where local conditions make it impossible for him to heat his nickel solution."

TABLE I. *Data for Nickel Plating from Hot Solutions.*

Location		Years Used	Product	Gallons	Composition of Bath oz./gal.			Temp. ° F.	C. D. amp./sq.ft.	pH	Tanks and Lining
					$NiSO_4$	$NiCl_2$	H_3BO_3				
A	Ont.	8	Mfg.	3,500	32	3	3	90	10 - 40	5.2 - 5.6	Concrete, asphalt-lined.
B	Conn.	1	Mfg.	3,000	28	10	4	90	10 - 12	5.8	Steel, hard rubber-lined.
C	N. J.	⅙	Mfg.	2,000	32	3	2	120	10	5.5	Steel, rubber-lined.
D	N. J.	..	Mfg.	700	17	3	3	120	20	6.0	Cypress, unlined.
E	N. Y.	0.5	Elec'type	660	..	..	..	100	18	6.2	Wood, lead-lined.
F	Pa.	4	Mfg.	32,000	32	4	4	120 - 150	10 - 50	1 - 6	Steel, lead-lined. Steel, rubber-lined.
G	Pa.	6	Mfg.	9,000	..	..	..	120	30 - 40	5.6 - 5.8	Steel, rubber-lined.
H	Ohio	..	Mfg.	19,000	..	..	..	90	12 - 15	6.3 - 6.5	Cypress, unlined.
I	Ohio	9	Mfg.	800	34	*	3	120 - 160	20 - 100	2.5 - 3.5	Wood, lead-lined.
J	Ill.	10	Mfg.	4,200	24	3	3	110	30	5.2 - 5.8	Cypress, unlined.
K	Ill.	1.5	Mfg.	750	35	3.5†	4	125 - 135	60 - 80	4.8 - 5.0	Steel, lead-lined.
L	Ind.	1	Job. pl.	500	24	3	3	120 - 140	35 - 50	......	Wood, lead-lined.
M	Mich.	7	Bumpers	25,000	32	..	..	100 - 120	35 - 50	2.3 - 2.6	Wood, lead-lined. Steel, rubber-lined.
N	Mich.	3.5	Auto acc'y	6,300	30	3	4	110 - 120	30	5.8	Cypress, unlined.
O	Mich.	7	Auto	30,000	38	8	4	105	25	5.8	Steel, lead-lined.
P	Mich.	4	Auto	12,000	30	4‡	4	120 - 130	12 - 15	5.2 - 5.5	......, lead-lined.
Q	Wis.	1	Bumpers	3,600	35	2.5‡	3	125	25	2.3	Wood, asphalt-lined.
R	Wis.	10	Job	2,000	32	3	3	120	20	5.0 - 5.2	Steel, lead-lined.
S	Calif.	7	Bumpers	2,250	45	3.5	4	118 - 128	30	4.0 - 4.5	Wood, lead-lined. Steel, lead-lined.
T	Calif.	9	Mfg.	1,400	45	9	3	124 - 128	40	6.2 - 6.3	Wood, unlined.
U	Ohio	0.5	Mfg.	500	25	3	..	125	80	2.5	Wood, lead-lined.
V	Mich.	1.5	Auto	16 000	40	1	5	160	25 - 30	2.5	Steel, rubber-lined.
W	Mich.	3	Auto	8,500	20	1.5	5	140	45	2.2	Steel, hard rubber-lined.
			Total ...	183,730							

* Hydrofluoric acid.

† NH_4Cl.

‡ NaCl.

NOTE: 90° F. = 32° C.

120° F. = 49° C.

140° F. = 61° C.

160° F. = 71° C.

1 gal. = 3.785 Liters.

10 amp./sq. ft. = 1.08 amp./sq. dm.

1 oz./gal. = 7.5 grams/Liter.

O. "The hot solution is much to be preferred to the cold. Since the application of hot nickel there has been a great improvement in the lasting and wearing quality of nickel-plated products."

P. "The hot solution is much better than the cold. We have no serious trouble with it. Have never used a cold deposit under chromium."

S. "Plating with cold nickel solution at low pH will cause pitting, and with high pH will cause peeling under chromium. Have had practically no trouble with the hot solution."

Three out of the twelve branch secretaries who replied stated that none of their members were using hot nickel, so it is evident that there are several regions engaged in plating to which the hot nickel solution has not yet penetrated. On the other hand, it is fairly certain that 30,000 to 40,000 gallons (110,000 to 150,000 liters) of hot nickel solution on which no reports were received are used by automobile manufacturers in Detroit and vicinity, and a large amount must be used by automobile makers elsewhere, so it is probable that the 184,000 gallons or 700,000 liters (approximately) is much less than the total hot nickel solution used in the United States and Canada. At present the hot nickel solution is used by manufacturers whose products are exposed out of doors or are subjected to very severe usage, like automobiles and flatirons. Few job-plating shops appear to be using hot nickel. Geographically, its use is mainly in the Middle West.

With three exceptions, all who reported the composition of their solutions are employing a fairly high nickel content, which in a hot solution should make very rapid plating possible. The wide variations in current density are due in part to differences in the class of articles plated, but evidently the possibilities of the hot nickel solution for rapid plating are not yet realized by some of its users. Tanks vary from cypress, through lead-lined wood or steel, to rubber-lined steel as the latest fashion. Lead pipe is universally used for the steam coil.

Advantages of the hot solution are: Three to ten times the output from the same volume of solution; the possibility of obtaining a thicker, more protective deposit in less time than from the cold solution; a softer, more ductile deposit that is less likely to peel in buffing or in subsequent use. Its disadvantages are a mat deposit which requires buffing, and increased liability to pitting of the deposit from hydrogen. The latter is controlled by additions of hydrogen peroxide or sodium perborate, the preference being three to one in favor of the former. It is reported that with a new solution pitting is often very serious, so that large and frequent additions of peroxide are necessary, but that this trouble ceases after about three months.

When a stainless alloy first appeared on the new Ford, other manufacturers of automobiles, fearing that the public might demand solid metal on all cars, with the consequent scrapping of hundreds of thousands of dollars worth of plating equipment, talked much and earnestly of the need for the production of better and more durable plating by everybody. Although much good plating is being done, in too many cases production managers and cost accountants control the quality of plating. The results of their policy of scrimping on plating costs are seen in rust on certain makes of cars after only a few months' use. Bright electroplate over steel for automobiles or other outdoor use cannot give good service unless the deposit is thick and non-porous. So far as now appears, nickel must constitute the major part of the protective coating. The hot, concentrated nickel solution offers a means, not yet fully utilized, for producing a thick, ductile coat of metal in the same time that is now used in depositing an inadequate coating from the cold solution.

The writer thanks the members of the American Electro-Platers' Society and those other platers who supplied the information which has made this paper possible.

Dept. of Chemical Engineering,
University of Wisconsin.

DISCUSSION.

OLIVER P. WATTS: Do you get a bright chromium deposit as it comes from the barrel?

COLIN G. FINK[3]: Yes, indeed.

OLIVER P. WATTS: I tried some experiments along that line myself a few years ago, but I could not get a bright deposit in the barrel. I experimented for quite a while and it was impossible for me to get a bright deposit.

E. M. BAKER[4]: When we first began nickel plating, we used the so-called "Watts' solution" and found in the article by Prof. Watts[5] all of the information which one skilled in the art needed to operate this solution. We first used a cathode current density of 200 amp./sq. ft. (21.6 amp./sq. dm.), but have since decreased this to around 50 amp./sq. ft.

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[3] Head, Div. of Electrochemistry, Columbia Univ., New York City.

[4] Asst. Prof. of Chem. Engineering, Univ. of Michigan, Ann Arbor, Mich.

[5] O. P. Watts, Trans. Am. Electrochem. Soc., 29, 403 (1916).

(5.4 amp./sq. dm.). Higher current densities are feasible for plating articles of relatively small area in a bath of relatively large cross-section. However, we have found it desirable to substantially fill the cross-section of the bath with work to be plated. This considerably increases the effective resistance between the anode and cathode, and, therefore, increases the voltage which is required to produce a given current density. Under these conditions, current densities of 75 or 100 amp./sq. ft. (8.1 to 10.8 amp./sq. dm.), let alone 200 amp./sq. ft. (21.6 amp./sq. dm.) are prohibitive from the standpoint of cost of power. As economic balance seems to dictate about the current densities which we have adopted.

When high current densities are employed, it is advantageous to use a high bath temperature, and conversely, better plating is secured at low current densities by using a low bath temperature.

Another objection to extremely high current densities is the large current required per tank. This is not an objection on a new installation, but rather applies to modifying the plating conditions in an old plant. If the current required per tank at a current density of 100 amp./sq. ft. (10.8 amp./sq. dm.) is 10,000 amperes, in most plants this would mean that two or more of the present generators would be required on a single tank. Under the usual plating conditions, it is not desirable, nor often even feasible, to operate two or more generators in parallel. Consequently, such plants would find little advantage in changing their plating conditions to adopt such high current densities as 100 amp./sq. ft. Let me make it clear that this statement does not apply to the plating of a few small articles in a large tank, but refers rather to large scale manufacturing conditions as they usually exist.

OLIVER P. WATTS: What voltage do you use?

E. M. BAKER: When operating at 50 amp./sq. ft. (5.4 amp./sq. dm.) the potential between the anode and cathode is practically 12 volts. To operate at 100 amp./sq. ft. (10.8 amp./sq. dm.) would require around 20 volts which would be prohibitive from a cost standpoint.

A paper presented at the Thirtieth General Meeting of the American Electrochemical Society, held in New York City, September 28, 1916, Mr. L. E. Saunders in the Chair.

22

THE PROTECTION OF IRON BY ELECTROPLATING.

By Oliver P. Watts and Paul L. DeVerter.

Although nickel-plated iron is satisfactory for use indoors, when exposed to the weather it almost invariably rusts. Brass-plated steel is extensively employed for the cheaper grades of builders' hardware, but is even more unsatisfactory than nickel plate for out of door use. In reply to an inquiry concerning the possibility of a durable brass plate on steel for use out of doors, *The Metal Industry*[1] says, "An electro-deposit of zinc on steel or iron is the only one that will withstand atmospheric conditions for any length of time, and a demand is now being made for hardware that has received an electro-deposit of zinc before being plated with any other metal for ornamental purposes, such as nickel, copper, brass or bronze. This double coating gives good service and is the only satisfactory one for hardware which is exposed to the weather."

The superior protective action of electro-galvanizing in comparison with deposits of other metals on iron is well recognized. This has generally been ascribed to voltaic action; whenever a hole is broken or worn through the plating a voltaic cell is formed between the metallic coating and the exposed iron. If the coating consists of a metal which is electro-positive to iron, the latter is cathode and is protected from corrosion, but if the coating is electro-negative to iron this becomes anode, and is corroded worse than if the "protective coating" were entirely absent. Examination of tables of potentials of the metals shows that, of the metals which can be satisfactorily plated out of aqueous solutions, only zinc and cadmium are electro-positive to iron. Since cadmium is not used for commercial plating on account of the expense, zinc remains as the only electroplate which can protect iron by voltaic or galvanic action. Theory and practice appear to be in harmony.

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[1] Metal Industry, 1915, p. 469.

Galvanic action requires that two unlike conductors be in electrical connection with each other and with an electrolyte. So long as the iron is completely covered by the electroplate there is no opportunity for voltaic action, either corrosive or protective, and, so far as rusting of the iron is concerned, it is immaterial what metal constitutes the coating. The protection of iron by deposits of zinc and its universal rusting when plated with other metals seems to indicate either that electro-deposits of zinc are less porous than those of other metals, or that in the thickness used commercially all electro-deposits are porous, or on exposure soon become so, and thus the superior protection by zinc is due solely to its galvanic action.

To investigate the porosity of electroplating, and to determine the protection afforded to iron by deposits of different metals, a series of experiments has recently been carried out in the electrochemical laboratory of the University, and it is thought that these are of sufficient interest to electroplaters to merit publication.

THE PROTECTION OF IRON BY DEPOSITS OF NICKEL, COPPER AND BRASS.

Since it is generally conceded that commercial plating with these metals does not protect iron from rust, it was decided to try much thicker deposits than those usually employed. A company which makes great quantities of an article in daily use by millions of people specifies ten milligrams of nickel per square inch as the minimum for good deposits, and fifteen for their heaviest plate. The latter corresponds to an average thickness of 0.00348 mm. or 0.000137 inches, and requires an hour at five amperes per square foot for its deposition. For indoor use this deposit stands well the constant handling to which these articles are subjected. The deposits of the tables which follow range from this thickness to ten and in a few cases even twenty times heavier.

Strips of sheet iron were pickled in sulphuric acid to remove scale, cleaned in the electric cleaner, dried, weighed, returned to the electric cleaner for a few seconds, rinsed, and hung in the plating bath. After plating the strips were reweighed, and the average thickness of the deposit calculated. The brass and copper deposits were made from hot cyanide baths containing caustic soda; the zinc solution consisted of the sulphate and a little chloride; the nickel was plated from a rapid solution recommended by the writer[2], which was used hot except for two samples. The conditions of deposition are given in Tables I to IV.

TABLE I.

Brass Deposits on Iron.

No.	Time Min.	Temp.	Amp./dm.^{2}	Thickness		Amp. Hrs./dm.^{2}	Cur. Eff. Percent
				Inches	m.m.		
1	55	Hot	11.5	0.00028	0.0071	1.0	26.7
2	10	Hot	11.5	0.00061	0.0155	1.9	30.1
4	15	Hot	12.3	0.0008	0.0203	3.07	25.5
6	30	Hot	12.6	0.00228	0.059	6.3	33.1
7	60	Hot	8.75	0.00327	0.0832	8.75	33.9
41	150	Hot	8.0	0.00607	0.1543	20.0	34.5

TABLE II.

Copper Deposits on Iron.

No.	Time Min.	Temp.	Amp./dm.^{2}	Thickness		Amp. Hrs./dm.^{2}	Cur. Eff. Percent
				Inches	m.m.		
36	3	Hot	7.32	0.00027	0.0069	.37	58.2
3	10	Hot	6.83	0.00096	0.0245	1.12	71.2
5	15	Hot	6.83	0.00099	0.0251	1.58	51.8
9	45	Hot	5.55	0.00129	0.0327	4.1	31.9
8	75	Hot	5.68	0.00271	0.0689	7.1	39.1
42	120	Hot	3.25	0.00248	0.063	6.5	33.1
46	180	Hot	3.27	0.00686	0.1745	9.81	60.8

TABLE III.

Zinc Deposits on Iron.

No.	Time Min.	Temp.	Amp./dm.^{2}	Thickness		Amp. Hrs./dm.^{2}	Cur. Eff. Percent
				Inches	m.m.		
21	4	Hot	4.88	0.00019	0.0049	0.32	71.6
19	1	Cold	14.7	0.000196	0.0050	0.24	97.4
14	3	Cold	13.25	0.00043	0.0109	0.66	85.3
10	5	Cold	13.65	0.00077	0.0195	1.14	86.2
11	12	Cold	12.5	0.00103	0.0263	2.3	63.1
13	30	Cold	9.55	0.00237	0.0603	4.77	60.5
12	25	Cold	14.7	0.00266	0.0667	6.1	52.0

TABLE IV.

Nickel Deposits on Iron.

No.	Time Min.	Temp.	Amp./dm.^{2}	Thickness		Amp. Hrs./dm.^{2}	Cur. Eff. Percent
				Inches	m.m.		
30	20	Cold	1.3	0.00016	0.0042	0.43	45.5
25	10	Cold	2.3	0.00022	0.0055	0.4	51.0
31	15	Hot	4.85	0.00069	0.0176	1.2	78.5
33	90	Cold	1.0	0.00091	0.0231	1.5	62.5
29	20	Hot	5.28	0.00102	0.0255	1.76	72.0
32	25	Hot	6.48	0.00146	0.0371	2.7	63.5
34	40	Hot	7.2	0.00249	0.0633	4.8	55.0
44	180	Hot	4.23	0.00598	0.152	12.75	48.1
45	165	Hot	5.56	0.00702	0.178	15.05	42.7

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[2] Trans. Am. Electrochem. Soc. (1916) 29, 126.

The samples were placed in wood racks, exposed to the weather, and examined occasionally for their appearance in regard to rust. The results are shown in Tables V to VIII.

RESULTS OF WEATHERING.

TABLE V.

Copper-plated Iron.

No.	Amp. Hrs./dm.^{2}	Thickness Inches	Days required for rusting Slight	Moderate	Very bad
36	0.37	0.00027	8	10	14
3	1.12	0.00096	47	73	88
5	1.58	0.00099	47	73	88
9	4.1	0.00129	47	73	88
8	7.1	0.00271	67	88	..
42	6.5	0.00248	No rust in 70 days.		
46	9.81	0.00686	No rust in 70 days.		

TABLE VI.

Brass-plated Iron.

No.	Amp. Hrs./dm.^{2}	Thickness Inches	Days required for rusting Slight	Moderate	Very bad
1	0.98	0.00023	20	32	73
2	1.9	0.00051	46	73	88
4	3.07	0.00066	47	73	88
6	6.3	0.00228	53	73	88
7	8.75	0.00327	53	73	88
41	20.0	0.00607	Tarnished, but no rust in 70 days.		

TABLE VII.

Nickel-plated Iron.

No.	Amp. Hrs./dm.^{2}	Thickness Inches	Days required for rusting Slight	Moderate	Very bad
30	0.43	0.00017	9	19	40
25	0.4	0.00022	9	19	40
31	1.21	0.00069	12	19	53
33	1.5	0.00091	19	40	73
29	1.76	0.00102	19	40	73
32	2.7	0.00146	Tarnished, but no rust in 122 days.		
34	4.8	0.00249	Tarnished, but no rust in 122 days.		
44	12.75	0.00598	Bright, not even tarnished in 70 days.		
45	15.02	0.00702	Bright, not even tarnished in 70 days.		

TABLE VIII.

Zinc-plated Iron.

No samples rusted in 122 days.

The most striking feature of the weathering tests is the complete protection against rust during four months of very wet weather afforded by electro-galvanizing less than 0.0002 inch thick, while rusting occurred through deposits of copper 0.0027, of brass 0.00327, and of nickel 0.00102 inch in thickness. With thin plating rusting was serious and widely distributed, but on the thicker deposits it was confined to a few widely scattered spots. Although Nos. 42, 46 and 41 showed no signs of rust after seventy days exposure, they had tarnished so badly that all resemblance to the original copper or brass was lost. Specimens Nos. 44 and 45 not only were free from rust, but the nickel plate appeared as bright as when deposited.

DOUBLE PLATING.

In addition to the quotation already cited in favor of a coating of zinc under brass or copper plating on iron, the current issue[3] of *The Metal Industry* contains the following: "Neither copper, brass or nickel gives a successful coating upon steel that will resist atmospheric influence and prevent the formation of rust. The large hardware manufacturing companies have realized these facts and are at the present time giving their product a preliminary coating of zinc from an alkaline cyanide zinc solution which is followed by direct deposition of copper, brass or nickel, or coating the zinc with copper or brass and then nickel plating. This method is the most effective for all purposes of plating upon steel when exposed to dampness or the action of salt air."

In view of such favorable reports from practical platers concerning the protective effect of a deposit of zinc beneath copper or brass plate, it was deemed advisable to test such double plating. Specimens were therefore prepared as shown in Table IX.

TABLE IX.

Double Plating on Iron.

No.	Metal	Time Min.	Temp.	Amp./dm.^{2}	Thickness Inches	m.m.	Amp. Hr./dm.^{2}	Cur. Eff.
15	Zinc	3	Cold	14.35	0.00041	0.0104	0.72	70.2
	Copper	15	Hot	7.18	0.00107	0.0272	1.79	47.3
16	Zinc	1	Cold	12.95	0.00013	0.0034	0.21	86.3
	Copper	20	Hot	5.95	0.00145	0.0368	1.98	70.0
20	Zinc	3	Hot	4.88	0.00018	0.0045	0.24	87.3
	Copper	15	Hot	7.32	0.00119	0.0304	1.83	50.5
17	Zinc	1	Cold	13.85	0.000157	0.0040	0.23	85.8
	Brass	25	Hot	12.15	0.00327	0.0832	5.5	58.3
18	Zinc	3	Cold	12.27	0.00040	0.0102	0.61	85.6
	Brass	20	Hot	11.7	0.00186	0.0473	3.9	48.4

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[3] June, 1916.

TABLE X.

Results of Weathering on Double Plating.

No.	Amp. Hrs./dm.²		Thickness Inches	Days required for rusting
17	0.23	Zinc	0.000157	53, slight; 70, six rust spots on one side.
	5.5	Brass	0.00327	
18	0.61	Zinc	0.00040	40, slight; 70, shows 25 rust spots.
	3.9	Brass	0.00186	
15	0.72	Zinc	0.00041	14, slight; 70, much rusted.
	1.79	Copper	0.00107	
16	0.21	Zinc	0.00013	20, slight; Zinc blistered and broken in 70 days, rusted in such spots.
	1.98	Copper	0.00145	
20	0.20	Zinc	0.00018	14, slight; 70, many blisters and rust spots.
	1.83	Copper	0.00012	
35	0.33	Zinc	0.00019*	73, slight; 122, eight rust spots.
	0.92	Copper	0.00062	
35a	0.33	Zinc	0.00019*	53, slight.
	0.92	Copper	0.00062	

* As the weights of these samples were not recorded the thickness of the deposits have been computed from the ampere hours by comparison with other deposits.

The results of weathering in Table X show slightly better protection by double plating than with the same total thickness of brass or copper alone; had the zinc deposits been free from blisters it is probable that the results would have been still more favorable to the double deposit. The final rusting of every sample of double plating is in marked contrast to the complete protection afforded by zinc alone.

The zinc in No. 17 is nearly as thick as in Nos. 19 and 21, which gave perfect protection. The result of covering the zinc in No. 17 with 0.003 inch of brass has been to nullify the protective action of the zinc and to induce rusting at nearly the same rate as Nos. 6 and 7, which were without the coating of zinc. A detailed comparison of the other double deposits with the single coatings leads to a similar conclusion: the protective effect of the zinc coating is almost, if not completely, nullified by plating it over with brass or copper. The reason for this is easily seen. Zinc protects by galvanic action at the expense of being itself corroded. (It should be noted that the relative size of the surfaces of the two metals is a factor of tremendous importance in determining the extent of the corrosion or protection of one metal by contact with another.) In No. 19 the surface is zinc, with here and there a pin-hole exposing a minute bit of iron. The corrosion of zinc necessary to protect these microscopic surfaces of iron is so small in amount, and is applied to so large a surface of zinc, that a deposit of the latter only 0.0002 in. (0.005 mm.) thick can protect the iron for months, if not for years, against ordinary atmospheric corrosion. In No. 20 such a deposit of zinc has been copper plated, with here and there a pin-hole through which the zinc is exposed. (The iron may or may not be exposed—the results as regards rusting will be the same.) Each pin-point of exposed zinc plate is surrounded by a relatively enormous surface of copper cathode, and in its endeavor to protect the copper against corrosion and tarnish the zinc is soon entirely dissolved, exposing the iron beneath it. This, like the zinc, acts as anode toward copper, and rusting is the result. Such a sub-coating of zinc can at best only slightly delay the rusting of iron plated with brass, copper, nickel, etc. If this practice is to be followed the zinc deposit should be made as thick as possible, in order to lengthen its life when once it is exposed and begins to act as anode. What is needed is a non-porous coating of nickel, brass or copper. Whether or not this can be obtained without going to the extreme thickness found necessary in these experiments is for someone of wider experience than the writer to say.

POROSITY OF ELECTRO-DEPOSITS.

The prompt rusting of the iron beneath the thinner deposits of all the metals except zinc seemed to indicate either that such deposits are porous in structure, or that there are small holes at certain points which leave the iron exposed. To study this question use was made of an ingenious, yet simple, method employed by W. H. Walker for detecting holes in tin plate.

A one and a half percent solution of agar was prepared, and to each hundred cubic centimeters of this 7 c.c. of a one percent solution of potassium ferrocyanide was added. The samples of plated iron were placed in a shallow glass dish and covered with the hot solution, which quickly set to a stiff jelly. In a short time numerous blue spots appeared on the thinner deposits.

With copper-plated iron the action is as follows: whenever there is a crack or hole in the plating a galvanic cell is formed in which the exposed iron is anode, goes into solution in the ferrous state, and is precipitated as Turnbull's blue, just as when a solution of potassium ferrocyanide is added to the solution of a ferrous salt in a test tube.

The results of this test are shown in Table XI. As these deposits were not weighed their thickness can only be estimated by a comparison of the ampere hours per square decimeter with those of Tables I, II, and IV.

TABLE XI.

Ferroxyl Test for Porosity.

Deposit	Time, min.	Temp.	Amp./dm.^{2}	Amp. Hrs./dm.^{2}	Blue-spots
Copper	1	Hot	5.5	0.09	Several
Copper	3	Hot	4.8	0.24	Few
Copper	5	Hot	5.6	0.47	None
Copper	10	Hot	5.6	0.94	None
Copper	20	Hot	5.9	1.99	None
Copper	40	Hot	5.9	3.91	None
Nickel	3	Hot	5.0	0.25	Many
Nickel	5	Hot	5.0	0.41	Many
Nickel	10	Hot	5.3	0.90	Many
Nickel	20	Hot	5.4	1.81	None
Nickel	40	Hot	5.1	3.4	None
Brass	3	Hot	11.1	0.55	None
Brass	5	Hot	10.4	0.87	None
Brass	10	Hot	11.8	1.96	None
Brass	20	Hot	11.8	3.93	None
Brass	40	Hot	11.3	5.65	None

All of the deposits were found to contain pin-holes with the exception of the brasses, but unfortunately no deposits of brass less than 0.55 ampere hours per square decimeter were prepared for this test. Copper coatings up to 0.47 and nickel up to 1.81 ampere hours per square decimeter contained pin-holes, but thicker deposits were free from them.

The remarkable protection afforded by very thin deposits of zinc must be due entirely to galvanic action, unless zinc coatings are free from the holes which have been shown to exist in thin deposits of all other metals tried in these experiments. The ferrocyanide test cannot be applied to zinc coatings however, since any exposed iron would be cathode, therefore would not dissolve, and so would not make its presence known by the blue precipitate. A test for the detection of pin-holes in electro-galvanizing, for which we are also indebted to Prof. Walker, consists in immersing the strips of galvanized iron in a hot, strong solution of sodium hydroxide; wherever a bit of iron is exposed it becomes the cathode of a voltaic cell, and hydrogen is evolved from it. The results of these tests are given in Table XII.

TABLE XII.

Porosity of Zinc Deposits by Sodium Hydroxide.

Deposit	Time Min.	Temp.	Amp./dm.^{2}	Amp.Hrs./dm.^{2}	Bubbles showing porosity
Zinc	1	Cold	12.1	0.20	Many
Zinc	3	Cold	16.6	0.83	Many
Zinc	5	Cold	11.8	0.98	Few
Zinc	10	Cold	9.1	1.52	None
Zinc	20	Cold	10.0	3.33	None

Thin zinc deposits proved to be as full of holes as were the coatings of other metals, and the freedom from rusting of lightly electro-galvanized iron is due solely to galvanic action. Deposits thicker than 1.5 ampere hours per square decimeter (14 amp. hrs. / ft.^{2}) were free from holes.

PIN-HOLES BY INSPECTION.

Another method of testing for porosity consisted in examining the electro-deposits by transmitted light. To secure zinc deposits advantage was taken of the poor adhesion of electroplating on aluminum. Sheets of aluminum were polished, immersed for a few seconds in the electric cleaner, rinsed, and plated with zinc. The edges of the sheet were then cut away, and the deposit was stripped off and examined. The results are given in Table XIII.

TABLE XIII.

Porosity of Zinc Deposited on Aluminum.

Time, min.	Temp.	Amp./dm.^{2}	Amp. Hrs./dm.^{2}	Holes
5	Cold	6.32	0.52	Many
10	Cold	6.57	1.09	Few
20	Cold	5.55	1.85	None
30	Cold	5.12	2.56	None

At and above 1.8 ampere hours per square decimeter no holes were found—a good agreement with the previous test.

The lack of adhesion of electroplating on aluminum is due, in part at least, to an invisible film of oxide on the surface of the metal, and in spite of the good agreement seen in the last two sets of tests, there remained a suspicion that this film of oxide might cause electroplating on aluminum to be less uniform than on other metals. It was therefore decided to avoid the use of aluminum for receiving the deposit, wherever possible. Nickel, copper, and brass deposits were obtained by plating on zinc, and dissolving this in dilute sulphuric acid. A description of the deposits and the results of inspection are shown in Table XIV.

TABLE XIV.

Porosity of Metal Deposits on Zinc.

Deposit	Time, min.	Temp.	Amp./dm.^{2}	Amp. Hrs./dm.^{2}	Holes
Copper	3	Hot	8.2	0.41	Few
Copper	6	Hot	6.1	0.61	None
Copper	6	Hot	6.8	1.14	Few
Copper	10	Hot	7.5	1.20	None
Copper	20	Hot	6.5	2.18	Few—6 per square inch
Copper	40	Hot	7.8	3.12	Few—4 per square inch
Brass	3	Hot	12.0	0.60	None
Brass	5	Hot	12.0	1.0	None
Brass	10	Hot	12.0	2.0	None
Brass	20	Hot	12.0	4.0	None
Nickel	3	Hot	9.2	0.46	Many
Nickel	5	Hot	9.5	0.79	Many
Nickel	10	Hot	9.0	1.50	Several
Nickel	20	Hot	12.9	4.30	None
Nickel	40	Hot	12.9	8.60	None

This study of the porosity of electroplating seems to show that brass (0.000154 in. (0.0039 mm.) thick) and copper (0.000347 in. (0.0087 mm.) thick) deposits from the cyanide solution up to 0.5 ampere hours per square decimeter (4.6 amp. hrs. / ft.^{2}) contain pin-holes, and that nickel plating requires 1.5 ampere hours per square decimeter (14 amp. hrs. / ft.^{2}, 0.00102 in. thick) before pin-holes disappear.

In weathering tests of two to four months duration, rusting occurred on brass and copper plate many times thicker than the minimum for the disappearance of pin-holes. In case of the heavier deposits rusting was confined to spots a millimeter or less in diameter, the spaces between spots giving perfect protection to the iron beneath. For nickel plate there was good agreement between the disappearance of holes and freedom from rust. The divergence shown in this respect by copper and brass plating may possibly be due to the greater difference of potential between these metals and iron than that which exists between nickel and iron. The greater the difference of potential or corrosive force, the more difficult will it be to prevent rusting. For copper deposits there were no holes at 4.4 ampere hours per square foot (0.000347 in., 0.0087 mm., thick) and no rusting at 60.4 ampere hours per square foot (0.00248 in., 0.062 mm., thick). Similar values for brass plate are 5.1 amp. hrs. / ft.^{2} (0.000154 in., 0.0039 mm.) for no holes, and 20 amp. hrs. / ft.^{2} (0.00607 in., 0.152 mm.) for no rusting. Nickel required 16.8 amp. hrs. / ft.^{2} (0.00108 in., 0.027 mm.) for the absence of holes, and 25.4 amp. hrs. / ft.^{2} (0.00146 in., 0.037 mm.) for freedom from rust.

The only hope of a general use of copper and brass plate on iron exposed to the weather seems to lie in securing a uniform deposit, free from pin-holes. In special cases it may be feasible to employ the extremely thick deposits of these metals which have been shown to be necessary to protect iron from the weather, but unless the plated article is fairly rigid there is danger of cracking and peeling of such heavy deposits, and the time and expense of producing them will prevent their general employment.

CONCLUSIONS.

1. These experiments confirm the orthodox view that the superiority of electro-galvanizing over deposits of other metals for the protection of iron is due to voltaic action.
2. It has been shown that thin electro-deposits of zinc, copper, nickel and brass are full of holes, and therefore only the first may be relied on to prevent rusting, unless deposits are made much heavier than is at present the rule.
3. Deposits of nickel should exceed 0.0015 in. (0.038 mm.) in thickness in order to protect iron out of doors, and copper or brass plate should have three times this thickness. Even then it is a question how long such coatings will afford protection.
4. For the protection by electroplating of iron which is to be exposed to the weather, zinc (or cadmium) is the only metal worthy of consideration.
5. The foregoing experiments do not show that double coatings—zinc followed by copper or brass—are distinctly superior to a single heavy coating of the latter metals. If zinc is to be used advantageously, it should form the outer coating.
6. It is very desirable that some method be found for producing a uniform electroplate, free from the holes which were responsible for rusting in these experiments. Could such plating be done deposits of nickel, copper and brass would form a far more effective protection to iron than at present.

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DISCUSSION.

G. B. HOGABOOM: The findings of Messrs. Watts and De Verter as given in their paper, with reference to double plating of zinc, and then either brass, nickel or copper, are in accordance with what we experienced about three years ago.

A door-check that was plated in a sulphate of zinc solution has been out, to my knowledge, three years, exposed at the side of a railroad track to the smoke of freight engines and it does not show a particle of rust, while some steel escutcheons that were given the same coating of zinc, and then given a coating of nickel, or of copper, or of brass, had in about one hundred and twenty days spots of rust. As soon as one spot developed then a greater number of them appeared quite rapidly. Why that happens is explained by Dr. Watts. According to his idea it is because one metal is electro-positive to the other and protects it. It is of vital importance to the hardware manufacturers to find some way of plating steel with a protective coating; brass, copper and nickel do not stand up under the usual atmospheric conditions very long.

CARL HERING: The paper refers frequently to pin-holes. Some years ago I read a paper before this Society describing experiments made with a microscope showing that suspended foreign particles in an electrolyte, like the dust from the room, traveled from anode to cathode, or the reverse, just like the ions do. It is not known what causes them to travel, but they do. Some of them will ultimately deposit on the cathode, and I am inclined to believe that is one of the causes of pin-holes. If, therefore, the solution around the cathode were kept perfectly free from suspended impurities, say by means of a diaphragm, there would be less likelihood of forming pin-holes.

Another thing which occurred to me in reading this paper was that the authors cleaned the iron by the ordinary pickling process. If they had cleaned it by electrolytic pickling, they would no doubt have gotten less pin-holes. If you examine iron under the microscope, iron that has been heated, like plates or castings, you will always find little specks of black oxide in the bottom of little depressions. In the ordinary pickling process many of these little specks do not come out. By looking at it afterward under a glass one will still find these little black specks in these depressions. By the electrolytic pickling all of these specks can be dissolved, as the action gets down into the bottom of the deepest pits and without any useless waste of good metal and acid, as the pure metal is not dissolved. If more care were taken, I think the plating of iron would be more successful.

G. B. HOGABOOM: In regard to the pin-holes, I do not think Mr. Hering's point is well taken for the reason that pin-holes will occur in the deposit of metal, even if there is a diaphragm. One of the hardest things to do in electro-plating is to deposit brass, copper or nickel upon electro-plated zinc without blistering, and these pin-holes seem to be the result of that. Better results can be had by sand blasting the surface, the zinc will adhere better, and even with that precaution little pin-holes will often form after it is plated with the brass or copper, while under the microscope the plate will not show any holes whatever. There is something in the action, in the nature of electrolysis, that causes the plate to blister.

CARL HERING: The particles I referred to are smaller than would be held back by your diaphragm. The only way they could be kept off would be by some diaphragm of organic material, or a porous cup, but not by means of any screen or bag, as they would go right through that.

J. W. RICHARDS: I find in the conclusions a recommendation that the thickness of the plating should be a certain minimum thickness in order to afford complete protection. I think that the thickness of the plating necessary to give complete protection depends considerably on the original roughness of the surface, since a roughened surface commences to plate on the high points, and it takes some time for the plate to grow smooth and the plating to become continuous.

Other things being equal, the smoother the object the more quickly it will be coated continuously, and the rougher the object the longer it will take and the heavier the deposit to make a continuous coating.

G. B. HOGABOOM: On a smooth article it is more difficult to make the nickel plate adhere than on a roughened object. For successful plating, it seems to me to be necessary to have a slightly roughened surface, that is, a surface in an active state.

A. S. CUSHMAN: It is not only in electro-plating operations one finds pin-holes. As a manufacturer of tin plate and terne plate, I do not think I have seen a fair-sized sample made by the hot-dip process that was free from pin-holes. It seems difficult to prepare the surfaces of iron and steel by any process whatsoever, to such a degree of excellence that other metals, either by electro-plating or hot-dip process, will cover them all up, and I think unless you do put on a heavy enough coating in order to build up on top of the pin-holes you could not get them filled up.

L. E. SAUNDERS: My attention was called today to the fact that on some of the shells which are being manufactured in this country for the European nations that plating is required. Has any one any facts to give on that point? I understand that the Russian Government requires that steel shells must be coated with some other material to prevent rusting. Do you know anything about that, Mr. Hogaboom?

G. B. HOGABOOM: I have had no experience with shells, but know that the finish depends upon the structure of the metal. Pin-holes will show if the metal has been overheated in the manufacturing process.

J. W. RICHARDS: These pin-holes appearing in the metals which are heated differently, appear to be due to irregularities in the surfaces which are caused by the heat treatment. These cause irregularities in the deposition, because of the different conductivity of the cleaned surfaces and of the coated surface, or spots, caused by the heat treatment.

G. B. HOGABOOM: I have seen deposits of silver which under a microscope showed the outlines of the structure of the steel upon which it was plated. The structure of the metal very materially affects the character of the deposit.

O. P. WATTS (*Communicated* 23 Nov., 1916): In the five months which have elapsed since this paper was written rust has appeared on only one of the specimens previously reported in perfect condition, viz., on No. 32 six spots of rust show through the nickel plating.

A paper presented at the Thirty-first General Meeting of the American Electrochemical Society, held in Detroit, May 5, 1917, President FitzGerald in the Chair.

23

THE EVOLUTION OF HYDROGEN FROM CYANIDE PLATING SOLUTIONS.

By Oliver P. Watts and Albert Brann.

[*Abstract*]

Experiments were made with silver and copper cyanide solutions, with the addition of varying amounts of free potassium cyanide, to determine the effect of the latter in producing liberation of hydrogen at the cathode. The effect is much greater with copper solutions than with silver solutions. Test experiments show that the liberation of hydrogen is direct, and not due to action of the free cyanide, but to raising of the single potential necessary to deposit the metal until it reaches that sufficient to electrolytically set free hydrogen.

The deposition of copper and brass from the cyanide solutions used in plating is accompanied by an evolution of hydrogen, which becomes greater as the amount of free cyanide is increased. In explanation of this it cannot be said that deposition of metal from cyanide solutions is always associated with the liberation of hydrogen, for in silver plating no hydrogen is evolved. Such evolution of hydrogen means that the efficiency of deposition of metal diminishes with increase of the free cyanide.

In seeking an explanation of this phenomenon, at least two possibilities must be considered. The first involves the well-known solvent power of cyanide solutions for many metals, and would explain the lowering of the current efficiency with increase of free cyanide as due to a solvent action of the electrolyte on the deposit. The second possibility is that the hydrogen does not come from reaction between the metal and cyanide, but that it is directly deposited by the current instead of a chemically equivalent amount of metal.

When it is considered that the addition of a very moderate proportion of potassium cyanide can entirely prevent the deposition of copper, even when high current densities are employed, the first supposition appears unlikely to be the correct explanation. This view is still further confirmed by a recent experiment with a nickel-plating solution. This was divided into two parts, to one of which one percent by volume of concentrated sulphuric acid was added; the two solutions were then electrolyzed in series for a half hour at 0.3 ampere per square decimeter, with nickel anodes and copper cathodes. The cathode in the original solution gained 0.021 gram, an efficiency of 85 percent, but that in the acid electrolyte did not show a trace of nickel, and had not increased in weight. To determine whether the hydrogen that appeared in place of nickel in the latter solution was deposited directly by the current, or came from the dissolving of nickel by the acid as fast as deposited, the nickel-plated cathode was hung in the acidified solution for a half hour. It lost only 0.0026 gram in weight. The lowering of the current efficiency of nickel baths which results from the addition of strong acids is due to the plating out of hydrogen in place of nickel, and not to attack of the deposit by the acid.

Although it was deemed certain that the same condition would be found true for the copper cyanide solution, a confirmatory test was made. Equal volumes of the laboratory copper-plating bath were taken, to one portion 30 grams per liter of sodium cyanide was added, and the two electrolyzed at 0.15 ampere for 30 minutes. The cathodes gained 0.1518 and 0.0295 gram, efficiencies of 87.3 and 17 percent. On allowing the cathodes to stand in their respective electrolytes for a half hour with no current passing, the former lost 0.0016 and the latter 0.040 gram. The low current efficiency of cyanide copper solutions containing much free cyanide is due to the direct deposition of hydrogen instead of copper, and not to corrosion of the cathode by cyanide.

It is recognized that in electrolysis of solutions containing two or more metals, deposition by the electric current acts selectively; there is a tendency to deposit first that metal whose potential is lowest, and only when the greater part or all of this has been deposited, is the metal next lowest in potential deposited. It is this selective action which has made possible the electrolytic refining of metals. Although the fundamental principle is as stated, its practical operation is not so simple as indicated above; for unless there is a considerable difference of potential between the metals a complete separation does not take place, but there is a simultaneous deposition of both metals. Even when the potentials are quite different a few cases are known in which both metals are found in the deposit, as when electrolyzing the sulphates of zinc and iron. Current density and the relative concentrations of the metals in the electrolyte are important factors.

It is in this tendency to deposit only the element of lower potential when the difference of potential is great, and for both to be deposited together when there is a small difference of potential, that we must look for an explanation of the peculiarities in regard to the evolution of hydrogen in cyanide plating baths.

First it will be well to review the facts. In a solution of the double cyanide of copper and potassium containing no free cyanide, Field[1] obtained a current efficiency of 97.6 percent; but in commercial plating baths it is necessary to have some free cyanide present in order to secure good anode corrosion, and consequently the current efficiency is reduced to 70 to 80 percent, and there is always a considerable evolution of hydrogen. Not only is there no hydrogen evolved from the standard silver-plating solution, but much free cyanide may be added without causing gas to be given off at normal current densities. By raising the current density to such a point that metal cannot be supplied at the cathode by diffusion as fast as needed, hydrogen must be deposited from either solution, even if no free cyanide be present.

Caspari[2] gives 0.23 volt as the overvoltage of hydrogen on copper in normal sulphuric acid, *i. e.*, a copper cathode must have a potential 0.23 volt higher than a cathode of platinum before hydrogen will be deposited on it. This corresponds to —0.13 volt for the discharge potential of hydrogen on copper. Since the potential of copper, —0.51 (normal calomel electrode = —0.56 volt) is 0.38 volt below the discharge potential of hydrogen, it is easy to see why there is no deposition of this gas when a copper sulphate solution is electrolyzed at any reasonable current density. Copper and hydrogen are so far apart in potential that only copper is deposited.

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[1] The Principles of Electrodeposition, p. 189.

[2] Z. phys. Chem., 1889, 30, 89.

In normal potassium cyanide copper may show a potential as great as 0.8 volt, and, if the discharge potential of hydrogen on copper is the same in this as in copper sulphate solution, hydrogen should be deposited more readily than copper, and the low current efficiency of copper solutions containing a large excess of potassium cyanide is readily understood.

To determine the effect of variations in concentration of cyanide on the single potential of the metal and on the discharge potential of hydrogen, measurements were carried out in four solutions made by dissolving 65, 32.5, 6.5, 0.65 grams of C. P. potassium cyanide per liter, *i. e.*, in approximately normal, half, tenth, and hundredth normal solutions. The results are given in Table I, in which the discharge potential was taken as the lowest potential at which gas escaped steadily from the cathode. Since potentials vary with the amount of air dissolved in the electrolyte, with the time, current density, etc., and because the instruments employed were not of the highest accuracy, the numerical values given should be regarded as approximations only; yet it is thought that they are sufficiently accurate to permit the drawing of certain general conclusions. All potentials are positive unless marked otherwise.

TABLE I.

Single Potential Measurements in KCN Solution.

Concentration of KCN Added	N/100	N/10	N/2	N/1
Silver:				
Single potential	0.04	0.18	0.28	0.31
Discharge potential of H	.59	.56	.62	.55
Difference	.55	.38	.34	.14
Copper:				
Single potential	.53	.67	.78	.82
Discharge potential of H	.67	.70	..	..
Difference	.14	.03	..	..
Brass:				
Single potential	.53	.67	.77	.80
Discharge potential of H	.55	.70	..	..
Difference	.02	.03	..	..
Iron:				
Single potential	—0.13	—0.10	—0.04	..
Discharge potential of H	.56	.59	.59	.64
Difference	.69	.69	.63	..

It is seen that the potentials of all the metals rise as the concentration of cyanide is increased, although with iron the change is so small as to be negligible in practical work. Allowing for the errors previously referred to, it appears that the discharge potential of hydrogen on the metals tested is independent of the strength of solution within the limits tested. The magnitude of the differences between the potential of the cathode metal and the discharge potential of hydrogen should be a measure of the difficulty of depositing this gas along with the metal in plating.

No values are given for the discharge potential of hydrogen on copper and brass in normal and half normal potassium cyanide, because gas was evolved on merely immersing these materials in the solutions; this would seem to show that the discharge potential of hydrogen is less than the potential of the metals in these solutions. The data of the table indicate that a very high current density would be required to deposit hydrogen from a silver-plating bath containing little free cyanide, that the current density required for this will become less as the amount of free cyanide is increased, and that in copper and brass baths gassing should occur at low current densities, even with the least amount of free cyanide that it is practicable to use.

Solutions of the double cyanides of the strength usually used for plating with silver and copper, but without free cyanide, were prepared by boiling an excess of the freshly precipitated metallic cyanide in a solution of potassium cyanide, and filtering. The potentials of silver and copper were measured, each in its own solution, without and with the addition of various amounts of free cyanide. The results appear in Table II.

TABLE II.

Potentials of Silver and Copper in their Double Cyanides.

Grams of Free Cyanide per Liter.	0	10	20	40	60
Silver in $KAg(CN)_2$.......	—0.62	—0.10	—0.06	—0.01	0.02
Copper in $KCu(CN)_2$......	—0.27	...	0.55	0.69	0.73

A larger amount of potassium cyanide appears to be necessary to produce the same elevation of potential in the presence of the double cyanide of the metal than in its absence; this indicates that the deposition of hydrogen from plating solutions will be less easy than was deduced from the measurements of Table I in potassium cyanide alone.

The above experiments were undertaken to furnish an explanation for the observed deposition of hydrogen from cyanide copper and brass baths, and its failure to appear in silver plating. The following conclusions may be drawn:

1. The great lowering of the current efficiency of copper and brass plating solutions caused by the addition of considerable amounts of sodium or potassium cyanide is due to elevation of the potential of the metal that is being deposited, until it equals, and finally exceeds, the discharge potential of hydrogen, so that this gas is deposited instead of metal, according to the long-known selective action at the cathode in electrodeposition.

2. The solvent action of cyanide on the deposit is comparatively unimportant.

3. The failure of the addition of free cyanide to the silver bath to produce the marked lowering of efficiency observed in copper and brass solutions, is due to the fact that the rise of potential of silver with increase of free cyanide is less marked than for copper and brass. Even 60 grams of free cyanide per liter leaves the potential of silver considerably below the discharge potential of hydrogen, instead of above this, as is the case for brass and copper.

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DISCUSSION.

F. C. **Frary**[1]: In regard to the potentials of silver in the double cyanides, at the San Francisco meeting of this Society, in 1915, Mr. Porter and I presented a paper[2] showing that the effect of free cyanide on the potential of silver was a function, not of the absolute quantity of free cyanide at all, but of the ratio of the free cyanide to the double cyanide. It seems to be, therefore, peculiarly unfortunate that on page 303 Dr. Watts did not specify the strength of the solution of double cyanide he used,

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[1] Research Chemist, Oldbury Electrochemical Co., Niagara Falls.

[2] Trans. Am. Electrochemical Society (1915), 28, 307.

as I am sure no one else would know what strength was used. I hope the information may be corrected in the discussion, and also if possible, that the vacant space in Table II, column 2, will be filled with the proper value, as that is the most interesting and important one of all, since it corresponds approximately with the free cyanide normally used in the plating bath, and it is in that part of the curve that the most rapid change of direction takes place, as is shown by both Dr. Watts' figures and our own.

With regard to the third conclusion, I would point out as a more apparent reason, from Dr. Watts' own figures, for the hydrogen being evolved in the copper bath and not in the silver bath, that in the silver bath you have 0.55 volt difference of potential between the metal and hydrogen, and in the copper bath only 0.14 volt. It is much easier to raise the cathode potential to 0.14 volt above the single potential of hydrogen than to raise it 0.55, and I suggest that this is more probably the principal factor in the case than the slightly different rate of increase of the copper potential with the addition of cyanide.

A. D. COWPERTHWAITE[3]: Is it not possible for the addition of cyanide to prevent the ionization of the double copper salt? That might explain the failure to deposit when the amount of free cyanide reached a certain point.

O. P. WATTS: I am not prepared to enter into a discussion of the ionization, but prefer to leave that to someone who is better acquainted with the ionization theory than I.

F. C. FRARY: As far as silver is concerned, the silver ion concentration calculated from our measurements in n/4 silver potassium cyanide solution is about 8×10^{-12}, while in the same solution containing also free cyanide to the extent of n/40, it is only 4×10^{-18}, or about one two-millionth as much as it was without free cyanide. Whether you believe the figures or not depends on how much trust you put in the formulae we have for the calculation of ionic concentration from electrode potentials.

O. P. WATTS: Since my remarks on page 303 had reference, as is perfectly clear, to all plating baths, Prof. Frary can hardly regard it as "peculiarly unfortunate" that the composition of

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[3] Chemical Engineer, The Edmunds & Jones Corp., Detroit.

these is omitted. The two solutions of Table II, page 307, contained, as made up initially, 46 grams of $KAg(CN)_2$ and 30.7 grams of $KCu(CN)_2$, respectively, per liter.

Perhaps the third conclusion will be less liable to be misunderstood if the following addition be made to it: If the potential of a metal is below the discharge potential of hydrogen upon it, as with silver, no hydrogen is electrolytically liberated, but if the potential of the metal exceeds the discharge potential of hydrogen upon it, as is the case with brass and copper in cyanide plating solutions containing the usual amount of free cyanide, hydrogen will be deposited.

A paper presented at the Thirty-fifth General Meeting of the American Electrochemical Society, in New York City, April 3, 1919, President Tone in the Chair.

24

REMARKABLE PITTING OF ELECTROPLATING[1]

By Oliver P. Watts.[2]

Abstract.

When making some lead platings, heavy pitting suddenly and irregularly appeared. After considerable study of the cause, it was finally found to be due to air dissolving in the electrolyte while it was resting over night and cooling, which was then expelled as minute air bubbles on the work when the bath was heated up by the passage of the current. The microscopic bubbles clinging to the work, which had been left immersed in the bath, started the pitting. [J. W. R.]

Although the conditions which led to the unusual pitting which is the subject of this brief paper are very seldom met with in plating, the possibility that others may encounter the same difficulty makes it seem desirable to describe the phenomenon, and to tell its cause.

The trouble occurred in giving steel articles a plating of lead 0.010 inch (0.25 mm.) thick from a solution of lead fluosilicate, and consisted in the lead coating being more or less completely perforated by hundreds of small holes, which, from their size, may best be called pin-holes, and which of course rendered the lead plating useless.

A peculiarity not shown in the accompanying picture is the tendency of the pits to appear first along a sharp edge, *e. g.*, where a line of slag had been removed by the pickling solution. The most surprising thing about this attack of pin-holes was its suddenness and severity. Plating had been going on for six weeks

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[1] Manuscript received February 3, 1919.

[2] Assistant Professor of Chemical Engineering, University of Wisconsin.

before the trouble developed, but at its first appearance a half day's output of the plating tanks was spoiled. The trouble then grew less, and soon ceased. Several days later it recurred, all plating from the three tanks being badly pitted. Plating was then stopped until the cause of trouble could be determined and a remedy found.

There was much mineral oil on the articles as received at the plating room, and some of this was found to be carried over from the electric cleaner employed to remove it into the acid pickle used to remove rust just previous to plating. The hydrogen set free from the acid broke this up into microscopic drops which were found floating on the surface of the pickle, through which the work must be withdrawn. Complete elimination of the oil, however, did not stop the pin-holes.

The observation that many of the holes extended only part way through the lead coating furnished the clue to the cause of the trouble, *viz.*, that the holes were due to the collection of bubbles of air which was being slowly expelled from the plating bath.

During the hot weather of July and August, when the temperature of the solution was 115 to 120° F. (44 to 47° C.) and the tanks were in use 24 hours a day, this trouble did not occur; but the coincidence of the cool nights of September with an insufficient supply of material to be plated, so that the tanks occasionally stood idle from 8 P. M. to 9 or 10 A. M., permitted the solution to cool from its working temperature to about 78° F. (25° C.); this cool solution then dissolved a considerable quantity of air. When the current of 900 amperes was turned on, four or five hours were required for the solution to regain its normal working temperature; during this time the dissolved air was slowly expelled and collected in minute bubbles, which clung to the articles that were being plated and so caused the pin-holes. A similar expulsion of dissolved air is seen when a tumbler of cold, aerated water is brought into a warm room; bubbles of air slowly gather on the sides of the tumbler. The large current used, the high resistivity of the solution in comparison with the copper sulphate bath, for example, the small surface exposed to the air (the tanks were 28 inches (70 cm.) deep and slightly less in width), and the heat insulation furnished by the 3-inch (7.5 cm.) plank of

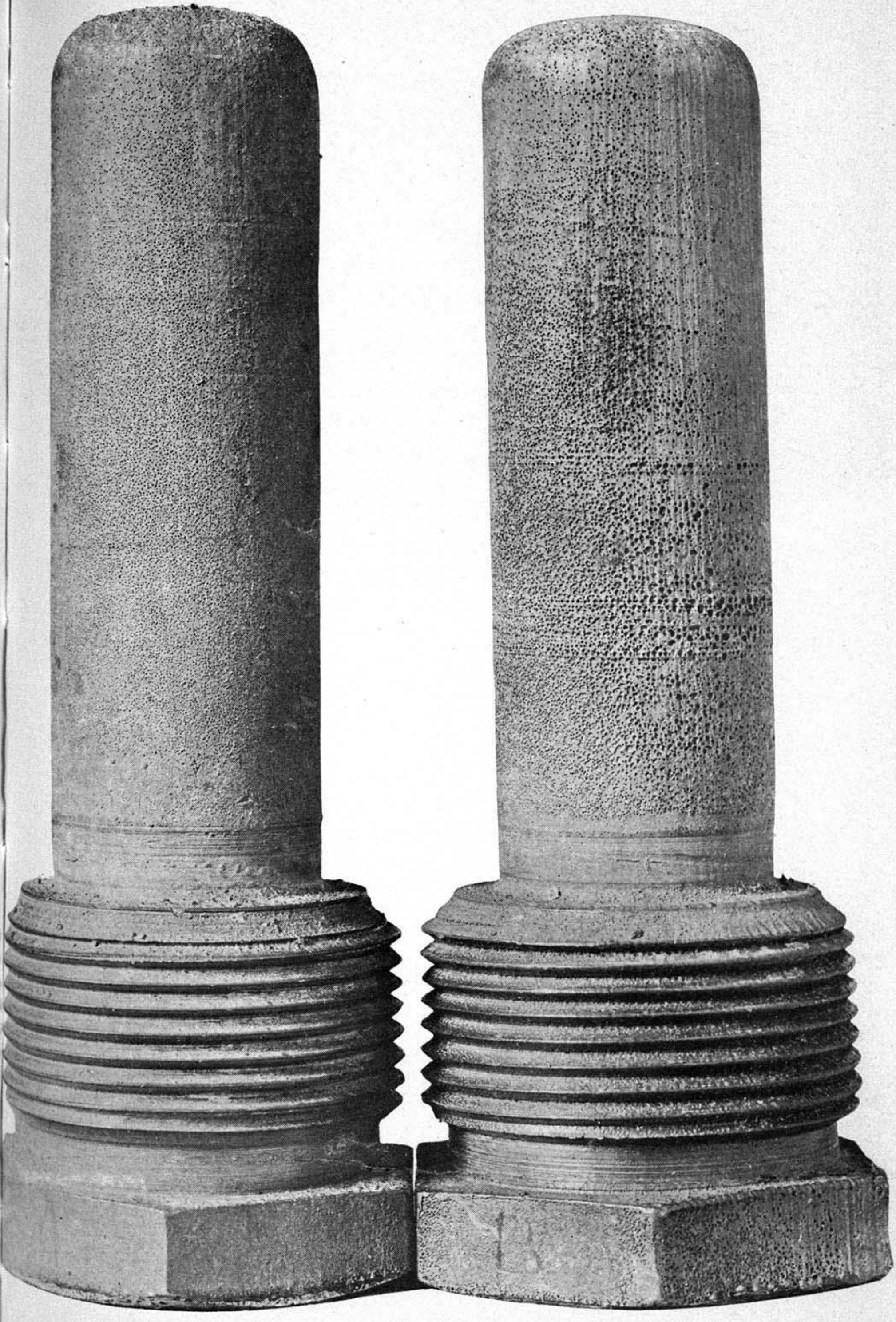

FIG. 1.

which the tanks were constructed, all contributed to the trouble since their combined effect was to make the operating temperature of the solution over 20° F. (11° C.) above that of the room. The three hours required for deposition gave ample time for bubbles of air to collect.

The difficulty was overcome by heating the solution to a little above its working temperature by means of a lead steam coil before resuming plating, whenever the tanks had been out of use for any considerable time.

Similar trouble by gas-pitting may be expected whenever a plating solution that is used for heavy deposits, and operates at an elevated temperature, stands idle and cold for many hours; but if there is a steady evolution of hydrogen from the cathode during normal operation of the bath, as with the cyanide copper or the brass solution, no trouble need be anticipated, for the stream of gas, ascending along the surface of the metal, will prevent bubbles from clinging long enough to form pits in the plating. Pitting may be expected only when the rate of evolution of gas from the work is extremely slow.

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DISCUSSION.

GEO. B. HOGABOOM[1]: Dr. Watts' paper opens up a discussion upon electroplating that I think is more broad than his paper would indicate. If you read any text book upon electroplating, one of the first postulates is to boil a new solution. In looking up some of the literature I find that Roseleur in 1852, was one of the first to recommend the boiling of solutions, as it would improve the deposit. It is quite evident that the boiling of the solution is to drive out whatever air there may have been in the water in mixing the solution.

Several years ago I was working on heavy silver deposits and after crystallizing out the carbonates by lowering the temperature of the solution they were filtered off. To each 100 gallons of

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[1] Electroplating Advisor, U. S. Bureau of Standards.

solution 20 gallons of very cold water directly from the faucet were added. I was required by the President of the Company to immediately place some work in that solution and run it. The deposits were run for twenty hours. Every piece that was put into the bath came out in exactly the same pitted condition as Dr. Watts' booster shell. That solution was then run with the porous cell for five hours and work put in it and the deposit became normal. The following day I tried it on another bath with some work and duplicated the condition and results, in fact, it was duplicated the day after. A year later it was tried again with the same pitting. It was evident that the pitting was due to the addition of cold water which had sufficient air in it to cause the pits.

A paper presented at the Thirty-fifth General Meeting of the American Electrochemical Society, in New York City, April 3, 1919, President Tone in the Chair.

ELECTRO-PLATING ON IRON FROM COPPER SULPHATE SOLUTION.[1]

By Oliver P. Watts.[2]

Abstract.

A discussion of getting good electro-platings of copper upon iron by preliminary dipping of the iron article in solutions of various metals which lie, electrochemically, between iron and copper. Arsenic, antimony, bismuth, lead and tin dipping solutions were tried, and arsenic, lead and antimony solutions found effective in securing a good subsequent electro-plating of copper. Even bismuth can be electro-deposited on iron by using a preliminary arsenic or antimony dip. Nickel can be deposited on aluminum by using a ferric chloride dipping solution; the author was not able to improve on this. [J. W. R.]

For electro-plating on iron or steel from a copper sulphate solution, platers have in the past found it necessary either to give the metal a preliminary coat of nickel or to plate it with copper from a cyanide solution before transferring the object to the copper sulphate plating bath. Since the sulphate solution is much more satisfactory than the cyanide for the production of heavy deposits of copper, where these are required the plater has been compelled to maintain two different plating solutions, and to perform two distinct plating operations. The desirability of being able to plate directly on steel in the copper sulphate solution is apparent, and many persons have tried to discover a method of doing so, but until recently in vain.

The difficulty which proved insuperable in the many years that copper plating on iron has been practiced is the attacking of the

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[1] Manuscript received February 3, 1919.

[2] Associate Professor of Chemical Engineering, University of Wisconsin.

steel by the electrolyte, and the deposition of copper "by immersion." When a strip of zinc or iron is dipped into a solution of copper sulphate, metal dissolves and a chemically equivalent amount of copper is deposited from the solution. This action is in its nature the same as the dissolving of a metal by sulphuric acid, differing only in that copper is plated out of solution instead of hydrogen. The trouble in plating upon a metal which receives such a deposit by immersion is two-fold: when reaction between the metal and the solution is rapid the character of the deposit is the same as that obtained in extremely rapid deposition by the current, it is rough, powdery, and non-adherent; and since the driving force which causes the metal to be deposited is the going into solution of an equivalent amount of metal from the object which is being plated, there is a continual undermining of the foundation upon which the deposited metal rests, so that the plating blisters or becomes entirely detached after a short period of service. The remedy which naturally suggests itself is to use a large current at the outset, and cover the object with an electrolytic deposit so quickly that there will not be time for the corrosive action of the electrolyte to do serious damage. This method is successful when the rate of attack by the electrolyte is slow, *i. e.*, when the E.M.F. between the object and the metal constituting the deposit is small, but when this E.M.F. is great, even starting in, or "striking," at a high current density fails to overcome the trouble. It is for these reasons that platers have found it impossible to secure from neutral or acid solutions of their common salts an adherent electro-plate of copper, silver, platinum, or gold on such electro-positive metals as magnesium, zinc, or iron.

At the annual convention of the American Electro-platers' Society held at Detroit in July of last year, a paper was presented by John Satka, of the Chicago Branch,[3] which gave a method of copper-plating on iron or steel from a copper sulphate solution without the usual preliminary plating in the copper cyanide or the nickel solution. The method consisted in immersing the cleaned steel in a solution of 8 ounces of arsenious oxide to a gallon of hydrochloric acid (60 g. per liter), rinsing, and plating in the copper sulphate bath at a current density of 10 to 15 am-

[3] August issue of Monthly Review of American Electroplaters' Society.

peres per square foot (1.10-1.65 A. per sq. dm.). Care should be taken that contact with the cathode rod is made as soon as the steel touches the solution. Since it is necessary that the arsenic dip shall reach every portion of the surface of the steel, the articles should be dipped in the solution several times to insure complete substitution of the rinse water by the arsenic dip. Under these conditions a bright copper coating is deposited, which will withstand polishing, scratch-brushing, and ball-burnishing. This method is already being used by a number of platers, and seems destined to wide usefulness.

In seeking a reason for the remarkable effect produced by immersion of iron in the arsenic solution, one naturally thinks of the prevention of the corrosion of iron by hydrochloric or sulphuric acid that is brought about by dissolving a little arsenic in the acid. Although a striking coincidence, this other effect of arsenic furnishes no key to the mystery under consideration. Arsenic prevents corrosion of iron by providing a cathode material on which the potential required for the evolution of hydrogen exceeds the potential of iron, so that iron is unable to displace hydrogen from the solution, and corrosion of the iron ceases;[4] but when plating on iron from copper sulphate solution the trouble heretofore experienced has been due to the displacement of copper, not hydrogen, and the ability of arsenic to prevent the displacement of hydrogen by iron seems to offer no explanation of the beneficial effect of its presence in this case.

During immersion in the arsenic dip used by Mr. Satka, a coating of arsenic, more or less perfect, must be deposited on the iron, and it is the presence of this coating of arsenic that makes it possible to secure an adherent deposit of copper. But how? Heretofore deposits produced by simple immersion have been regarded with suspicion by the plater; if thin, they do not protect the iron, but rather accelerate rusting, and if an attempt be made to secure a thick deposit by prolonged immersion of the iron, the entire deposit is liable to come off. Does this film of arsenic differ in some fundamental way from all other deposits produced by immersion, or can its beneficial effect in plating on iron with copper be brought about by other metals? Experiment alone can answer this question.

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[4] Trans. Am. Electrochemical Society (1912), **21**, 337; (1917), **32**, 257.

The only metals which give any promise of furnishing a substitute for arsenic are those which are below iron, and are above or but a trifle below copper in the electrochemical series. The other metal must be below iron in order to deposit on iron by immersion, and should be above copper or but little below it, else the remedy will prove worse than the disease which it is hoped to cure. According to Neumann, the common metals which lie within these limits are the following:

	Sulphate	Chloride
Iron	+0.093	+0.087
Nickel	—0.022	—0.020
Tin	....	—0.085
Lead	....	—0.095
Bismuth	....	—0.315
Antimony	....	—0.376
Copper	—0.515	....
Arsenic	....	—0.550

Measurements, by the writer, of the E.M.F. between copper and copper plated with arsenic, antimony, and bismuth, gave values of 0.034, 0.068, and 0.042 volts, respectively. All three metals were positive to copper, but only bismuth precipitated copper from the acid sulphate plating bath used in the experiments which follow. The failure of antimony to do so is probably due to the formation of an insoluble basic sulphate.

Of the metals in the list above, nickel lies too close to iron to yield a deposit by immersion, hence none of its salts were tried as dips for iron, but solutions of each of the others were used as preliminary dips before copper-plating.

It is of course essential that the coat of metal obtained by immersion shall be smooth and fairly adherent; much trouble was experienced in obtaining such a deposit with some of the above metals.

THE ARSENIC DIP.

In using the arsenic dip the concentration of arsenious oxide was varied from 10 to 60 grams per liter of hydrochloric acid, and the acid was also diluted with two volumes of water without detriment to the effectiveness of the dip. Good results in copper-plating were obtained with a variation of the time of immersion in the arsenic dip from 10 seconds to 6 minutes. Several specimens failed to take a perfect coat of arsenic, as was shown by removal of the copper plate from portions of the sheet by the scratch brush. The reason for these failures was not apparent, as the sheet iron had been put through the usual cleaning process, *viz.*, removal of mill scale by hydrochloric acid, rinsing, brushing with a brass scratch brush to brighten the surface, dipping for an instant in the pickling acid, rinsing, immersion in the arsenic dip, rinsing, and plating. Sulphuric acid was tried as a solvent for the arsenic instead of muriatic, with only slightly less satisfactory results.

THE LEAD DIP.

A lead dip was prepared by diluting 40 c.c. of the lead fluosilicate plating bath with 400 c.c. of water, adding 100 c.c. of fluosilicic acid, and a solution of 4 grams of gelatine. This acted slower than the arsenic dip, and required about 30 seconds' immersion to insure a good copper plate on iron. There were less failures from bad spots in the copper plating than with the arsenic dip. Solutions of lead nitrate acidified by nitric acid and of lead acetate made acid by acetic acid were also tried, but the copper plate could be rubbed off in every case in which these dips were used. Their failure as dips is probably due to the crystalline nature of the lead deposited from them.

THE ANTIMONY DIP.

In experimenting with antimony chloride a very concentrated solution of magnesium chloride, strongly acidified with hydrochloric acid, was used as a solvent, in order to lessen the amount of hydrochloric acid which would otherwise have been necessary to keep the antimony in solution and to prevent a black, spongy deposit of antimony on the iron. About 1 c.c. of formalin was added per 100 c.c. of solution, to diminish attack of the iron by the hydrochloric acid. In order to obtain uniformly good deposits of copper by the use of this dip it was found necessary to acidify the copper plating bath more strongly than when using the arsenic and lead dips.

THE BISMUTH DIP.

From solutions of bismuth chloride it proved very difficult to get a smooth, bright deposit on iron by immersion. In spite of the use of magnesium chloride and hydrochloric acid in the dip, a trace of water on the iron when immersed would cause a black smut to be deposited. By dipping the iron in concentrated hydrochloric acid just before immersing in the bismuth dip some fair-looking coats of bismuth were obtained, but except in the case of two narrow strips of iron, a good copper plating could not be obtained over the bismuth; the copper solution seemed to get through the bismuth coating and attack the iron, for the copper plate was easily rubbed off. Deposition of copper on bismuth by immersion was found to take place slowly, and to give a coating of copper which stood severe scratch-brushing.

THE TIN DIP.

An acidified solution of tin chloride seemed to give a good deposit of tin on iron by immersion, but it was impossible to obtain a good plate of copper after using the tin dip, although copper deposits on tin rather quickly by immersion. A good copper plate was obtained on a bar of tin. The reason for the failure of the tin dip is not clear.

THE COPPER DIP.

Success with the antimony, arsenic, and lead dips suggested an attempt to copper-plate iron by the use of a copper dip made up on similar lines, *i. e.*, a solution weak in copper and highly acidified. It was found that increase of acid in a dilute solution of copper sulphate slows down the rate of deposition by immersion on iron, and with a solution of copper sulphate in concentrated sulphuric acid the deposition of copper becomes very slow. All attempts to plate upon such deposits failed.

The finding of several other metals which may be substituted for arsenic as the basis of a dip for the plating of iron from a solution of copper sulphate, seems to indicate that the beneficial action of arsenic consists merely in its forming a coating over the iron which adheres fairly well, and protects the iron beneath for the brief time, 4 or 5 minutes, needed to give it a coat of copper by the current. To confirm this view it seemed desirable to try the arsenic dip as an aid to plating with some other metal than copper from a solution that does not give an adherent deposit on iron. For this purpose bismuth was selected as the substitute for copper.

PLATING ON IRON WITH BISMUTH BY AID OF THE ARSENIC DIP.

Fifty grams of bismuth oxide was dissolved in 100 c.c. of concentrated hydrochloric acid, to which 10 c.c. of formalin was added to minimize attack of the iron by the acid. When tested by plating on copper, a gray, adherent deposit was obtained. On iron the deposit by the current peeled in spots at the end of five minutes, and a scratch brush removed most of what remained. However, both the arsenic and antimony dips made it possible to get a good, adherent plate of bismuth on iron. Use of the lead dip resulted in the bismuth plate taking the form of a black smut. An attempt to plate on sheet lead with bismuth showed the failure of the lead dip to be due to attack of the lead by the plating bath, with deposition of the smut. Owing to the brittleness of bismuth, it cannot be recommended as suitable for general use in plating.

SILVER-PLATING BY AID OF THE DIPS.

Acid solutions of silver salts give a spongy deposit on iron by immersion, and plating from them is therefore a failure on iron. Tests of the above dips as aids to plating on iron from an acid solution of silver fluoborate resulted in non-adherent deposits in every case. This is not surprising in view of the distance that silver is below arsenic, antimony, and lead in the electrochemical series. On dipping these three metals in the silver-plating solution a black, spongy deposit instantly formed on each metal. This failure of the dips for silver-plating made their testing for plating with gold and platinum, metals of still lower potential, unnecessary.

THE ARSENIC DIP FOR COPPER-PLATING ON ALUMINUM.

One of the most successful methods of plating on aluminum, a problem that long baffled the plater, consists in dipping the cleaned aluminum for a half minute into dilute hydrochloric acid which contains 1 percent of ferric chloride, and then plating with nickel. The beneficial effect of this treatment is believed to lie in the deposition of iron by immersion, to which metal the nickel plate adheres well. If a perfect coating of arsenic, antimony, or lead could be given to aluminum by the dips previously employed, it should be possible to plate aluminum with copper instead of nickel, which, for obvious reasons, it is now necessary to use.

On immersing aluminum in the bismuth and tin dips, a black smut at once formed, so these were abandoned. Several samples of copper plate on aluminum were prepared by aid of the arsenic and lead dips; they stood polishing, but on cutting away the edges of the sheet and stripping off the copper plate, adhesion seemed slightly poorer where the sheet had been immersed in the dip than it was above this point. No beneficial effect was observed for any of the dips used.

In the experiments in copper-plating on iron, flat sheets, 2 by 6 inches (5 by 15 cm.) were employed; it is therefore impossible to draw conclusions regarding the effectiveness of the dips on the large and irregular material that frequently must be plated in commercial work. Objects with deep recesses, into which the copper sulphate solution will not "throw" well, may be expected to cause trouble in using the arsenic dip, and may prove impossible to plate by this means. Although adhesion was good enough to stand polishing, it is inferior to that of the ordinary electroplate, in the production of which deposition by immersion has played no part.

Some misanthrope, who would discourage human endeavor, once said "There is nothing new under the sun," and a study of the history of the most revolutionary discoveries in science seems to bear out this statement. In spite of the novelty of the arsenic dip, and the accomplishment by its use of that which had been regarded as impossible, the principle underlying its action has long been employed by platers in the "blue" or "quick" dip. This consists of a salt of mercury dissolved in potassium cyanide, into which articles of copper or brass are dipped before silver-plating. Its purpose and method of operation are exactly those already set forth in explanation of the arsenic dip; mercury is deposited on the other metal by immersion, and lowers the potential of the object to be plated so that corrosion by the electrolyte is diminished, and in consequence there is a slightly better adhesion of silver plate when the "quick" dip is used. Since the potentials of copper and brass in dilute cyanide solutions are not much greater than that of silver, the attack of these metals by the silver bath is not severe, and a very satisfactory silver plate can be secured on copper or brass without employing the "quick" dip.

The arsenic dip is merely the latest case in which the plater's old enemy, deposition by immersion, has been made an ally by the simple expedient of introducing an intermediate stage—the deposition by immersion of a metal that is only part way down to the potential of the metal with which it is desired to plate the electro-positive metal.

SUMMARY.

It has been discovered recently that by immersing iron for a few moments in an acidified solution of arsenious oxide, an adherent copper-plate may be deposited from an acid electrolyte, but no adequate explanation had been offered for this unique effect of arsenic. In this paper it has been shown that certain solutions of lead and antimony may be substituted for the arsenic dip, previous to direct-current plating of copper on iron from copper sulphate.

It appears to be impossible to obtain a perfect plate on iron from solutions of bismuth chloride by the usual methods of electro-plating; but use of the arsenic or antimony dip is attended with the same successes as in copper plating.

The successful substitution of solutions of antimony and lead for arsenic, and the application of these dips to plating on iron with bismuth, show that the beneficial effect of the arsenic dip is not due to a property peculiar to arsenic alone, but is the result of coating the iron with a metal whose potential in acid solutions is so near to that of copper that it is possible to deposit a good copper plate upon it, yet whose potential is not so far below iron that it will deposit on iron in a powdery, non-adherent form.

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University of Wisconsin.

DISCUSSION.

W. D. MAINWARING[1] (*Communicated*): One of the problems upon which I was consulted recently was the electrodeposition of nickel upon steel tools. The particular articles were surgical chisels for government uses.

Upon first being consulted, the question was asked, are you

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[1] Production Eng., Cleveland, Ohio.

giving the tools a preliminary copper plate, the answer returned was no. An investigation was next conducted to find out if possible what kind of surgical tools were double plated. I was greatly surprised to find that practically all such articles were nickel plated directly upon the instruments.

The tools themselves were next examined and it was found that the nickel plate was peeling from them in various manners, at the point, along the edges and down the sides. The next step considered was the reasons for the peeling of the nickel. Every factor was considered in the problem, the thickness of coating, on point and sides, the effect of honing the tool after plating was completed. This operation had to be done at this stage in order to have cutting edges in excellent shape. It was contended that no matter when the honing was done the nickel-plating should stick. During the examination of the tools, it was found that every tool on which the nickel plate was stripping had a film of dirt and oxide between the plate and surface of tool.

This report relating to the above caused more care to be taken in cleansing the tools, but still the thing kept occurring. It had been observed that the tanks were uncovered and anodes and surface of liquid were very dirty, this was also pointed out. Better results were finally obtained, but the percentage of waste remained extremely high.

Since working upon this problem, an effort has been made to arrive at an answer to the question, how did the dirt get between the nickel-plating and surface of the tool, the tools being perfectly clean when placed in the tank. It has been stated that the surface of tanks and anodes were extremely dirty. When the articles to be plated are placed in a tank and the current is turned on, an active decomposition of the water at once takes place, a flow of water to the surface of the tool immediately begins to make up for that decomposed, any dirt that would be on the surface of the tank would be drawn down and deposited with the nickel, just as long as the tools remained in the tank.

I might say that the particles that covered the surface of the tank were not all dirt; some of the particles were salts, nickel salts that had crystallized out; they were floating on the surface of the tank, and also the anodes. This was pointed out. In these tools after the tool was honed, just breaking the nickel, the entire nickel plate would strip off and you could see the flow of dirt from here down the tool, and it all settled in the point.

This discussion is written to emphasize the point that in any method of plating used, the fundamental principle of success is cleanliness, not only of tools but tanks; they should be thoroughly cleaned out at times and not allowed to become covered with dirt and dust.

It seems to me that all kinds of steel articles should receive a preliminary coating of copper before the nickel-plating is done. The process described by Mr. Watts seems to give an efficient method for doing this.

GEO. B. HOGABOOM[2]: In the gentleman's discussion, I think his argument in regard to the dirt on top of the solution going down into the solution and depositing on the work is equally applicable, whether the article was copper plated or not copper plated. And copper plating would not prevent the dirt from appearing.

The question of depositing nickel upon steel directly is influenced more by the amount of current that is used. You can get a current that would deposit hydrogen primarily, or you can get a current that would deposit hydrogen with the nickel. In the first place, you would have a distinct peeling; in the second place, you would have a peeling at the edges and pitting. It is not a question of cleanliness. If the solution had some crystals of nickel sulphate on the anodes it would show that there was something radically wrong with his nickel solution. If he was using a double sulphate solution he would not be able to use over 12 oz. per gallon (90 gm. per liter), and if the temperature of the room should decrease to 50° F. (10° C.), there would be crystallization of the salts, but, if a single sulphate solution was used, that would eliminate crystallization.

There should not be, nor is, any difficulty in depositing nickel directly upon steel. Shears are plated with nickel without previous copper plating. After they are plated, they are ground, that is, the nickel on the inside of the shear is ground off, and the edges are sharpened. The adherence of the nickel depends entirely upon the condition of the solution and the amount of

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[2] Electroplating Advisor, U. S. Bureau of Standards, Washington, D. C.

current used, and the same thing should be true for surgical instruments.

W. D. MAINWARING: During the working out of that problem we tried all the current densities, and also the question was taken up with certain physicians in Philadelphia as to the advisability of first plating the article with copper. We did not plate the tools with copper, but we finally succeeded in getting a coating of nickel to stick.

A. G. REEVE[3]: We plated our surgical instruments with nickel. The plating may perhaps have peeled from a few of them, but I think the plating held pretty well on nearly all, and we did not plate any of them with copper. We plate a great deal of our cutlery and deposit nickel on much of it, not on all; on some we deposit silver directly on the steel, and I heartily agree with what Mr. Hogaboom has said about causing the nickel to adhere directly to the steel. The idea of the dirt being drawn from the surface of the tank is a new one to me. In all my experience I never saw anything that gave me the idea that that could take place. Perhaps it does; but I have noticed this, in passing a well-cleaned steel article from a rinse-tank into a nickel-plating bath, if there is dirt or anything on the top of the bath, the film of liquid covering the articles to be plated will spread immediately when it strikes the surface of the bath, as the work enters, so that the dirt that was there in minute floating particles immediately spreads out, making a clean place through which the work passes and is clean after it gets into the bath. Of course, if the dirt, by some means or other, is drawn down on to the work after that, harm will be done, but, for myself, I never saw any work which I thought was caused to be defectively plated in that manner. We have found, however, that holding the work up and looking at it as it is coated with water and observing the water-break, as we call it, to see if the water will run off or stand on the article, in drops, is quite an inadequate test for determining the cleanliness of steel. Steel used in cutlery frequently has more or less numerous very minute pinholes which can only be observed with the aid of the microscope and are absolutely invisible to the naked eye, and these reach in to a sufficient depth

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[3] Res. Dept., Oneida Community Ltd., Kenwood, N. Y.

and seem to be capable of holding enough foreign materials, grease, buff dirt, pickling acid, or most anything of that kind, so that when you hold the article up to observe as to its cleanliness, you possibly do not get a water-break because the main surface is absolutely clean, and the water cannot break away from it, but sufficient foreign matter exudes from the pinholes to prevent deposition immediately adjacent thereto, and the imperfection is not bridged over, so that the water-break is very inadequate as a test for the degree of cleanliness required by our line of plating. Our experience has been that if we get the work properly and thoroughly cleaned, and, as we say, cleaned to a sufficient depth, nickel plating, if put on as Mr. Hogaboom says, with sufficiently low current density, will adhere with great tenacity and can not be pried off by mechanical means.

C. P. MADSEN[4]: I regard this paper as a very important contribution to the art of copper deposition on ferrous metals, I, however, question the suggested value of the process outlined in this paper as a means of copper plating iron before nickel plating. So long as metals are deposited in the porous condition shown by Dr. Watts' former paper entitled "The Protection of Iron by Electroplating," the advantage of first plating the iron with copper is questionable, especially for such articles as cooking vessels and surgical instruments, whether the copper deposit made by these new processes of treating the iron surface is more impervious than that made from a cyanide bath or not, because verdigris can still form through the porous nickel deposit.

I agree with Mr. Hogaboom that nickel can be deposited directly upon iron at least as adherently as copper, and that, therefore, an intermediary coating of copper is not necessary for this purpose.

The origin of the dirt which Mr. Reeves refers to may not be so mysterious when the character of commercial nickel anodes is understood. These anodes not only contain considerable iron but also many insoluble impurities. Under certain conditions a considerable quantity of nickel oxide in the form of a black insoluble powder is also formed. While normally this oxide and insoluble impurities should settle in the bottom of the bath it can under certain conditions be carried across the cathode, which may account for the dirty surface mentioned.

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[4] Consulting Engineer, New York City.

I may also add that I do not quite agree with Mr. Reeves that dirt in the bath is the only cause of pinholes. It is true, of course, that any kind of impurity in a deposition bath causes imperfections in the deposits, but I have also encountered pinholes in deposits made from chemically pure and clean baths and have, therefore, concluded that they may be an inherent result of certain factors of deposition.

WM. BLUM[5]: It is interesting to note that Dr. Watts (as well as Mr. Satka, the author of this method), was able to obtain good deposits of copper upon steel covered with a preliminary coating of arsenic, a metal usually placed below copper in the electrochemical series; but was unable to substitute for the arsenic certain of the metals which are intermediate between iron and copper. This behavior illustrates the fact, emphasized a few years ago in a paper by Dr. Frary, that the question as to whether and in what form a metal will deposit upon another metal by immersion, will depend upon the relative potentials between the two metals and the particular solution employed. This relation in turn will depend not so much upon the normal position of the elements in the electrochemical series, as upon the character, and especially the metal ion concentration of the solution.

J. W. RICHARDS[6]: In regard to the use of nickel plating on surgical instruments, it is interesting to note that one of our members, Mr. Haines, manufactures an alloy called stellite, which is a substitute for tool steel and makes an excellent material for surgical instruments. I understand that a large amount of his activities during the war has been in the manufacture of surgical instruments out of stellite, that being one metal that is not attacked by solutions.

GEO. B. HOGABOOM: Why would not chromium steel act as well? I have some knives on my table made of chromium steel which have been used five years, and you can cut any kind of fruit with them and leave the juice standing on them over night or any length of time, and they are absolutely free from stains.

J. W. RICHARDS: I think one question is that of resisting the antiseptic solutions which are used and may attack the chrome steel but are said not to attack the stellite.

[5] Chemist, Bureau of Standards, Washington, D. C.

[6] Prof. of Metallurgy, Lehigh University.

A paper presented at the Forty-second General Meeting of the American Electrochemical Society held in Montreal, September 21, 1922, President Schluederberg in the Chair.

26

ELECTROPLATED ZINC AND THE DIFFUSION OF ELECTRODEPOSITS INTO ZINC.[1]

By WALTER G. TRAUB[2]

ABSTRACT.

Experiments were made to determine the cause of the disappearance of certain metals that had been deposited on zinc. The results indicate that copper, brass, gold and silver are diffused into zinc; whereas nickel, which does not diffuse into zinc, can be used as a preventive against diffusion of other metals deposited over it. [A. D. S.]

Several instances have been reported where thin plates of metal deposited electrolytically on zinc have disappeared after a few months. This fact seems first to have been brought to the attention of C. F. Burgess, formerly head of the chemical engineering department of the University of Wisconsin. In attempting to gold-plate some articles made of aluminum, he first deposited a coating of zinc, and then covered this with a deposit of gold. After two or three months, the party for whom he did the plating called his attention to the fact that the gold had disappeared entirely.

About a year ago, the Apollo Metal Works of La Salle, Illinois, who electroplate sheet metals on a large scale, reported trouble from the disappearance of brass and copper plate that had been deposited on zinc.

The experiments which follow were undertaken to learn whether coatings of these particular metals are diffused into zinc, or merely fall off, and in case of diffusion, what other electrodeposited metals behave similarly.

To carry out these experiments, a large number of zinc strips

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[1] Manuscript received August 7, 1922.

[2] Senior in Chemical Engineering, University of Wisconsin.

TABLE I.

Electrodeposits on Zinc.

No.	Plate	Weight of Zn Strip Grams	Weight of Zn Strip + Deposit Grams	Weight of Zn Strip + Deposit After Heating Grams	Weight of Deposit Grams
1	Cu	21.4987	Deposits unsatisfactory		
2	Ni	21.0374			
3	Cu	21.0982			
4	Cu	21.5045			
5	Ni	20.2197			
6	Cu	20.2365			
7	Brass	20.3709	20.4414	20.4414	0.0705
8	Brass	19.3744	19.4100	19.4098	0.0356
9	Brass	21.3318	21.3781	21.3781	0.0463
10	Brass	20.5427	20.5525	20.5524	0.0098
11	Cu	20.7171	20.7733	20.7730	0.0562
12	Cu	20.7626	20.9370	20.9370	0.1744
13	Ni	20.6561	20.7219	20.7219	0.0658
14	Cu	19.3450	19.4963	19.4963	0.1513
15	Cu	18.7269	18.8067	18.8064	0.0798
16	Ni	19.7058	19.9800	19.9800	0.2742
17	Ni	20.3665	20.6320	20.6320	0.2655
18	Cu	18.8304	18.9809	18.9809	0.1505
19	Cu	19.0864	19.0880	19.0877	0.0016
20	Cu	18.9690	18.9734	18.9734	0.0044
21	Cu	19.0140	19.0290	19.0290	0.0150
22	Cu	19.6371	19.6424	19.6423	0.0053
23	Cu	19.6100	19.6694	19.6694	0.0594
24	Cu	18.3009	18.3111	18.3108	0.0102
25	Brass	20.4950	20.5138	20.5136	0.0188
26	Brass	20.4380	20.4426	20.4424	0.0046
27	Brass	19.3645	19.3667	19.3666	0.0022
28	Brass	19.7490	19.7497	19.7496	0.0007
29	Brass	20.2290	20.2297	20.2297	0.0007
30	Au	9.8780	9.8975	9.8972	0.0195
31	Au	10.2237	10.2300	10.2298	0.0063
32	Au	10.1100	10.1132	10.1129	0.0032
33	Au	9.9000	9.9055	9.9055	0.0055
34	Ag	9.5677	Deposits unsatisfactory		
35	Ag	10.5875			
36	Cu+Ag	10.4766	10.5500	10.5492	0.0734
37	Ag	11.1725	Deposits unsatisfactory		
38	Ag	9.2498			
39	Ag	8.8972			
40	Ni+Au	9.5600	Good results.		
41	Ag	10.5600	10.5865	10.5865	0.0265
42	Ag	10.0919	10.1199	10.1199	0.0280
43	Ag	9.3700	9.4093	9.4093	0.0393

Specimens 34, 35, 37, 38, 39—very small amount of copper plus silver plate.

were cleaned in the electrolytic cleaner, dried, and weighed. These strips were then plated with different metals and alloys, such as copper, brass, nickel, gold and silver. Preliminary experiments had previously shown that these metals disappeared when plated on zinc in thin layers. The strips were then reweighed to obtain the actual amount of metal or alloy deposited. Because of limited time for observation, they were placed in an electric heater at a temperature of 60° to 80° C. for a period of two weeks.

At the end of that time, the specimens were taken out and examined. They were found to be discolored due to a thin film of oxide, which had formed on the surface. This was removed by immersion in the electrolytic cleaner. Most of the specimens then appeared like ordinary zinc strips. They were polished slightly, but the surface did not change in appearance to any appreciable extent. The deposited metals were only slightly absorbed around the edges of the strips where the deposit was thicker due to the higher current density.

The specimens were then weighed for a third time. It was found that the weight of each strip was practically the same as at the time of the second weighing just after the metal had been deposited. All specimens had been thoroughly washed and dried in all the operations to obviate any unnecessary error. Some specimens had not changed at all in weight, others had lost a few tenths of a milligram, perhaps due to the removal of the dark film spoken of above.

Specimen No. 36 was plated first with copper and then with silver. Both coatings disappeared. Specimen No. 40 was plated first with nickel and then with gold, so that a portion of the gold plate was deposited directly on the zinc. The specimen was then given the same treatment as that described above. Upon final examination it was found that the zinc had absorbed the gold in places where the gold had been deposited directly on the zinc. In places where there was a nickel layer between the gold and the zinc no change took place. Similar results were obtained with the nickel-plated zinc specimens; there was no disappearance of the deposited metal.

When plating zinc with silver, it was found necessary to use the standard silver "striking solution." This was done by first cleaning the specimen, then making it the cathode in a cell containing the "striking solution." The anode was silver. The specimen was plunged into the electrolyte for just a brief instant. It was then washed and placed in the usual cyanide bath for silver deposition. A beautiful deposit of silver was obtained which was permanent and did not come off by rubbing or by wear, but was absorbed on heating.

TABLE II.

Appearance of Specimens.

No.	Plate	Dimensions Cm.	Before Cleaning (Oxide)	After Cleaning
8	Brass...	10.3 x 4	dark gray	gray
10	Brass...	10.9 x 4	dark gray	gray
11	Cu......	11.1 x 4	grayish brown, edges brown	grayish brown mottled
12	Cu......	10.3 x 4	same as No. 11	gray, brown edges
13	Ni......	9.7 x 4	not affected	not affected
14	Cu......	9.9 x 4	gray, reddish brown edges	gray and brown, mottled
15	Cu......	10.1 x 4	same as No. 14	same as No. 14
16	Ni......	9.8 x 4	not affected	not affected
17	Ni......	9.7 x 4	not affected	not affected
18	Cu......	10.4 x 4	brownish	gray and brown
19	Cu......	10.3 x 4	gray, brown edges	gray
20	Cu......	10.3 x 4	same as No. 19	gray
21	Cu......	10.3 x 4	gray, purple edges	gray
22	Cu......	10.2 x 4	same as No. 21	gray
23	Cu......	10.5 x 4	brown and purple	gray, brown edges
24	Cu......	10.4 x 4	gray, purple edges	same as No. 23
25	Brass...	11.9 x 4	brown, reddish	gray
26	Brass...	11.6 x 4	same as No. 25	gray
27	Brass...	11.7 x 4	gray, brown edges	gray
28	Brass...	11.6 x 4	yellowish gray	gray
29	Brass...	11.8 x 4	yellowish gray	gray
30	Au......	11.5 x 4	gray	gray
31	Au......	5.2 x 2	very dark gray	gray, silvery
32	Au......	5.9 x 2	grayish black	gray
33	Au......	5.9 x 2	grayish black	gray
36	Cu+Ag.	11.6 x 2	gray	gray
41	Ag......	11.3 x 2	gray	gray
42	Ag......	12.0 x 2	gray	gray
43	Ag......	10.8 x 2	gray	gray
40	Ni+Au.	....	....	gray where Au directly on Zn; with layer of Ni between, no change

The nickel plates were deposited from a solution designed especially for the direct nickeling of zinc. The solution contained sodium citrate. The gold, silver, brass, and copper were, of course, deposited from cyanide solutions.

These experiments show conclusively that thin plates of copper, brass, gold, and silver are diffused into zinc. Nickel is not diffused into zinc, and it can act as a preventive against diffusion of other metals deposited over it.

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DISCUSSION.

H. M. WILLIAMS[1]: I noticed this same phenomenon about two years ago. There was a name plate manufacturer who had substituted zinc sheet for brass on account of the difference in price. The zinc was plated with brass and copper for the various color effects. The plated sheets were placed in storage and in less than six months the plate had entirely disappeared. It would have been well if this investigation had been followed up with some micrographs. Probably that would have proven the theory advanced in the paper.

WM. BLUM[2]: Two or three years ago we had an inquiry from a manufacturer who had used brass plated zinc for electric light fixtures. With the unfavorable conditions caused by the elevated temperature on certain parts of the fixtures, absorption of the brass took place in a very short time.

The question is often asked, "Is the adhesion of an electrodeposit to the base metal due to alloying?" It seems at least possible that if this alloying does take place slowly between certain metals, there may be incipient alloying as soon as the one metal is deposited on the other.

R. J. MCKAY[3]: I believe you will find that this difference is a difference in rate, rather than an absolute difference, in the case of nickel, in view of a similar occurrence in the metallurgy of

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[2] Chemist, Bureau of Standards, Washington, D. C.
[3] International Nickel Co., New York City.

nickel. In electrodeposition, if the current is shut off, the cathodes will take on a rosy color, due to the cementation of a slight amount of copper out of the solution. If these cathodes are then raised out of the solution and stored for a few months, the rosy color has entirely disappeared, probably due to the diffusion of the copper into the nickel; but this rate is very slow, and if the deposit is thick the color remains.

A deposit of copper on nickel will diffuse very rapidly at temperatures of cherry red and low red heat.

A. G. REEVE[4]: It might be interesting to say in this connection that we noticed quite a number of years ago in the case of certain ornamental objects stamped out of pure block tin plated with gold, upon these objects subsequently lying around, the plating was not worn off, but in the course of a year or two it completely disappeared. We assumed that the gold was absorbed in some way.

MEMBER: Regarding the junction of the tin and iron, if the tin is put on by the standard hot process there is considerable alloying. In our tinning work, we find that when the tin left in the iron amounts to about 0.3 percent, so-called "flowers" appear; that is, the tin that is left on is alloyed with the iron and forms figures in the form of flowers.

We have carried out some experiments in putting tin on iron electrolytically, and upon taking the tin off, the flowers do not appear. Of course the electrolytic deposit is put on only a short time before being removed, so that in time there may be an alloying feature. In that case, however, the tin apparently does not alloy appreciably with the iron electrolytically, while it does when deposited hot.

W. H. FINKELDEY[5] (*Communicated*): Mr. Traub's interesting paper recalls several similar experiments which were made in our laboratory a few years ago. We became interested in the absorption of zinc base electrodeposited metallic coatings during the course of an investigation to determine the reasons for the disappearance of plated coatings on spun and drawn zinc articles. Our experiments were confined entirely to electrodeposits of copper, inas-

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[5] Research Division, New Jersey Zinc Co., Palmerton, Pa.

much as it is a rather general practice in the plating industry to coat or flash zinc articles with copper previous to plating with other metals. We were interested in determining whether there was an absorption of the copper plate and, if it did take place, its approximate rate. There was considerable doubt in the minds of several manufacturers who were plating zinc articles, whether the possible absorption of the copper flashing might not materially influence the adhesion of subsequent electrodeposited coatings. In some cases they considered it to be the cause of serious peeling and blistering.

Briefly, our experiments consisted of electroplating specimens of strip zinc with three thicknesses of copper plating, exposing the same to temperatures ranging from 60° to 400° C. and noting the time required to produce total absorption of the copper plating. The thickness of the copper plate coatings are given in Table I.

TABLE I

Specimen No.	Weight of Copper g./sq. cm.	Thickness of Copper Plate in cm.
1	0.00026	0.000029
2	0.00030	0.000034
3	0.0037	0.0038

The results of our experiments are given in Table II.

TABLE II

Specimen No.	Thickness of Copper Plate in Cm.	Length of time after which absorption was complete at									
		400°C Min.	350°C Min.	300°C Min.	250°C Min.	200°C Min.	150°C Min.	125°C Min.	100°C Hr.	75°C Days	60°C
1	0.000029	1	1	2	2	5	15	40	4	2	(*b*)
2	0.000034	1	1	2	3	7½	25	90	5	2	. . .
3	0.0038	3	5	15	25	140	7 Ds.	. .	(*a*)	. . .	. . .

(*a*) Not after one month. (*b*) Not after one week.

Our experiments with copper plating confirm those of Mr. Traub, and we agree with the conclusions which he has drawn. However, there is one point which we wish to bring out. In the case of a copper plate, the rate of absorption is dependent to no little extent upon the thickness of the copper plate, since the diffusion rate will be materially lowered as the surface of the zinc metal under the coating becomes richer in the constituent which is being absorbed. Thus we noted from our experiments that our heaviest plated coatings were not absorbed after heating at 100° C. for over one month. As would be expected, the rate of absorption is greatly influenced by the temperature. At a higher temperature, absorption of the thinner coatings was completed in some instances within a few minutes.

From our examinations of actual plated articles which had previously been flashed with a coating of copper, we could find no indication that peeling was due to any absorption of the underlying copper plate. In many instances, where the plated coating could be peeled off, the underlying copper flashing was found to have peeled from the zinc base and to be tightly adherent to the outer coating.

It is apparent, also, that trouble resulting from diffusion of plated coatings can be overcome to a considerable extent by increasing the thickness of the copper flashing which is usually deposited preparatory to the finished plating.

The writer has recently examined microscopically a number of nickel plated zinc sheets of German origin, which were several years old, in which the "flash" coat of copper is still clearly visible. This material carried a copper coating of 0.024 g./sq. dm. over which had been deposited a nickel coating of 0.204 g./sq. dm.

A paper to be presented at the Forty-eighth General Meeting of the American Electrochemical Society, to be held in Chattanooga, Tenn., September 24, 25 and 26, 1925.

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EFFECTS OF NITRATES ON CURRENT EFFICIENCY OF PLATING SOLUTIONS.[1]

By P. A. NICHOL[2] and O. P. WATTS.[3]

ABSTRACT.

Upon the addition of 40 g. per liter of sodium nitrate to a nickel-sulfate plating bath no nickel deposit was obtained. Solutions of the nitrates of Zn, Cd, Co, Ni and Fe were tried, but no satisfactory results obtained. On the other hand Pb and Cu nitrate baths gave cathode efficiencies of 97 and 99 per cent respectively. An appreciable drop in current efficiency was obtained upon the addition of $NaNO_3$ to silver cyanide baths. In general, nitrates are to be avoided in plating baths. [C. G. F.]

The brittleness of nickel deposits is usually ascribed to absorption of hydrogen. Noting the failure of hydrogen to appear on an iron cathode in a solution of sodium nitrate, contrary to the behavior of sodium salts in general, led one of the authors to think that the addition of sodium nitrate to nickel plating solutions might perhaps prevent the absorption of hydrogen by the deposit, and so overcome one of the troubles with nickel plating.

A trial of this anticipated remedy had the entirely unexpected effect of practically preventing the deposition of nickel. Tests on the same nickel solution before and after adding 40 grams of sodium nitrate per liter gave efficiencies of 93 and 0.5 per cent respectively. It is apparent that when there is a choice offered between deposition of nickel and reduction of a nitrate, there is a decided preference for the latter action, and that at ordinary current densities practically all the current will be utilized in reduction with a cathode of copper or nickel.

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[1] Manuscript received June 15, 1925.

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There is a conspicuous absence of nitrates from the myriad of formulas that have been given for nickel-plating solutions, supposed to be because of the tendency of nitrates to induce passivity of the anodes, with consequent production of acidity in the bath. It is now apparent that there is another reason for the avoidance of any considerable quantity of nitrate in nickel solutions. One of the few exceptions to this embargo against nitrates in nickel solutions is Brucker's solution[4] consisting of 100 parts of a saturated solution of nickel in nitric acid and 3 parts cream of tartar. In the light of our experiment Brucker's solution appears to be valueless.

Although silver nitrate is almost universally used in the preparation of silver-plating solutions, the standard books on plating all direct that the silver be precipitated, usually as cyanide, chloride or carbonate, and that all nitrate be washed out before redissolving in sodium cyanide. Since silver nitrate is used with good current efficiency in the electrolytic refining of silver, the reason for this studied avoidance of nitrates in the cyanide silver solution is not apparent.

To get some first-hand information on the effect of nitrate in the deposition of metals commonly used in electroplating, efficiency tests were made in nitrate solutions of several metals, both with and without the addition of sodium nitrate.

EXPERIMENTS WITH METAL NITRATE SOLUTIONS.

Normal solutions of the nitrates of zinc, cadmium, cobalt and nickel were electrolyzed at a current density of 0.6 amp. per sq. dm. The trifling deposit obtained was loose, and non-metallic in appearance, apparently consisting of oxide or hydroxide. The addition of 30 grams of sodium nitrate per liter made no difference in the results. The addition of the same quantity of sodium nitrate to a normal solution of ferrous ammonium sulfate, which by itself gives an excellent deposit of iron at about 100 per cent efficiency, caused the deposit to become loose and non-metallic looking, the same as with the four metals above mentioned.

Normal solutions of lead and copper nitrates at 0.6 amp. per sq. dm. gave efficiencies of 97 and 99 per cent respectively, and

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[4] U. S. Patent 242,263, May 31, 1881.

these were unchanged by the addition of 30 grams per liter of sodium nitrate.

Two equal quantities of an old cyanide silver-plating solution were taken, and 75 grams per liter of sodium nitrate added to one lot. At a current density of 0.25 amp. per sq. dm. the efficiencies were 91.5 and 84.2 per cent.

A cyanide-copper solution that showed a current efficiency of 37.6 per cent at a current density of 0.6 amp. gave 34.15 per cent when 80 grams per liter of sodium nitrate had been added. The same solutions at 0.3 amp. per sq. dm. gave efficiencies of 42.9 and 36.9 per cent. At the higher current density the effect of the nitrate is smaller, as would be expected; but at 0.077 amp. per sq. dm. the efficiencies were 73.5 and 69.0 per cent. The lessened effect of nitrate on current efficiency at this still lower current density is possibly connected with the different nature of the two deposits, that from the solution containing nitrate being dull and brownish, while the other was smooth and had the appearance of bright copper.

CONCLUSIONS.

The plater's avoidance of nitrates in the majority of plating solutions is thus seen to be well-founded, and even in the cyanide silver and copper solutions, where the falling off in efficiency does not look serious, it would mean an increase in current of 250 to 300 amperes to secure the present daily output of some of the larger plating establishments. It is also possible that the formation of nitrites and other reduction products may, in continued use, have some injurious effect not encountered in electrolysis for an hour only.

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Written discussion, preferably typewritten and in triplicate, of this paper is invited and should be sent to the American Electrochemical Society, Columbia University, New York City.

A paper presented at the Keokuk session of the Fifty-second General Meeting of the American Electrochemical Society, on its Northwestern Trip, Sept. 4-21, 1927, Dr. A. W. Burwell in the Chair.

28

ANODES FOR CHROMIUM PLATING.[1]

By Oliver P. Watts.[2]

Abstract.

Various materials including chromium, lead, iron, nickel, ferrosilicon, and certain other ferrous alloys were tried out in a chromic acid plating bath. It was found that lead anodes are most serviceable for long continued operation of the bath.

[C. G. F.]

For electroplating with chromium several different materials have been recommended for use as anodes. In his epochal experiments G. K. Sargent[3] used and recommended lead anodes; K. W. Schwartz[4] says, "Chromium anodes are cheaper than platinum and better than lead"; C. H. Proctor[5] says that lead, sheet steel or chrome steel may be used as anodes, and recommends the last. It has been reported that at least one plater has used the steel tank containing the solution as anode, and that there is no noticeable corrosion of the tank or other bad result after a year's use. Tests of the effect of these anode materials and of several others upon the solution and upon the deposit are presented. The anodes used were chromium, lead, iron and steel, nickel and iron silicon, iron-chromium, nickel-chromium, nickel-silicon and nickel-chromium-silicon alloys.

THE REQUIREMENTS FOR AN ANODE.

It is customary in electroplating to make up a solution of such materials and concentration as experience has shown to be best

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[1] Manuscript received July 11, 1927.

[2] Assoc. Prof Chem. Eng., Univ. of Wisconsin, Madison, Wis.

[3] Trans. Am. Electrochem. Soc., 37, 485 (1920).

[4] Trans. Am. Electrochem. Soc., 44, 462 (1923).

[5] Mo. Rev., May, 1927, p. 11.

suited for the particular temperature and current density at which it is desired to operate, and then to maintain the initial conditions by the use of soluble anodes, with such an amount of exposed surface as will cause metal to dissolve at the same rate as it is deposited. One exception to this practice is in platinum plating, where the insolubility of a platinum anode in all solutions yet found, from which a good deposit of platinum can be obtained, has made it necessary to replace the metal deposited by the addition of platinum salts.

At the time of its introduction one of the features of the Udylite process for plating with cadmium was the use of a carbon anode; but this has since been abandoned and the metal is now supplied from anodes of cadmium. Because of the impossibility of buying rods or sheets of chromium, the earlier chromium plating was all done by the use of insoluble anodes, and it was not until 1923 that Schwartz tried and advocated chromium anodes. While general plating practice is practically unanimous in favor of soluble anodes, the situation in chromium plating is so peculiar that the use of chromium or insoluble anodes must be decided on their individual merits.

The solution used in these tests contained 250 grams of chromic acid and 4 grams of chromic sulfate per liter. Each anode was placed in 150 cc. of solution, and the several cells electrolyzed in series 24 hours a day without interruption, except for weighing anodes and introducing new cathodes. Every two or three days a half-hour efficiency test on a steel cathode was made at a constant current, which was read by an ammeter. The average current density was about 13 amp./sq. dm. (121 amp./sq. ft.) The temperature was 32 to 35° C., except in those cases where the resistance increased abnormally with use, when tempratures of 43 to 45° C. were reached.

In computing the efficiency of anodes containing chromium, this is considered to dissolve as trivalent chromium, hence to find the rate at which chromium is accumulating in the solution grams-per-ampere-hour should be considered rather than the relation between anode and cathode efficiencies. Ferro-chromium and stainless steel corroded uniformly, and efficiencies are based on solution of the metals in the proportions in which they exist in the alloys.

CHROMIUM.

A bar cast from commercial chromium made by aluminothermic reduction was used as anode for 131 hours (157 ampere hours) at various current densities without visible evolution of gas at any time. Based on trivalent chromium the efficiency of corrosion was 57.3 per cent and the average rate of corrosion was 0.371 gram per ampere hour. At all times after the start the efficiency of deposition was less than when a lead anode was used, and fell from 9.2 per cent at the end of 48 hours to 2 per cent at the end of 131 hours. During the test 4.1 grams of chromium was deposited and 58.2 grams dissolved.

Assuming no loss of chromium by spray and solution adhering to the electrodes, which is not true, the result of plating for 131 hours (157 ampere hours) would be to increase the metallic chromium in this 150 cc. of solution from 19.5 grams to 73.6 grams, or 377 per cent of the initial quantity. The viscosity of the solution was enormously increased, and also its electrical resistance, though to a less degree. Deposits were at first bright; later ones were white but matte, and toward the end were gray and rough.

On account of the great difference between the rates of solution and deposition, the chromium anode is not suited to long-continued use in chromic acid plating solutions. It is also a much more expensive way of maintaining the chromium content than the addition of chromic acid.

LEAD.

The lead anode was per-oxidized in dilute sulfuric acid to minimize the formation of lead chromate outside the vessel by the spray thrown up. Distilled water was added to make up for evaporation and loss by spray, and spraying was lessened by covering all vessels by pieces of watch glass. The solution which originally contained 19.5 grams of chromium was electrolyzed for 342 hours (410 ampere hours), when 15 grams (77 per cent of the metal originally in solution) had been deposited. From an initial value of 3.8 per cent the cathode efficiency had risen to 13 per cent in 24 hours, and at the end of five days attained a maximum of 22 per cent.

At the close of the test the cathode efficiency was 12.3 per cent. The deposits were excellent. After 277 hours (333 ampere hours) two 30-hour deposits were fringed with fine trees along the edges, indicating that the chromium content was becoming too low for the current density used, but half-hour deposits were still bright and free from trees.

If the loss of metal by spray and by solution carried out on articles plated were no greater in commercial plating than in these experiments, to exhaust a 100-gallon (378 liters) solution to the same degree would require the plating of 1867 radiator shells at 1,000 amperes for half-hour deposits, or 5,600 shells for 10-minute deposits. A well-known authority on plating has estimated that the two sources of loss mentioned above may account for half the chromium in the solution in some cases of commercial plating. Even with this extremely high loss of metal, half the plating mentioned above could be done without replenishing the solution. The use of a more dilute solution, which these experiments seem to show to be feasible, would diminish both losses.

At the end of the test 100 grams per liter of chromic acid was added to the exhausted solution. This increased the brightness of the deposit, and increased the efficiency of deposition from 12.3 to 13.8 per cent. It is, of course, not advisable to allow a chromium plating solution to become so depleted in metal as in this experiment, which was for the purpose of finding the effect of depletion.

IRON.

The well-known passivity of iron and steel in bichromate solutions would lead one to expect little or no corrosion of these materials as anode in the Sargent chromium solution. Both steel and Armco iron became covered with a dark brown coating, presumably manganese dioxide from the manganese which they contain, and were very slowly corroded. The efficiency of corrosion diminished with time, dropping from a maximum of 2.4 per cent at the beginning to 0.3 per cent at the end. A run of 410 ampere hours dissolved 3.45 grams of steel, 0.0084 gram per ampere hour, at a current density of 18 amperes per square decimeter, an average efficiency of 0.80 per cent.

The first difference noted in the deposits from the solutions with lead and iron anodes was in their brightness. A small quantity of iron acts as a "brightener," but also gives the deposit a darker tone. This observation has been verified by adding iron as phosphate and as ferrous sulfate to the chromium solution. The accumulation of a larger amount of iron in the solution causes a diminution of cathode efficiency, 246 ampere hours depositing 8.8 grams of chromium from solution with a lead anode, but only 6.1 grams when an iron anode was used. In 342 hours electrolysis of two cells in series 15 grams (0.0317 gram per ampere hour) of chromium were deposited by use of a lead anode, but only 9.23 grams of metal (0.0225 gram per ampere hour) when the anode was iron.

Other unfavorable effects of the iron anode were the covering of the deposit with a brownish film that was difficult to remove, a decidedly greater tendency to "treeing" on the edges of the cathode, and after a number of days, a marked increase in resistance. After 204 hours electrolysis (246 ampere hours) and at a temperature of 40 to 45° C. instead of 32 to 35° for the solution with a lead anode, the resistance of the solution in which the iron anode was used was 2.05 times that with the lead anode. All these effects are detrimental, and on their face would indicate that iron or steel anodes should not be used continuously in chromium plating.

Two operators of commercial chromium plating solutions, however, have reported the use of steel anodes for a year or more without encountering the objectionable features above noted. The only explanation that the writer can offer for these different results is that the amount of solution lost from the commercial baths through spray and "drag out" on the work is sufficient to keep the iron from attaining a harmful concentration. The tendency is as shown by these experiments.

HIGH-SILICON IRON.

Since high-silicon iron is noted for its resistance to attack by acids, it was thought that this might prove more insoluble as anode than steel. An alloy of Armco iron and 16 per cent commercial silicon was cast and used at 5 amperes per square decimeter. A loss of 3.14 grams resulted from the passage of 232 ampere hours, equal to 0.0135 gram per ampere hour. The addition of silicon has increased corrosion. The surface of the anode had a beautiful satiny luster, without the formation of the film observed with iron or steel anodes. There was no diminution in the rate of corrosion with time.

All deposits were white and free from the brownish film or stain encountered when iron anodes had been used for a long time. This may, however, be due to lack of sufficient use instead of any specific virtue of iron-silicon alloys as anodes, for this experiment ended at the point where use of iron anodes only began to cause the film on cathodes. A more extended use of iron-silicon anodes will be needed to decide this question.

NICKEL.

Like iron, nickel tends to become passive in oxidizing solutions, and it was therefore thought that nickel might prove more satisfactory as an anode than iron, for any nickel which might dissolve should not cut down the efficiency of deposition by undergoing alternate oxidation and reduction, as is the case with iron. The usual amount of solution was electrolyzed for 130 hours (155 ampere hours) with an anode of pure sheet nickel. The efficiency of corrosion was 7 per cent for the first two days, and dropped to 5 per cent near the end; the average was 5.7 per cent. Corrosion was at the rate of 0.0624 gram per ampere hour.

The efficiency of deposition rose to a maximum of 19 per cent after two days, and fell to 5.4 per cent at the end. Early deposits were bright and satisfactory, but toward the end they became black and worthless. Nickel is not a satisfactory anode.

FERROCHROMIUM.

A bar was cast from commercial ferrochromium, probably 64 per cent chromium, and this was operated for 64 hours. The first cathode, removed after 47 hours, was black and sooty in appearance, as were all others, not excepting a half-hour deposit. The rate of corrosion was 0.323 gram per ampere hour, an efficiency of 43.2 per cent, based on ferrous iron and trivalent chromium. Ferrochromium is worthless as an anode.

STAINLESS STEEL

An anode of stainless cutlery steel, presumably 13 per cent chromium and 0.30 per cent carbon, was tested at 8.7 amperes per square decimeter. The rate of corrosion was 0.432 gram per ampere hour, an efficiency of 44.8 per cent. Chromium in steel increases its corrosion as anode in chromic acid solutions, and renders it unfit for that use.

NICKEL-SILICON.

Thinking that addition of silicon to nickel might increase its resistance to anodic corrosion, alloys were made containing 15 and 5 per cent silicon. The former was so brittle that it could not be used. The latter corroded so readily that its use was abandoned after a single trial.

FERROCHROMIUM-SILICON

Fifteen per cent of silicon was added to the ferrochromium previously mentioned. This made it very brittle. The alloy corroded at the high rate of 0.75 gram per ampere hour, and is of no value as an anode.

NICKEL-CHROMIUM

The nickel-chromium alloys sold under the names chromel, nichrome, etc., are notable for their resistance to corrosion by sulfuric acid. A strip of "Chromel A" ribbon lost 0.663 gram per ampere hour, and is entirely unsuitable for an anode in the chromic acid solution.

THE CHEMICAL CORROSION OF STEEL.

Since steel tanks have often been used to contain chromium plating solutions, strips of cleaned Armco iron and low-carbon steel were suspended in the solution to find the rates of corrosion. The time was 26 days at room temperature (21° C.) and 5 days at 60° C.

Loss of Iron and Steel in Chromium Plating Solution, per Year

	Temperature			
	21° C.		60° C.	
	Oz./sq. ft.	g./sq. dm.	Oz./sq. ft.	g./sq. dm.
Armco iron	0.0038	0.0117	2.17	6.64
Steel	0.00129	0.00393	2.30	7.02

The Armco iron was covered with a tightly-adhering brown film and the steel by an iridescent green film. These films mean that the rates of corrosion diminish with time, and hence that losses per year calculated from these short-time experiments are too high. But the weight of the specimen included the film, and to that extent the calculated results are too low. The figures should be taken as merely an approximation. The figures seem to show that the cold solution does not attack iron or steel appreciably, but there may be decided corrosion by the solution when hot.

One efficiency test with chromium-plated steel as anode and cathode was carried out in a Hoffman apparatus for the collection of the gaseous products of electrolysis. No gas was evolved from the anode, which lost 0.331 gram per ampere hour, an efficiency of 51.2 per cent for trivalent chromium, or 102.4 per cent for the hexavalent metal. At the cathode the efficiency of metal deposition was 24 per cent (0.0768 gram per ampere hour) and that of hydrogen deposition 59.6 per cent, leaving 16.4 per cent of the current not visibly accounted for.

TABLE I.

Efficiency of Anodes in Chromium Plating.

Anode	g./amp. hr.	Per Cent Efficiency
Chromium	0.371	57.3^{III} or 114.6^{VI}
Ferrochromium	0.324	43.2
Stainless steel	0.383	44.8
Steel	0.0084	0.80
Nickel	0.062	5.6
Nickel-silicon, 5 per cent	0.973	....
Nickel-chromium	0.663	....
Ferrochromium-silicon	0.740	....
Duriron	0.0135	....
Chromium deposited	0.0453	14.0

This probably was spent in reducing from hexavalent to trivalent chromium some metal which wandered from the cathode without being reduced further to the metallic state and deposited. This experiment favors the view that chromium either dissolves as hexavalent metal, or that if it goes into solution as a trivalent metal, it is all oxidized to the hexavalent form, the extra 2.4 per cent corrosion being due to chemical attack of the anode by the solution.

By comparing the rate of corrosion of the different anodes with that of the deposition of chromium the effect on metal concentration under the conditions of these experiments can be seen. For comparison a cathode efficiency of 14 per cent (0.045 gram deposit per ampere hour) was chosen as about the average. The results are recorded in Table I.

CONCLUSION.

If these experiments are taken at their face value they indicate that of all materials tested lead is the only one that should be used as anode in chromic acid solutions for long-continued operation. An exception to that conclusion may, however, have to be made in the case of iron or steel, for the reason pointed out under that topic. Iron-silicon alloys are at least the equal of, and on further test may prove superior to, pure iron or steel as anodes.

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DISCUSSION.

RAY L. SHEPARD[6]: This sample of a chromium plated automobile door handle confirms the statement that lead is the most satisfactory anode. It has a zinc base with nickel plate and chromium plate on top. The anode was made of lead placed so as to give equal spacing around the cathode. Lead is easily adapted for this kind of work and proved very satisfactory. This particular handle is used as an automobile outside door handle. It will soon be the only kind used on the higher priced cars.

AUGUST M. KUHLMANN[7]: How thick is the deposit?

R. L. SHEPARD: Less than 0.1 mil (0.0025 mm.).

COLIN G. FINK[8]: The three valuable properties of chromium are:

1. Extreme hardness. We can produce chromium plate harder than a steel file.

2. Resistance to oxidation. Corrosion tests on various metals show that chromium is a better protective metal than any other.

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[6] Production Manager, C. B. Shepard Co., Detroit, Mich.

[7] Research Dept., Electrometallurgical Co., Niagara Falls, N. Y.

[8] Head, Division Electrochemistry, Columbia University, New York City.

3. Resistance to scaling at high temperature. Many companies are using chromium plated steel parts because they will resist a white heat and will not scale. The parts will turn dark green, but the chromium oxide plus chromium plate protects the steel underneath.

Another valuable property of chromium is the difficulty with which it forms a sulfide. Chromium sulfide is very hard to produce. The instability of chromium sulfide makes chromium valuable in vulcanizing apparatus. It prevents the rubber from sticking to the molds. I believe chromium plate will take care of 80 to 90 per cent of base metal plating in a short time.

GEORGE B. HOGABOOM[9]: In using lead anodes, it is well to state that it has been found advisable to remove the lead anodes during the time the bath is not in use, on account of the lead bichromate formation. I do not think chromium is going to replace other metals. Bright finishes are seldom acceptable. Most hardware dealers prefer the satin finish, and it is very hard to get a good dull chromium plate.

R. L. SHEPARD: As far as a bright finish is concerned, you are right about interior trimmings, Mr. Hogaboom. However, dealers prefer a bright finish for outside door handles. We do not find any difficulty in getting a good dull finish.

G. B. HOGABOOM: The finish in chromium is dependent upon the metal to be plated on. If it is to be bright plated, it must be plated on a polished surface, which has first been nickel plated. I cannot see where 80 to 90 per cent of our work is to be chromium plated.

COLIN G. FINK: The exact reproduction of the under surface is very important. Designs in the base metal can be reproduced in every detail.

G. B. HOGABOOM: We can bright nickel plate, and we can bright brass plate. In Bridgeport the silver shops are plating silverware of fancy designs in bright solutions. There is a firm in the East manufacturing bumper bars. They found that one lot had a very high luster, but the other needed buffing. Investigation proved that it was due to the carbon content of the steel. When the carbon was "combined" with iron, they obtained a high

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[9] Plater, Hanson and Van Winkle Co., Newark, N. J.

luster. When they had steel with graphitic carbon, they obtained a dull luster. They changed their carbon content to 0.90.

The question of preparation of the surface is important. The color of the brass deposit is affected by both the cathode and anode. With a brass anode containing 63 per cent Cu and 37 per cent Zn, the composition of your deposit will be 76 per cent Cu and 24 per cent Zn.

A paper presented at the Fifty-eighth General Meeting of the American Electrochemical Society, held at Detroit, Mich., September 25, 1930, Dr. Frank N. Speller presiding.

29

THE PLATING ON RADIATOR SHELLS.[1]

By Oliver P. Watts.[2]

Abstract.

Photographs of the plating on radiator shells are shown, accompanied by a description of the preparation of the steel and the details of plating. Heavy electrodeposits on steel are prescribed, to insure lasting protection against corrosion. The proper preparation of the steel surface preliminary to plating is an important factor. The actual thickness of various copper, nickel and chromium deposits was determined microscopically. Tests were made for pin holes and cracks in the plates. Finally samples were immersed in a 35 g./L. NaCl solution. Many specimens were in good condition after 23 days' immersion.

[C. G. F.]

The plating most in the public eye is that on automobiles, and the reputation of electroplating as a whole must stand or fall largely by the impression which this makes on car owners. Some car manufacturers are doing an excellent job of plating, with results which are a credit to them and a source of satisfaction and pride to the owners of their cars. Other makers of cars, either through ignorance of what constitutes good plating, or through a false economy of giving the plating contract to the lowest bidder that their purchasing agents can find, are decorating their cars with a brand of plating that is calculated to discredit all plating with the public. Poor plating is not always done designedly, but may result from neglect of some one or more of the many factors which contribute to a uniform, thick, non-porous deposit.

It was therefore thought by the writer that a presentation of photographs of the plating on radiator shells, accompanied by a description of the preparation of the steel and the details of plating, would show manufacturers exactly what results are produced by current methods of plating, and would thus contribute somewhat to the improvement of the plating on automobiles. The radiator shell was chosen for investiga-

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[1] Manuscript received July 15, 1930.

[2] Assoc. Prof. of Chemical Engineering, Univ. of Wisconsin, Madison, Wis.

tion because it is usually made of steel, and is more commonly plated by the manufacturer of the car than are some other parts.

At present the general practice in producing a "chromium-plated" radiator shell is to deposit first a coat of copper, which is usually buffed, then a coat of nickel, which is always buffed, and finally a very thin coat of chromium. To prevent the rusting of steel it must either be plated with a metal which protects galvanically, that is, zinc or cadmium, or the coating of protective metal must be water-tight. It has been the

TABLE I.

Preparation of Steel Surface.

Shell	1st wheel	2d wheel	3d wheel	4th wheel
A	150 dry	180 grease	180 color	
B	150 dry	150 grease	180 sub felt	
C	150 dry	150 grease	180 sub felt	200 sheepskin
D	150 dry	180 grease		
E	120 dry	120 grease	150 grease	
F	80 dry	120 grease	150 grease	180 grease
G	120 grease	150 grease	200 grease	
H	150 dry	180 grease	180 color	

TABLE II.

Plating Data.

Shell	Time Min.	Amp./ sq. ft.	Amp./ sq. dm.	Amp.-hr./ sq. ft.	Amp.-hr./ sq. dm.
A	Cy-Cu 25	14	1.5	5.8	0.62
B C D	Cy-Cu 6	18	1.9	1.8	0.19
	SO_4-Cu 20	28	3.0	9.3	1.00
E	Cy-Cu 25	23	2.5	9.7	1.04
F	Cy-Cu 39	24	2.6	15.6	1.68
G	Cy-Cu 13	12	1.3	2.6	0.28
H	Cy-Cu 25	14	1.5	5.8	0.62

Shell	Time Min.	Amp./ sq. ft.	Amp./ sq. dm.	Amp.-hr./ sq. ft.	Amp.-hr./ sq. dm.	Amp.-hr./ sq. ft.	Amp.-hr./ sq. dm.
A	Ni 25	14	1.5	5.8	0.62	Cr 3	0.32
B C D	Ni 30	11	1.2	5.5	0.59	Cr 15	1.61
E	Ni 35	10	1.1	5.8	0.62	Cr 7.4	0.8
F	Ni 33	11	1.2	6.0	0.65	Cr 8.8	0.95
G	Ni 22	13	1.4	4.6	0.5	Cr 3.3	0.36
H	Ni 25	14	1.5	5.8	0.62	Cr 3	0.32

writer's experience that a thin electroplate, 0.0001 in. to 0.0002 in. (0.0025 to 0.005 mm.) of any metal either has initially many holes in it, or these quickly develop with use. Only thick electroplates are free from these holes. Unfortunately chromium is so brittle that it is not feasible to apply thick coatings except upon rigid articles, hence for the prevention of rusting on "chromium-plated" steel, protection must be secured by the deposition of a thick layer of other metal or metals beneath the chromium.

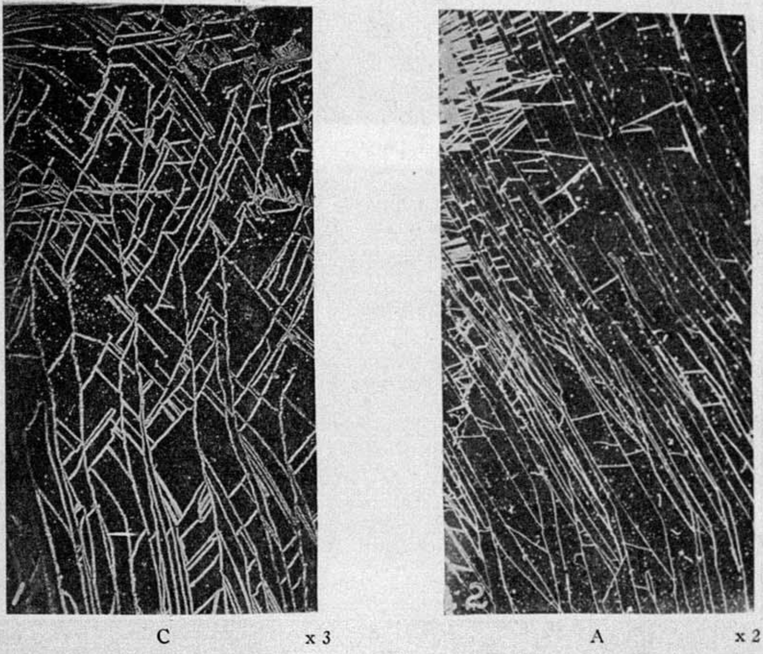
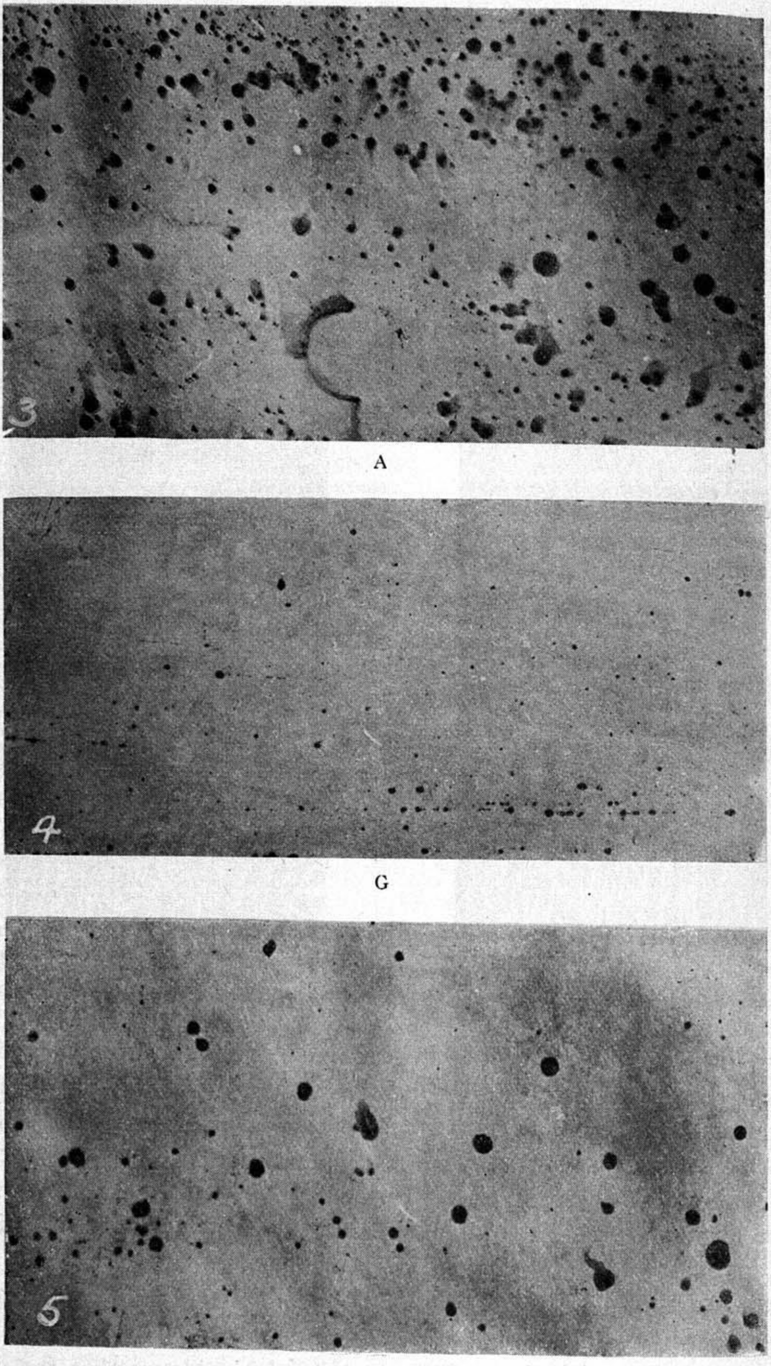

C x 3 A x 2

FIG. 1. Cracks in chromium plate. Detected by the copper deposition method.

The fineness and uniformity in grain size of the different grades of abrasive used in preparation of the steel is an important factor in the protective value of the subsequent plating, as well as in its appearance. For this reason specifications for the preparation of the steel surface are given, as well as of the plating. According to information furnished by the makers the shells studied were prepared by the operations indicated in Table I and were plated as specified in Table II.

On shells B, C and D the cyanide copper was followed by a heavier deposit from the sulfate solution. The copper plate on A, G and H was not buffed before nickeling. It is a curious coincidence that the companies that do not buff the copper plate, thereby saving a few cents per



A

G

H

FIG. 2. Pinholes in coatings. Detected by ferricyanide paper. ¾ natural size.

shell, are putting on so little copper that it could not have been buffed without removing most of the copper. They are, whether they know it or not, depending almost entirely on the nickel and chromium for protection of the steel. When informed of the practical absence of copper from shell A, the manufacturers sent another shell, H, which they "believed to have a very satisfactory coating of copper." As shown in Table III, the average thickness of the copper on H was not much better than on A. This was confirmed by a test of an exposed part of the copper plate on H. A six-inch (15 cm.) loose cotton buff with rouge, running at 2,600 r.p.m., exposed no steel after 5 seconds, but at the end of another 5-second period of buffing the copper had been entirely removed from a spot the size of a dime on a flat surface!

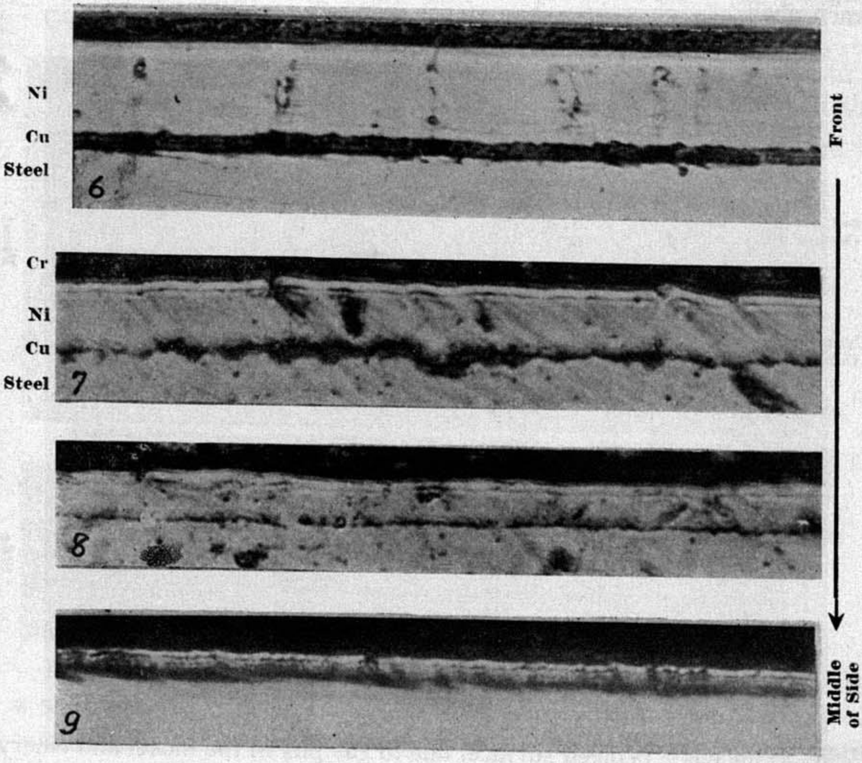


FIG. 3. Section of composite electroplate A. x 1000.

VISUAL INSPECTION OF THE SHELLS.

Inspection of the shells by eye and with the aid of a binocular microscope at a magnification of about 30 diameters indicated several defects in the polishing of the steel and in the plating. In some cases sufficient finishing with fine emery had not been done after cutting down with coarse emery, and consequently marks made by the coarse emery showed on the finished shell. Gas pits formed during nickel plating were another source of roughness, and greatly lessened the thickness of the nickel in these spots. Following are details of the condition of each shell.

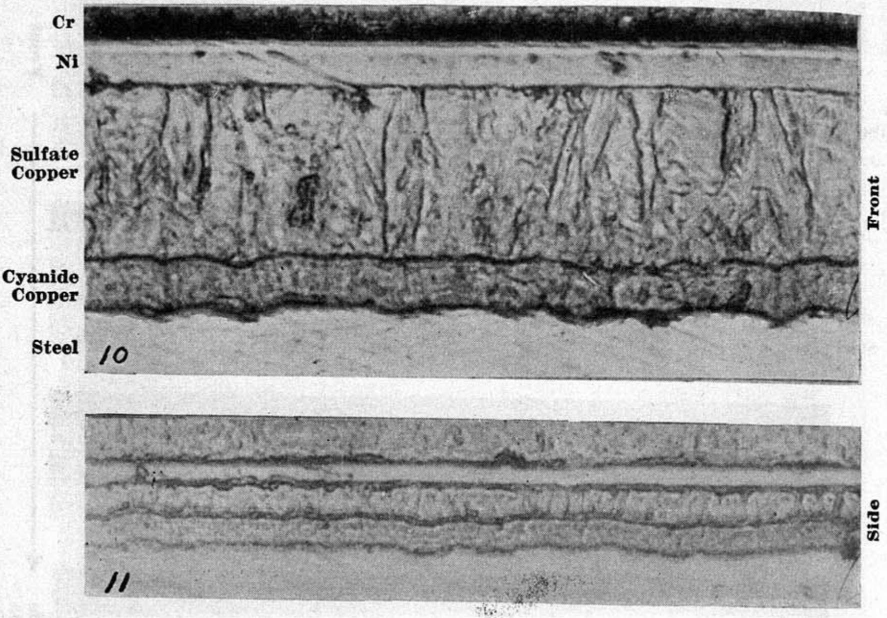


FIG. 4a. Section of composite electroplate B. x 1000.

A—This has a pebbled surface, due to gas pits in the nickel and emery marks not fully removed from the steel.

B—No emery marks, but the luster of the surface is dimmed by very fine longitudinal scratches, as if the nickel had been buffed with a slightly scratchy material.

C—An excellent surface. No emery marks, but an occasional longitudinal scratch, as if a few coarse grains had been mixed with the fine emery. No gas pits. The chromium plate shows fine cracks on the front at the top and sides, where the chromium is thickest.

D—No emery marks, but elongated pits (gas pits in the nickel?) and faint scratches like those mentioned in C. The chromium is cracked along the back edge of one side near the top.

E—An excellent finish. A few emery marks are visible on the top of the shell, which was buffed crosswise, differing from all other shells in this respect. A few gas pits can be seen on the sides, with a streak running upward from each pit. This shell, like all others, was plated bottom up.

F—A very good finish, but shows a few emery marks. No gas pits.

G—A faintly pebbled surface. No emery marks.

H—A pebbled surface, which the microscope shows to be due to a host of elongated gas pits in the nickel plate and emery marks in the steel.

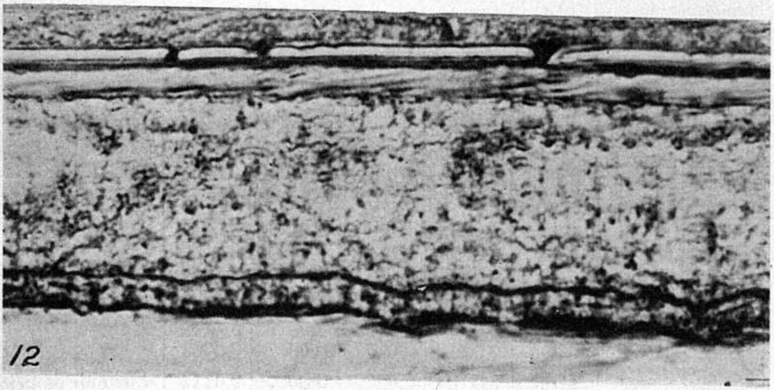


Fig. 4b. Front; cracks in chromium C. x 1000.

PREPARATION OF SPECIMENS FOR THE MICROSCOPE.

In order to prepare specimens for examination with the microscope a slice was cut entirely across the shell with a hack saw; this was cut into lengths of about three-fourths of an inch (19 mm.), and plated with copper for 10 to 16 hours from a sulfate solution in order to protect the edges during polishing, and to provide a background against which the chromium might be visible. Many metals and solutions were tried in the endeavor to make a metal deposit adhere well to the polished chromium plate. The method finally adopted was to flash the specimen for a minute in an alkaline solution of antimony in order that it might cover with copper quickly, and then to plate with copper in the sulfate solution.

The plated specimens were stood on edge in a brass ring and the voids filled with solder. Since the high temperature of the solder often caused the copper plate to lift from the chromium, fusible metal was later substituted for the solder. "Smooth On" cement was also tried, but particles of this dislodged during polishing and rendered it very difficult to secure a surface free from scratches. About an eighth of an inch (3 mm.) of the mounted specimen was sawed off and the exposed surface of the remainder was ground down, polished and etched with ammonia and hydrogen peroxide to make the copper stand out distinctly from the nickel and steel adjacent to it.

TABLE III.

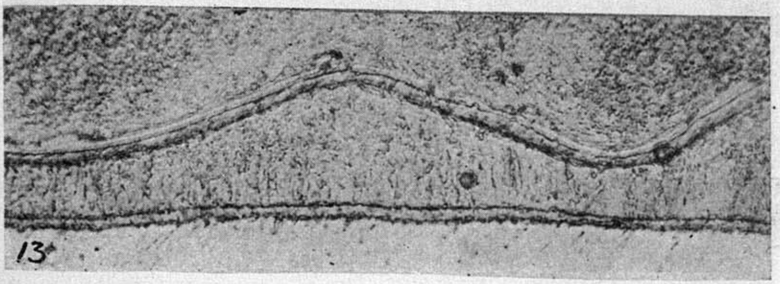
Variations in Thickness of Plating.

Shell	Deposit	Amp.-hr./sq. ft.	Amp.-hr./sq. dm.	Theoretical Thickness		Observed Thickness				Min./Max. %
						Max.		Min.		
				Inches	mm.	Inches	mm.	Inches	mm.	
A	Cy-Cu	5.8	0.62	0.00065	0.0165	0.0009	0.0229	0.00003	0.00076	33
	Ni	5.8	0.62	0.00030	0.0076	0.00044	0.0112	0.00022	0.0056	50
B	Cy-Cu	1.8	0.19	0.00020	0.005	0.00021	0.0053	0.00015	0.0038	65
	SO_4-Cu	9.3	1.00	0.00052	0.0132	0.00103	0.0262	0.00017	0.0043	18
	Ni	5.5	0.59	0.00028	0.0071	0.00028	0.0071	0.00014	0.0036	42
C	Cy-Cu	1.8	0.19	0.00020	0.005	0.00016	0.0041	0.00008	0.0020	50
	SO_4-Cu	9.3	1.00	0.00052	0.0132	0.00144	0.0366	0.00010	0.0025	7
	Ni	5.5	0.59	0.00028	0.0071	0.00033	0.0084	0.00008	0.0020	30.5
D	Cy-Cu	1.8	0.19	0.00020	0.005	0.00017	0.0043	0.00009	0.0023	59
	SO_4-Cu	9.3	1.00	0.00052	0.0132	0.00103	0.0262	0.00016	0.0041	15.5
	Ni	5.5	0.59	0.00028	0.0071	0.00024	0.0061	0.00009	0.0023	42
E	Cy-Cu	9.75	1.05	0.00109	0.0277	0.00045	0.0114	0.00030	0.0076	67
	Ni	5.7	0.61	0.00029	0.0074	0.00065	0.0165	0.00022	0.0056	34
F	Cy-Cu	15.6	1.68	0.00176	0.0447	0.00027	0.0069	0.00008	0.0020	30
	Ni	6.0	0.65	0.00031	0.0079	0.00025	0.0064	0.00010	0.0025	40
G	Cy-Cu	2.4	0.26	0.00027	0.0069	0.00009	0.0023	0.00005	0.0013	55
	Ni	4.6	0.5	0.00024	0.0061	0.00105	0.0267	0.00029	0.0074	30.5
H	Cy-Cu	5.8	0.62	0.00065	0.0165	0.00009	0.0023	0.00006	0.0015	67
	Ni	5.8	0.62	0.00030	0.0076	0.00033	0.0084	0.00020	0.005	61

VARIATION IN THICKNESS OF DEPOSITS.

The thicknesses of the different deposits were measured by means of a micrometer eyepiece on the microscope. Both the sulfate-copper and nickel deposits varied greatly in thickness at different points on the same shell. The maximum and minimum thickness of each metal in a single cut across the shell are shown in Table III, together with the theoretical thickness computed from the time of plating and the current density, assuming 100 per cent efficiency and uniform distribution of plating over the whole shell.

The comparative uniformity in thickness of the copper deposited from cyanide solutions is in marked contrast to the wide variation in thickness of the nickel and copper from the sulfate solution. The great importance of good throwing power when plating for protection of a corrodible metal like steel is shown by a study of Table III and of the photographs which appear later. The column marked per cent in the table gives the ratio in per cent of the thinnest to the thickest portion of the deposit observed in a cut across the shell. A deposit of copper may be secured from a cyanide solution with a maximum thickness not more than twice the minimum; but from the sulfate solution the thickest deposit is likely to be five to six times the minimum, and hence unnecessarily thick. It is highly important that the plater maintain his solutions at or near the best throwing power attainable in each type of solution.



Wavy deposits from copper sulfate. x 500.

Deposit on side of shell. x 1000.

Fig. 5. Section of composite electroplate C.

Both the relative and actual thickness of deposits of the different metals, and the variations in thickness of the same metal, may be seen and measured on the photographs, Fig. 3 to 10, which are at a magnification of 1,000 diameters.

At first glance some of the figures in Table III seem incredible, *e. g.*, that on C the copper deposit from the sulfate solution should be at any point, nearly three times the calculated thickness; but with a poorly throwing solution like this, very little copper will be deposited on the inside of the shell, and since the actual cathode efficiency is nearly 100 per cent, much more than the theoretical thickness must be reached at some points on the outside nearest the anodes. The relatively thin copper deposits of A, F, G and H show that these solutions are being operated mainly as electric cleaners. Although F has a fair thickness of copper, eight times the number of ampere-hours per square foot was required to produce it that gave in B a deposit of about equal thickness.

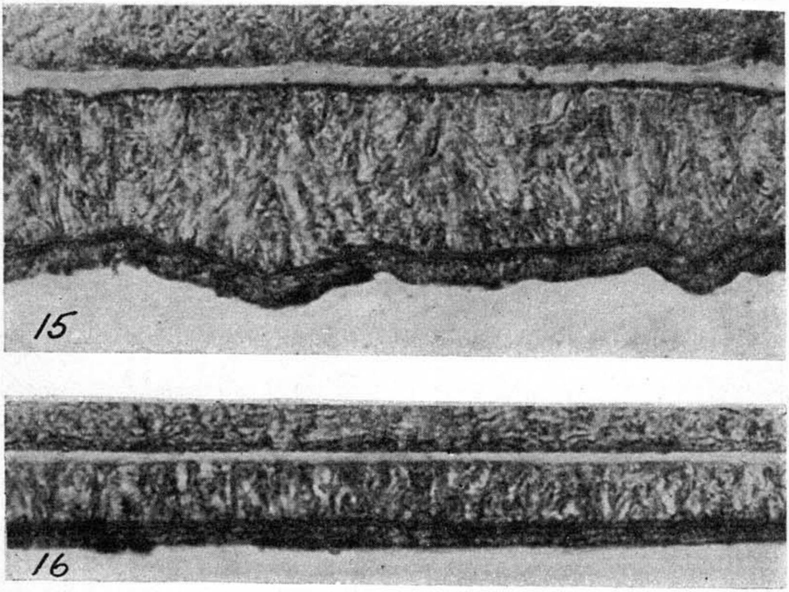


FIG. 6. Section of composite electroplate D. x 1000.

The thickness is greatest on the front of the shell, and falls gradually or rapidly, according to the throwing power of the solution, across the side to the back edge. Sometimes a minimum may be reached about the middle of the side, from which the thickness increases slightly toward the back edge.

TESTS FOR PINHOLES.

Wet test paper containing potassium ferricyanide, sodium chloride and dimethyl glyoxime was applied to each shell. The papers from A and H were peppered with blue spots, indicating corrosion of the steel through all the metal coatings, and the paper from G which was best of the three, had a hundred blue spots in eight square inches (51.6 sq. cm.). Broad pink streaks on the front of each of these shells indicated holes through the chromium but not through the nickel. The other shells showed no holes except through the chromium. Photographs of the test papers from A, G and H are shown in Fig. 2 at 0.75 diameters (three-fourths size). The failure of G, in view of its very heavy deposit of nickel, was unexpected. All three are shells with little or no copper plate, which, if present, was unbuffed.

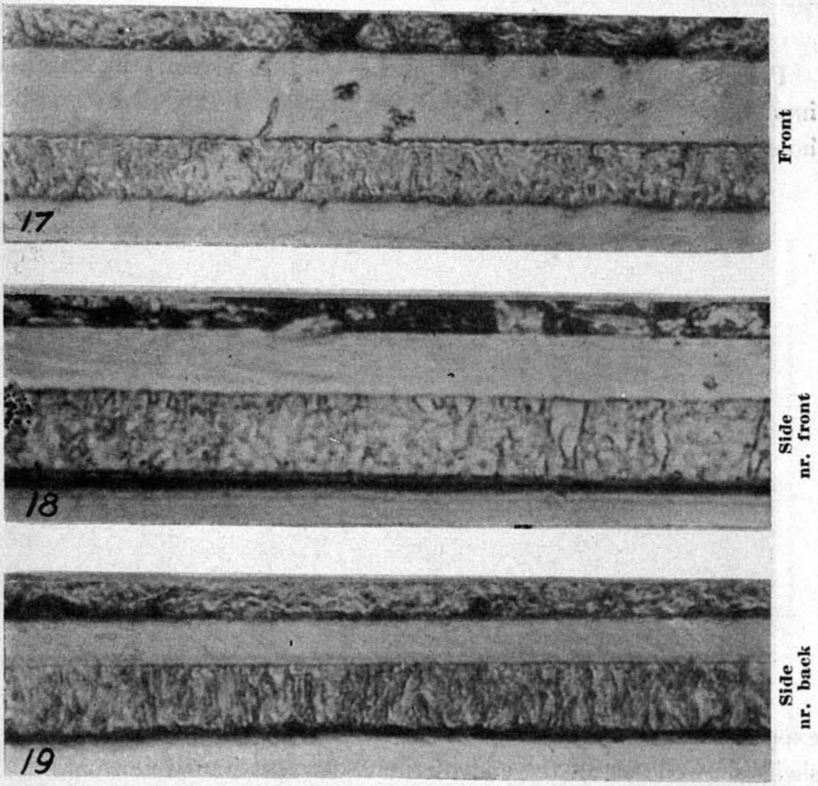


FIG. 7. Section of composite electroplate. Shell E. x 1000.

CRACKS IN CHROMIUM PLATE.

Although cracks in the chromium plate may not be visible on new shells, application of the test paper or exposure out of doors or in salt water will bring them to light, if any exist. Cracks and pinholes in chromium plate are brought out more distinctly by Dubpernell's test.[3] This consists of plating at a low current density in a copper sulfate solution. Under these conditions copper deposits first and most readily in the cracks and spots bare of chromium. The photographs of Dub-

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[3] E. M. Baker and W. L. Pinner. Soc. Automotive Eng., **23**, 200 (1928).
[4] E. M. Baker and A. M. Rente, Trans. Am. Electrochem. Soc., **54**, 337 (1928).

pernell's test on C and A, Fig. 1, show the same pattern of cracks as did the test paper. It has been stated that under certain conditions, cracks in chromium plate do not become serious until the total quantity of current exceeds 300 ampere minutes per square foot. However, A received only 180 ampere minutes per square foot in the chromium bath.

IMMERSION TESTS IN LAKE WATER AND IN SEA WATER.

Pieces of the shells 12 to 18 inches (30 to 54 cm.) in length were immersed in a tank of lake water. Because of the great number of holes through to the steel, that were indicated by the test paper, it was expected that A, G and H would rust at once. However, none of the shells showed rust at the end of the two-weeks immersion period. The same pieces were then placed in a tank of water containing thirty-five grams of common salt per liter (4.7 oz./gal.). After three days no rust was apparent on any of the shells. In 13 days A was peppered with tiny rust tubercules and many fine parallel cracks were visible. The other specimens were free from rust. After 23 days all specimens were removed, washed, wiped dry and examined, with the following results:

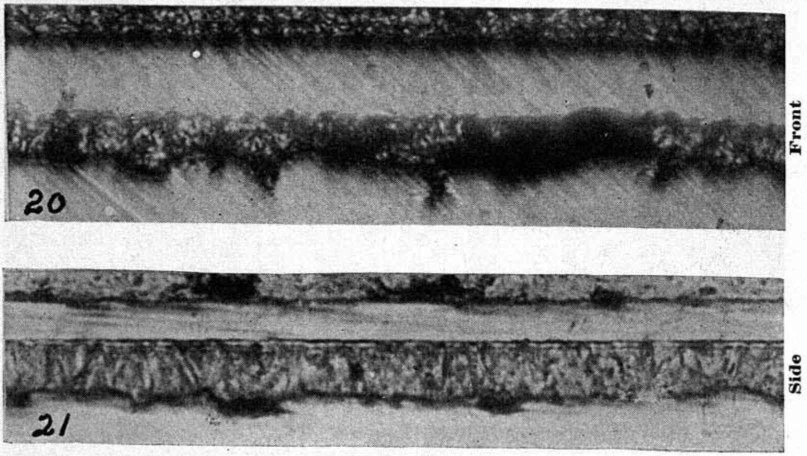


FIG. 8. Section of composite electroplate. Shell F. x 1000.

A—Utterly ruined. It had rusted badly at the pinholes indicated by the test paper, and in addition had corroded deeply at many cracks in the chromium plate.

B—Still perfect. No rust. On the front, four groups of cracks are now visible for the first time.

C—No rust, but a host of parallel cracks are now visible on the front and on both edges of the side of the shell. It is noteworthy that these are places of highest current density, where the chromium plate is thickest. On rubbing vigorously with a cloth the cracks disappear.

D—No rust. A few cracks in the chromium are visible on the top of the shell near the back edge.

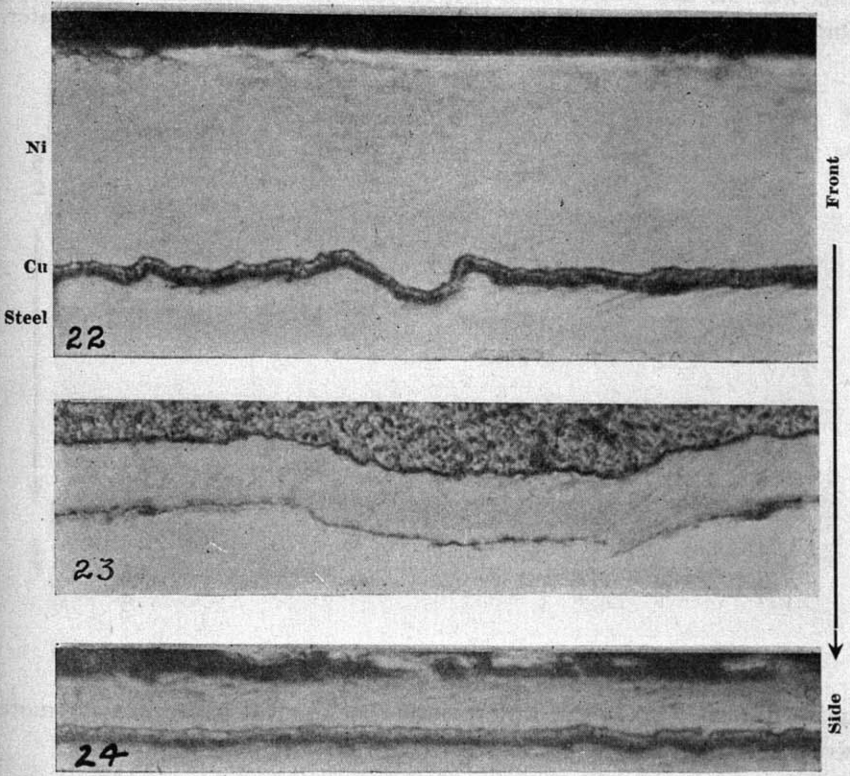


FIG. 9. Section of composite electroplate. Shell G. x 1000.

E—No rust. A few cracks are seen on the front near the top only.

F—No rust. No cracks in the chromium, but many dull spots are noted. These, like the cracks, can be wiped off with a cloth, and are doubtless due to the same cause, a microscopic hole in the chromium through which the products of corrosion of the nickel have oozed out and spread over the chromium widely enough to be visible to the eye. When these are wiped off the crack itself is too small to be visible.

G—No rust. A few tiny cracks on the front edge, and many dull spots scattered over the surface. These are more easily rubbed off than those on F and leave no trace behind.

H—No rust and fewer dull spots than on F or G.

The corrosion tests in fresh and in salt water corroborate the findings of the test paper in that the only shell which failed in the corrosion tests was the one which the test paper showed to be by far the worst. On the other hand, the failure of A, G and H to rust in fresh water, and of the last two in salt water, show that the test paper is a far more severe test than one would expect from its short duration.

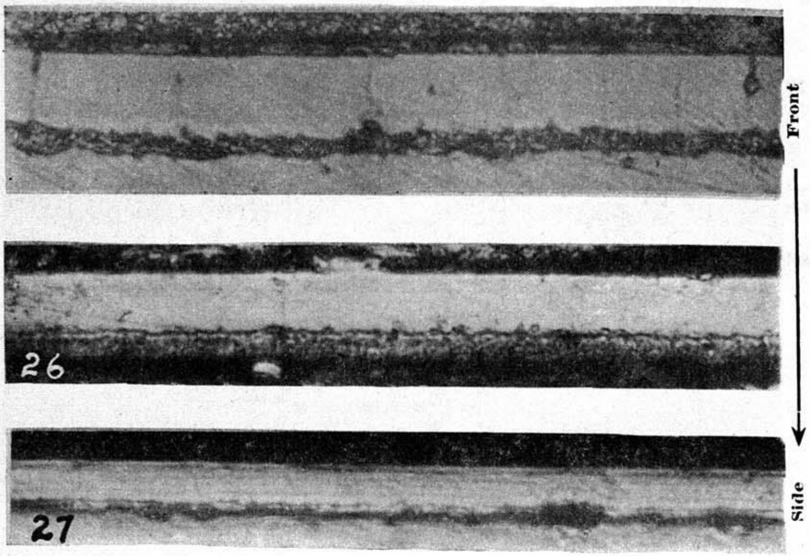


FIG. 10. Section of composite electroplate. Shell H. x 1000.

The function of chromium plate and of the plate immediately underlying it seems clearly indicated by these corrosion experiments. Chromium plate applied in the extremely thin layer at present used for ornament cannot be expected to protect a corrodible metal like steel; the only function of the chromium is to prevent the tarnishing of some other metal beneath it. The latter metal must be applied with sufficient continuity and thickness to keep corrosive agents from contact with the steel. It is well-known that electroplates of metals other than chromium, and having the slight thickness of the usual chromium plate, are not water-tight. Chromium plate is slightly, if at all, superior to other metals in this respect. It is therefore necessary that chromium plating be of such thickness that the uncovered spots and cracks are so small that the eye cannot see the tarnished metal that is exposed through the holes and cracks in the chromium. For out-of-doors use nickel appears to be superior to other metals for the electroplate immediately underlying chromium. If chromium plating is to survive, its friends must be jealous of its reputation, and eliminate the poor work which is discrediting "chromium" with the public.

PHOTOGRAPHS OF ELECTRO-DEPOSITS.

Photographs of cross sections of the plating are shown in Fig. 3 to 14, usually at a magnification of 1,000. In each photograph the steel is at the bottom, and next is the darker copper, followed by nickel, and then the chromium, which shows as a whiter line (if at all visible) between the nickel and the darker protective coat of copper which was applied before polishing the specimens.

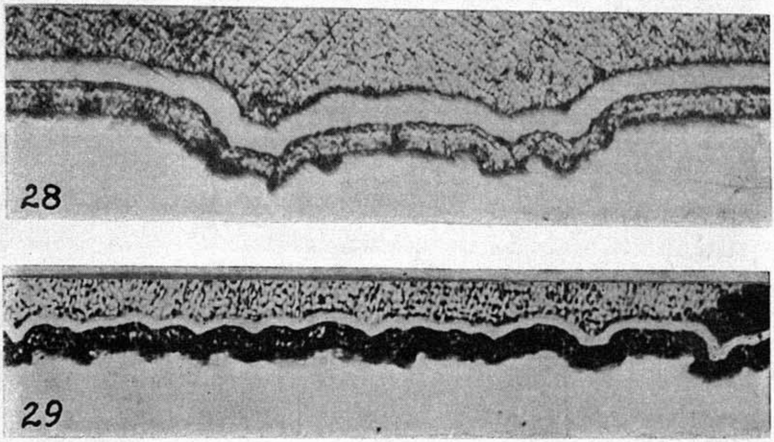


FIG. 11. Plating on unpolished steel on the back of shells. x 1000.

Fig. 3 consists of four sections from shell A, and shows the diminution in thickness of nickel in passing from the front to the middle of the side of the shell. The copper deposit on this shell varies from a very thin line to none at all, so that protection is due mainly to the nickel.

Fig. 4 shows sections from the front (upper picture) and from the side of B, in which the chief dependence for resistance to corrosion is placed on an extra thick plate of copper, which consists of a layer of cyanide copper followed by a heavier deposit from the acid sulfate solution. The disadvantage of a poorly throwing solution is indicated by the great difference in thickness of the sulfate copper on the front and that on the side of the shell.

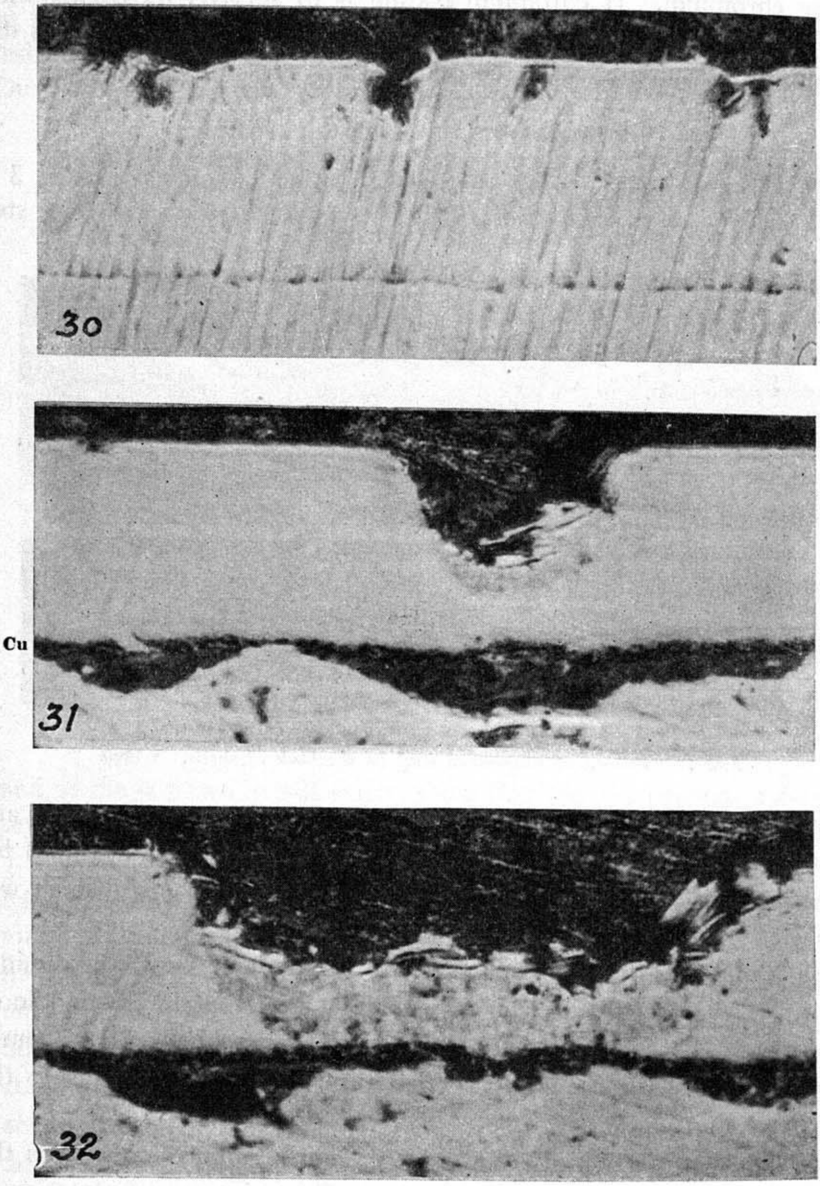
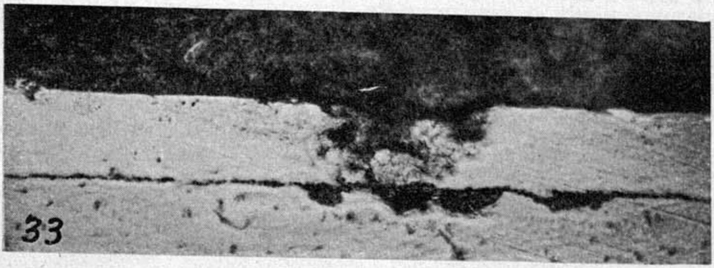
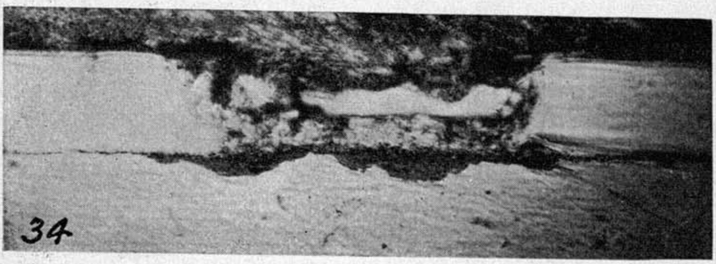


FIG. 12. Pinholes in nickel of Shell G. x 1000.

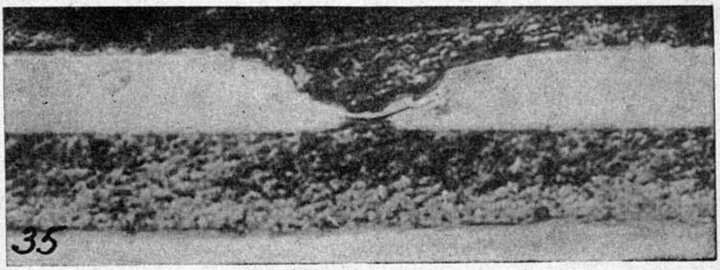
Fig. 5 shows shell C, which differs from B only in having had a better preparation of the steel before plating. The waves in the sulfate copper were so long that it was necessary to lower the magnification to 500 diameters in order to show the whole of a single wave on the photographic plate.



G x 500



G x 500



C x 1000

FIG. 13. Pinholes in electroplates.

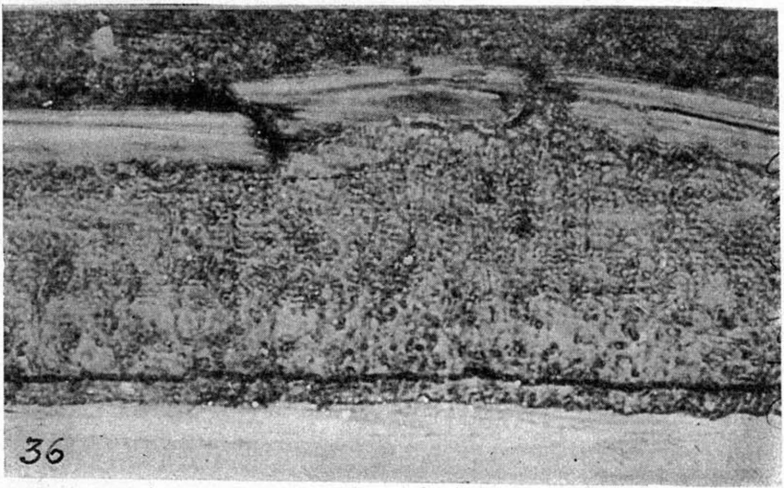
Fig. 6 shows sections from the front and far back on the side of D. The plating is similar to that on B and C, but much less time and labor were given to the preparation of the steel surface for plating. This shows on the front of the shell, but, strangely, not on the side.

Fig. 7 shows three sections from E, the front, the side toward the front, and the side near the back edge. An extra good finish on the steel and uniformity in the electroplate are apparent.

Fig. 8 shows sections from the front and side of F. The roughness of the copper on its lower edge indicates poor preparation of the steel, in spite of the great labor devoted to subsequently buffing the copper. Protection is about equally divided between the copper and nickel coats.

Fig. 9 shows shell G, which depends for protection on an unusually thick deposit of nickel, the cyanide copper solution functioning chiefly as an electric cleaner. The steel shows poor preparation.

Fig. 10 is shell H, supposed to be a duplicate of A. Although copper was found everywhere that the shell was examined with the microscope, it is very thin. Since its upper surface is little if any rougher than the lower surface, the omission of buffing before nickeling is probably justified.



C x 1000

Fig. 14. A "fault" in electroplate.

Steel that was left pitted or scratched has been referred to as poorly prepared for the reason that a leveling process must be carried out in the subsequent buffing, and the metal coating is cut away more than if the leveling off had been done before plating. The thinner the electroplate, the more serious is the failure to remove all pits and scratches from the steel before plating. Fig. 11 shows the plating on the backs of shells, where no polishing has been done on the steel. If an attempt were made to polish the plate, it is evident that the nickel would be cut through on a considerable portion of the surface. The buffing of an electroplate that has been deposited over poorly prepared steel differs from buffing an electroplate on unprepared metal only in the degree to which the deposit must be cut away to produce a good finish.

PINHOLES.

An unfortunate characteristic of electroplates is the occurrence of tiny holes entirely or partly through the deposit. On account of their small size they are usually referred to as pinholes. Fig. 12 consists of three pictures at a magnification of 1,000 diameters of pinholes in the nickel plate of G. The first photograph (upper) shows five shallow cavities, with the three at the right bridged over by chromium. In the second and third pictures the holes are deeper and the chromium plate lies in fragments on what appears to be a spongy nickel deposit.

Fig. 13 shows two holes which go entirely through the nickel of G to the film of copper beneath. The extra thickness and roughness of the copper plate immediately beneath the holes, and the fact that the copper was not buffed before nickeling, leads to the suggestion that the holes may have been due to rough or spongy spots on the copper. The third picture at a magnification of 1,000 diameters shows a hole in the nickel of E that is bridged by the chromium plate.

Fig. 14 is a picture of a catastrophe similar to a geological "fault"—a fracture and slipping of the nickel and chromium plates which occurred in shell C. Besides the fracture an inverted pinhole with the top nearly closed is to be seen at the right.

One cause of holes in electrodeposits, most common in nickel plating, is the clinging of gas bubbles to the cathode. Another cause is insoluble matter suspended in the plating solution. The photographs seem to indicate that a third cause may lie in rough or porous spots on the surface which is being plated. The greatest single improvement that could be made in electroplating would be the elimination of these weak spots or pinholes.

The writer wishes to acknowledge his indebtedness to the manufacturers who supplied the radiator shells used in this study, and to the following students for assistance in the preparation of specimens: J. W. Schutt, H. J. Kinney, F. J. Kristof, A. B. Crane, A. T. Johannsen, A. R. Kreutz.

Chemical Engineering Laboratories,
University of Wisconsin.

DISCUSSION.

Edwin M. Baker[5]: I note in looking over this paper that in many cases the minimum total thickness in the thin parts of some deposits is not in excess of 0.00036 in. (0.0091 mm.), and in some cases it is even less. Now, in order to have good protective value, against either an adequate accelerated corrosion test or weather conditions, the preponderance of evidence is that a greater thickness of deposit than this is required.

One advantage of composite deposits such as, for example, nickel-copper-nickel, is that if the buffing cuts away any great thickness of the deposit, the underlying copper is rapidly seen on visual inspection and the excessive buffing is thus made apparent. To obtain a uniformly satisfactory deposit, the whole set-up should be such that visual inspection methods that can be used in the plating shop can be relied on to detect excessive buffing, which is evidently the cause of at least a portion of the areas of thin deposit reported in the paper. This is particularly necessary if the polishing is such that dependence is placed on the buffing to do work that should have been done in the original polishing. In general, one not only obtains superior protection where a multiplicity of deposits is employed, but by visual inspection he at least is sure that not more than the top deposit has been cut through. If the underlying deposits are substantial, he is then certain of the protection these deposits afford.

F. N. Speller[6]: Prof. Baker has touched on one of the principles of applications of various layers of paint. The color of the layer has a very useful purpose. I never thought of that before in this connection, as a base coating. I was talking to Prof. C. H. Desch this summer in regard to replacing worn parts by electrodeposition in Sheffield, and he told me that he found lead to be the best material there, that is, the British Navy Department were using that as a base for nickel in building up worn parts.

Wm. M. Phillips[7]: I do not want to be too critical of a paper that is certainly very useful, and which gives an idea of the actual distribution of metal we are getting on radiator shells, but if you will refer to p. 68, on shell G, you will find that Mr. Faraday would be probably somewhat offended if he were alive. The theoretical thickness there is 0.00024 in. (0.0061 mm.), the minimum shown is 0.00029 in.

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[5] Asst. Prof. of Chem. Eng., Univ. of Michigan, Ann Arbor, Mich.

[6] Director, Dept. of Metallurgy and Research, National Tube Co., Pittsburgh, Pa.

[7] Advisor on Finishes and Plating, General Motors Corp., Detroit, Mich.

(0.0074 mm.), showing that the minimum is a little more than the theoretical, and the maximum, of course, greatly more, because it is over 0.001 in. (0.025 mm.).

Now, when it comes to this question of the distribution of metal, in the first place a few years ago we did not get anything like a sufficient amount of metal to protect radiator shells or anything else. Prof. Watts shows that the amount of metal deposited has been greatly increased in the past few years, which is a very desirable thing.

Often, as Prof. Watts mentioned, just by accident we get the metal thickest just where we want it thickest, which is a very good thing. Further than that, we are accustomed to considering thicknesses as average thicknesses. That is the way we have been figuring them for years. The average thickness on automobile parts was at one time only 0.0002 in. (0.005 mm.). I remember examining a number of the parts of an old automobile and found that the average thickness was about that figure, 0.0002 in. (0.005 mm.). That was about five years ago, and if we take the average thickness now we will find a marked improvement. If you look at a thousand radiator shells that are copper-nickel and chrome plated, you will be fortunate, if you are looking for rust, if you find two that are rusty. This refers to cars that have been out for a year. That is a vast improvement over what we had a few years ago.

I think that this distribution should be made better, and one of the means that has been taken to bring this about is to use greater electrode distances. Many of the full automatic machines now designed, instead of having electrode distances of 4 to 6 inches (10 to 15 cm.), may have as much as 10 to 12 inches (25 to 30 cm.), which does bring about a fair distribution, and even if you were to get, as some of these shells show, a thickness of 0.0003 in. (0.008 mm.) or under, on the thinnest portions, at least, for radiator shell plating, that is tolerably satisfactory, as compared to the other finishes on cars. We would like to have more, of course, but it is tolerably satisfactory.

A radiator shell is the easiest part of an automobile to protect with electroplate, for the reason that when you drive your car into the garage, even if it has been out in the rain, you have the hot radiator core inside, which dries it off. There are other parts of the car that need much better plates than radiator shells. However, the radiator shell, nevertheless, serves as a good example for Prof. Watts' paper.

Polishing in every case is the most expensive part of plating. If by any method of plating we can eliminate some of the polishing it is a good economic move. Another factor is that the abrasive grain in use in the past has been in a large measure responsible for lack of uniform accurate polishing. It is only recently that the grain has been graded. Formerly it was only about 30 per cent. accurate, many oversize particles being present, that is, you would get only about 30 per cent. of the grain size specified. Recently grading has been brought up to about 70 per cent. With a careful selection of wheels the polishing can be done quickly and the quality of the work improved. This improvement in abrasive grading occurred after Prof. Watts' work was completed.

WILLIAM BLUM[8]: There is at present considerable difficulty in preparing or enforcing specifications for plating from the standpoint of the purchaser. The manufacturer of automobile parts can specify the thicknesses of copper, nickel, etc., and within reasonable limits can control them, especially with automatic plating machinery. It is difficult, however, for even a large purchaser to inspect the plating on an automobile to determine whether it is of good quality or not. The large amount of work that Prof. Watts has done illustrates the difficulty of getting even approximate data on the average thickness or distribution of coating on an article like an automobile. A great responsibility therefore rests on the manufacturers to insure within the plant, where they do have control of processes, that they are getting a product that, so far as their knowledge goes, will be satisfactory.

PAUL W. C. STRAUSSER[9]: Prof. Watts, what was the mounting material made up of, and also the etching agent? We have had difficulty in finding a satisfactory metal for holding the specimen which would not drag over its face.

OLIVER P. WATTS: The first mounting material that I tried was ordinary soft solder, in which a little antimony had been added to harden it, but the trouble with that was the heat necessary in order to apply it. It had to be melted and put on the specimen, which was mounted in a little sawed-off section of brass tubing. We stood the specimen on edge and poured the melted solder in around it, and the heat in that process would sometimes cause the plate to lift in tiny spots that you could not see with the eye, but when examined with the microscope you would find little blisters on the metal.

Then we went to one of the fusible metals, which melted at about 65° C. This was an improvement, but did not completely cure the trouble. "Smooth-on" which had been recommended as a mounting

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[8] Chemist, Bureau of Standards, Washington, D. C.

[9] Electrochemical Engr., Chrysler Motor Corp., Detroit, Mich.

agent was next tried. This was moistened with water and tamped in around the specimen in the ring. It was a failure because abrasive particles of iron or other material in the cement would become loosened and scratch the surface of the specimen.

Many etching reagents were tried, but that most commonly used was hydrochloric acid with formalin to etch the chromium and leave the steel and nickel bright. This was followed by ammonia and hydrogen peroxide to etch the copper. All that was desired was that one layer should be bright and the adjacent layers should be roughened, so that the boundaries between the layers might be clearly seen under the microscope. There is a point of weakness toward almost any reagent, and you have the difficulty of etching a dark line (on vertical section).

In the case of etching the chromium I was sometimes uncertain as to whether the dark line was chromium or simply the dark line that is produced where two metal structures go together. You can see that by looking at the pictures for duplex copper, that is, where there is cyanide and sulfate copper you will find a dark line right between those two metals. There they are—copper—nothing but copper, and yet it etches in deeply where the two plates of copper touch each other. That is the point of weakness, and that is true of all the deposits we have etched.

So finally I gave up trying to etch. I would have this dark line between the metals and a bright shell at the bottom—dark copper and bright nickel. I wanted to etch chromium, and I could tell exactly where the surface commenced and the other left off, and I always had this fear that the dark line which I saw, where the chromium ought to be, might be much wider than the chromium itself, so I abandoned that attempt to have this nice "sandwich" of light and dark so I could measure it. I preferred to get the chromium in a few cases by leaving the chromium bright.

COLIN G. FINK[10]: Do you find etching necessary in bringing out the structure?

OLIVER P. WATTS: Yes. What I wanted was to measure the thickness of the different deposits, not to reveal their micro-structure. Without etching it is always difficult and frequently impossible to tell where one layer of metal ends and the next begins.

W. W. MCCORD[11] (*Communicated*): On reading this very illuminating and valuable paper, I was rather led to one impression which I do

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[10] Head, Div. of Electrochemistry, Columbia Univ., New York City.

[11] Research Engr., McCord Radiator & Mfg. Co., Detroit, Mich.

not think is borne out by Prof. Watts' own results. On page 69 he states, "A deposit of copper may be secured from a cyanide solution with a maximum thickness not more than twice the minimum; but from the sulfate solution the thickest deposit is likely to be five or six times the minimum, and hence unnecessarily thick."

In the first place, I question that the plating on any section of any part of any automobile can reasonably be accused of being unnecessarily thick, but the point I want to discuss primarily is the impression inferred, though not directly stated, that the cyanide solution is to be preferred over the sulfate, due to its greater throwing power.

At the bottom of the same page Prof. Watts states in discussing the sulfate solution, "but with a poorly throwing solution like this, very little copper will be deposited on the inside of the shell, and since the actual cathode efficiency is nearly 100 per cent., much more than the theoretical thickness must be reached at some points on the outside nearest the anodes." Far from being an argument against the use of the sulfate solution, this strikes me as being the principal argument in favor of it. With many articles, such as lamps, radiator shells, etc., the protection on the inside is of little consequence, and this concentration of most of the plate on the outside would seem of distinct advantage.

In the shells examined by Prof. Watts, A, E, F, G and H were plated with cyanide copper, while B, C and D were composite, using both cyanide and sulfate solutions. The copper plating time for the composite was 26 minutes, while an average of the five cyanide shells showed 25.4 minutes. Thus tank capacity to get out a given number of shells per day would be approximately equal under both systems. However, the average ampere-hours per square foot in the case of the cyanide is 7.8 (0.86 amp. hr./sq. dm.) while the composite requires 11.1 (1.22 amp. hr./sq. dm.). In other words, generator capacity would have to be about 50 per cent larger in the case of the composite.

But let us look at the results. Assume that the observed maximum of both cyanide and sulfate copper occurs at the same point, and also that the same conditions apply to the minimum. This is probably not true in either case, with the result that the total maximum copper would be somewhat less, and the minimum somewhat more than the figures to follow. However, this assumption would make the worst possible case against the sulfate, so I am using that basis.

Averaging the maximum thickness of copper in the composite shows 0.00134 in. (0.034 mm.), whereas the average of the maximum with the cyanide shows 0.00036 in. (0.0091 mm.) or approximately four times as heavy with the composite. I hardly agree with Prof. Watts that one and a third thousandths inch (0.034 mm.) is unnecessarily thick, and I do not believe many consumers would object because they were receiving it, but his point is correct that there is a wide variance between the two systems.

There is no accurate way of determining the average amount of copper on the outside of the shell, but making the rather broad and obviously questionable assumption that it is probably somewhere close to the mean between the observed maximum and minimums, we find that an average of these means in the case of the cyanide gives 0.00023 in. (0.0058 mm.) against 0.00079 in. (0.020 mm.) for the composite. In other words, by using 50 per cent more current, by the use of the composite, apparently the average thickness of the copper on the outside of the shell is increased over three times beyond that attained by the straight cyanide. I recognize that these figures are open to criticism as not being exact, but I believe they are at least indicative.

However, what we are mainly concerned with, is not high spots, or even average thickness, but with weak spots in the plate. Averaging the minimum thicknesses in each case, and putting the worst possible construction on the figures by assuming that the thin points in the cyanide occur in conjunction with the thin spots in the sulfate, the composite shows 0.00025 in. (0.0063 mm.) against 0.00010 in. (0.0025 mm.) for the cyanide. In spite of its unequal distribution, the sulfate still plastered enough metal on the outside of the shell, so that its average thin spots were 2.5 times as heavy as the average thin spots of the cyanide.

In this connection, I may mention that shell E, a cyanide shell, far outstripped the others of its class, pushing shell B closely for first honors, and being better than either of the other two composite shells, whereas the rest of the cyanide shells were trailing far in the rear.

However, in the main, I believe my contention is sound that the sulfate is apt to give a heavier deposit in proportion to current used, on the outside of the shell, where it is needed, than with the cyanide. There are many other arguments pro and con, but I wanted to bring out this point, on which I felt that Prof. Watts was perhaps leaving an opposite impression.

OLIVER P. WATTS (*Communicated*): I am in hearty agreement with Mr. McCord when he says that the plating on no part of an automobile is unnecessarily thick, and also agree with him that our chief concern should be with the thin places rather than with the average or maximum thickness of plate. I should like to see a minimum of 0.001 in. (0.025 mm.) specified and obtained. It is of course economical both in metal and electric current to have most of the metal deposited on the outside of the shell where protection is desired, and comparatively little on the inside, as happens with the copper sulfate solution. But this is possible only with a solution of very poor throwing power, and therefore is accompanied by a serious variation in thickness of plate on the front of the shell, which it is the purpose of plating to protect.

In Table III above the ampere-hours used in depositing copper on shells B, C and D from the sulfate solution was five times that employed in depositing from the cyanide solution, yet the minimum thickness of sulfate copper was only 1.1, 1.3 and 1.8 times, respectively, that of the cyanide deposit on the outside of the shells. It is true that the maximum thickness of sulfate copper was 5, 8 and 6 times that of the cyanide deposits, but this does not help the thin spots to endure against wear and rust.

It is only this excess of copper plate that was referred to as unnecessarily thick. The copper sulfate solution has a nearly constant current efficiency, and hence the weight of copper deposited may be relied upon as proportional to the ampere-hours per square foot, but from the cyanide solution the weight deposited may vary from 30 to 170 per cent of that given by the sulfate solution, according to the amount of free cyanide, temperature, current density and copper content of the solution.

Mr. Phillips points to an apparent discrepancy between Faraday's law and the thickness of nickel stated to have been found on shell G. In the data furnished regarding the plating of this shell the total current on the tank was given as 8,000 to 10,000 amperes, hence a considerable deviation from the calculated thickness for the average current of 9,000 amperes is allowable. The nickel solution had a pH of 2, and consequently a much poorer throwing power than the usual solution with a pH of 5.8. The distribution of metal is therefore much like that from the sulfate copper solution, mainly piled up on the outside of the shell, with a great variation in thickness between the thickest and thinnest deposits. It is quite possible that three-fourths of the nickel is on the outside of the shell, so that a minimum thickness here nearly equal to that calculated for a uniform thickness over the entire shell is not the impossibility that it is inferred to be.

The recent improvement in sizing abrasives, referred to by Mr. Phillips, should result in a better steel surface on which to plate. It is highly important that the abrasives contain no oversize grains when purchased, and that no coarse grains be allowed to get on the finer wheels in the process of setting up. The admixture of a considerable quantity of grains finer than normal will not damage the steel surface, but only slow down the polishing.

The writer has stressed the importance of adequate preparation of the steel before plating. Instead of this, there is the option of giving poorly prepared steel a heavy coat of copper and doing the cutting down to a smooth surface on this soft steel, with a saving of labor over that required for finishing the harder steel. If the production of a smooth surface is delayed until after nickeling there is danger that the nickel will be nearly cut through over the ridges of the underlying metal, unless the nickel deposit is much thicker than is now common practice in nickel plating.

30

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A NEW BATH FOR THE DIRECT NICKELING OF ZINC.[1]

By George W. Nichols.[2]

Abstract.

Methods of direct nickeling of zinc are briefly reviewed. It is shown that several agents, notably lactates, retard displacement of nickel by zinc, thereby permitting direct nickeling of zinc. It is also shown that these agents affect the rate at which the potential of zinc in nickel solutions changes with time.

INTRODUCTION.

An early investigation of the problem of direct nickeling of zinc was made by Hammond.[3] He showed that the addition of sodium citrate to dilute nickel baths makes it possible to deposit nickel direct on zinc. Pfannhauser[4] had previously advocated the use of citrates in the direct nickeling of zinc, but Hammond showed the possibilities of the method.

The use of a separate striking bath was proposed by Graham.[5] He showed that the problem of directly nickeling zinc is greatly simplified by covering the zinc with a layer of nickel *quickly,* thereby minmizing the possibility of streaking.

In the past, various investigators[6] have advocated the use of aluminum magnesium or alkali sulfates in nickel baths. Thompson[7] showed that the use of a high concentration of alkali sulfate in dilute nickel baths permits nickel to be directly deposited on zinc.

Hammond ascribed the beneficial effect of citrates to their ability to retard the rate of deposition by immersion of nickel on zinc. This paper

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[1] Manuscript received June 29, 1933.

[2] Graduate student, University of Wisconsin.

[3] Hammond, Trans. Am. Electrochem. Soc., 30, 103 (1916).

[4] Pfannhauser, Die Elektrochemie (1900).

[5] Graham, Trans. Am. Electrochem. Soc., 44, 347 (1923).

[6] Watts, *ibid,* 23, 99 (1913).

[7] Thompson, *ibid,* 47, 163 (1925).

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* Headquarters, Columbia University, New York City.

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shows that many other substances, notably lactates possess the property to a marked degree.

EXPERIMENTAL METHODS.

In testing the effect of the various agents on the rate of deposition, strips of zinc were uniformly polished, cleaned cathodically in the alkali cleaner, rinsed in dilute sulfuric acid, and immersed in the various nickel baths (at room temperatures) for the same lengths of time (varying from one-half to five minutes). The zinc strips were then compared with each other.

In measuring the rate of change of potential of zinc in the various baths, the metal was scoured with No. 0 emery paper and wiped with a clean cloth immediately before starting the tests. The potentials were taken with a student type L. & N. potentiometer. Preliminary trials were resorted to in order to obtain the first readings in as close to zero time as possible.

Sheet zinc cathodes, 2 x 5 cm. (0.79 in. x 1.97 in.), flanked by nickel anodes were used in testing the plating properties of the baths. Both flat and bent specimens were used, the latter being crimped at 90 degrees along the long axis.

TABLE I.

Stock Solutions.

Bath No.	1		2		3	
	g./L.	oz./gal.	g./L.	oz./gal.	g./L.	oz./gal.
Nickel ammonium sulfate	75	10	..	..	...	..
Nickel sulfate	..	..	54	7	70	9
Ammonium chloride	..	..	..	..	15	2
Sodium chloride	38	5	38	5	...	..
Boric acid	15	2	15	2	15	2
Sodium sulfate (anhyd.)	..	..	..	..	100	13

The concentrations are given in terms of the hydrated salts.

To the above solutions, varying amounts of citrates, malates, lactates, alcohols (menthanol, ethanol, glycerol), and dextrose were added. The effect of the added agents on deposition by immersion of nickel on zinc, and their effect on the plating properties (on zinc) were investigated. The baths were also tested at increased nickel concentrations and over a wide range of pH.

RESULTS.

The most effective agents found for retarding the rate of displacement of nickel by zinc are lactates. Bright, soft and adherent deposits of nickel may be obtained on zinc from baths containing lactates.

Five g./L. (0.7 oz./gal.) of ammonium lactate added to solution No. 1 permits good deposits on zinc. Further additions up to 10 g./L. (1.3 oz./gal) have little or no effect; but excessive amounts of lactate are injurious, causing treeing at points of high current density.

Solution No. 1 is more suitable than No. 2 as a stock solution, the deposits being more adherent. The appearance of the deposits is very much the same from either bath.

Raising the nickel content of the bath increases the lactate-nickel ratio necessary to prevent streaking. Thus, increasing the nickel content of bath No. 2 from 54 to 70 g. of nickel sulfate per L. makes it necessary to double the lactate content. If the nickel sulfate concentration is increased to as much as 140 g./L., 50 g./L. of ammonium lactate must be added to prevent streaking. Moreover, under such conditions, the deposits are marred by numerous fine cracks. Hence, it is advisable to use a bath low in nickel.

The optimum current density in bath No. 1 to which five g./L. ammonium lactate has been added is 1.5 amp./dm.^{2} (14 amp./ft.^{2}), preceded by a strike for one minute at 2.0 amp./dm.^{2} (19 amp./ft.^{2}). Lower current densities tend toward streaking and higher current densities cause embrittlement and peeling. After four to six minutes plating, the deposit is impervious and the object may be transferred to a rapid plating bath if desired.

Streak-free deposits may be obtained from bath No. 1 to which has been added 10 g./L. of dextrose or sodium citrate or malate. The matte deposits are easily polished, but have a yellowish tone even when highly polished. On the other hand, the addition of 20 cc./L. of methyl alcohol permits very bright, smooth deposits; but such baths have a greater tendency to produce streaks.

The addition of ammonia to lactate bearing baths lessens the tendency to streak, but it also lowers the adhesion of the nickel to the zinc markedly. The addition of sulfuric acid increases the adhesion, but increases gassing, thus lowering the current efficiency, increasing the time necessary to cover the zinc, and increasing the possibility of streaks. Very bright deposits are obtained from acidified baths. Variations in acidity caused by unequal anode and cathode efficiencies may be controlled by pH measurements, since the buffering action of the ammonium lactate *in the concentration used* (5 g./L.) is slight. The best results are obtained at a pH between 3.7 and 4.3, determined colorimetrically with bromphenol blue.

The pH of the lactate bearing baths without the addition of acid or ammonia is from 4.0 to 4.2. The addition of large amounts of lactate buffers highly acid baths (pH below 2.0) or ammoniacal baths (pH above 6.0) toward a pH of 4.0. But the character of the deposits is not changed by the addition of the buffer to such baths. In other words, the acid or ammonia concentration is the controlling factor in highly buffered baths, rather than the pH.

The addition of lactate to high sodium sulfate baths (No. 3) increases the tendency to streak instead of lowering it. Presumably this is due to a lowering of the cathode polarization by the lactate since Thompson[8] points out that the effectiveness of such baths is probably due mainly to high polarization. Deposition by immersion from such baths is retarded by the addition of lactate.

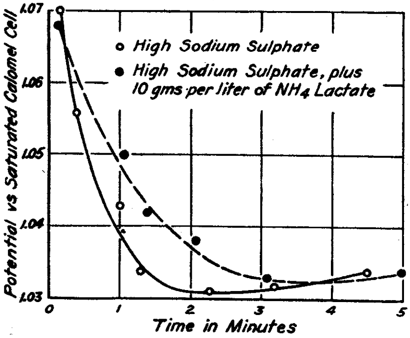

FIG. 1. Potential of zinc in nickel solutions, Bath No. 3.

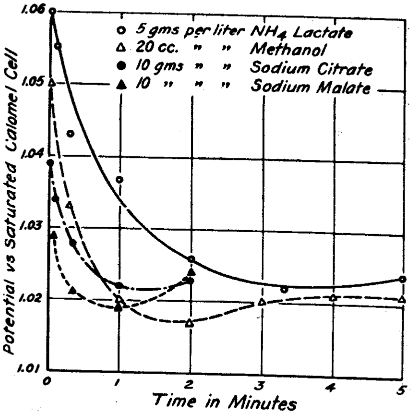

FIG. 2. Potential of zinc in nickel solutions, Bath No. 1.

Visual examination of zinc strips immersed in the various solutions show that many substances are capable of retarding the rate of chemical deposition of nickel. This property is possessed by hydroxy acids such as citric, malic and lactic; by certain alcohols, methanol and ethanol, but not by glycerol; and by at least one sugar, dextrose.

Visual examination and comparison of immersed specimens is unsatisfactory. Measurement of the change of potential (with time) of zinc in nickel solutions offers some advantages. The potential of a metal against a given solution depends partly on the concentration of that metal in the solution immediately adjacent to the surface of the metal. When zinc is immersed in nickel solutions, it displaces nickel

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[8] *loc. cit.*

in the solution and accumulates in the film surrounding the metal, since the process of diffusion requires time. Assuming the rate of diffusion to be substantially the same in all cases, the rate of change of potential corresponds to the rate at which zinc accumulates in the solution which in turn is roughly equal to the rate at which nickel is displaced by zinc. The attached curves show that the various added agents have characteristic effects on the reactions taking place, and consequently on the rate of change of potential. The curve for citrates is similar to that for malates. The curve for lactates differs materially from that for citrates or malates (Fig. 2). The curve for the high sodium sulfate bath (Fig. 1) is at higher potentials than for the other baths. Apparently the sodium sulfate affects the rate of change of potential. The effect of the lactate is still perceptible in the solution high in sodium sulfate. Acids lower the potential and ammonia raises it (Fig. 3).

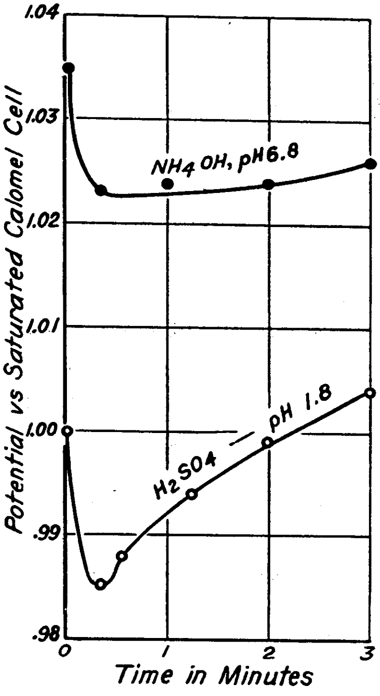

FIG. 3. Potential of zinc in nickel solutions, Bath No. 1.

Fig. 1 shows the effect of adding 10 g./L. of ammonium lactate to the high sodium sulfate bath, pH 4.0 to 4.3.

Fig. 2 shows the effect of 20 cc. methanol, 5 g. ammonium lactate, and 10 g. sodium citrate and malate per L., pH 4.0 to 4.3.

Fig. 3 shows the effect of adding ammonia or sulfuric acid.

CONCLUSIONS..

1. Displacement of nickel from its solutions by zinc is retarded by salts of hydroxy acids, alcohols and dextrose.
2. Lactates are especially effective in retarding deposition by immersion.
3. Good deposits of nickel on zinc can be obtained from solutions containing lactates. The yellow tone of deposits from citrate bearing baths is not met with.
4. The best deposits are obtained at a pH between 3.7 and 4.3. More acid baths increase the possibility of streaking; more basic baths decrease the adhesion.
5. Highly acid or ammoniacal baths may be buffered to the optimum pH by the addition of excessive amounts of ammonium lactate, but the plating characteristics of such baths are not altered by the buffering.
6. The ratio of lactate to nickel in the baths must be increased as the concentration of nickel is increased.

ACKNOWLEDGMENT.

The author wishes to express sincere thanks to Professor O. P. Watts for advice and encouragement received in conducting this investigation.

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Written discussion, preferably typewritten and in triplicate, of this paper is invited and should be sent to The Electrochemical Society, Columbia University, New York City.

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31

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THROWING POWER AND CURRENT EFFICIENCY OF THE NICKEL PLATING SOLUTION AT LOW AND AT HIGH pH.[1]

By RUSSEL HARR.[2]

ABSTRACT.

The throwing power of high pH solutions is better than that of low pH solutions under all conditions of temperature and current density. The throwing power of all solutions is improved by raising the temperature. Low pH solutions, which have very poor throwing power at room temperature, give a greater increase of throwing power with a given increase of temperature. The throwing power of low pH solutions increases with increase of current density, while that of high pH solutions decreases. Increasing the concentration of nickel sulfate from 300 g./L. (40.1 oz./gal.) to 450 g./L. (60.2 oz./gal.) causes a small decrease of throwing power for high pH solutions and a small increase of throwing power for low pH solutions. Hydrogen peroxide has very little effect on throwing power in solutions of high pH due to its rapid decomposition. In low pH solutions it may reduce throwing power very seriously due to the formation of soluble ferric salts. Iron in the ferrous state has no effect on throwing power. Iron in the ferric state (only soluble in low pH solutions) is most effective in reducing throwing power. More reproducible results are obtainable in the determination of throwing power by the use of small wire cathodes.

The only outstanding development in the field of nickel plating since the introduction of the Watts rapid-plating bath in 1916 is that of the low pH plating bath which was first proposed by W. M. Phillips to both the Electroplaters' and The Electrochemical Societies in 1930. The commercial development and application of chromium plating which

[1] Manuscript received June 28, 1933.

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started about 1923 has made it necessary to improve the quality of nickel plating since for most applications, nickel is used as an undercoating. As an undercoating for chromium plating, nickel must be of better quality, especially with regard to toughness and adherence if trouble is to be avoided. It is therefore of great commercial importance to know the advantages and disadvantages of the best nickel solutions. For this purpose tests were selected requiring no personal judgment, since biased opinions have too often been accepted as facts, especially in plating literature. The throwing power and current efficiency have been determined for medium and high nickel concentration solutions, at high and low pH, for several conditions of current density and temperature which are being used in industrial practice.

METHODS.

Preparation of Solutions.

A good commercial grade of salts for use in electroplating was used in the following experiments. After dissolving the salts according to the concentrations given in Table I, 20 cc./L. (3 oz./gal.) of 3 per cent hydrogen peroxide was added to oxidize the iron (contained as an impurity) to the ferric state and then an excess of nickel hydroxide was added and the solution was boiled. Boiling decomposes the excess hydrogen peroxide and brings the solution more rapidly to an equilibrium pH. After cooling to room temperature the excess nickel hydroxide and the precipitated iron were removed by filtering. It has been stated[3] that this treatment may reduce the boric acid content of the solution. However, there was no appreciable loss of boric acid when a solution of boric acid alone was boiled with an excess of nickel hydroxide.

As indicated in Table I, two concentrations of nickel were employed at high and low pH. The high pH values were obtained by boiling the solutions with nickel hydroxide. This procedure does not give the same pH for both concentrations of nickel sulfate; the high concentration solution came to an equilibrium pH value of 5.4 (quinhydrone) while the medium concentration solution came to equilibrium at 5.7. The value of 2.0 pH (colorimetric) was selected for the low pH solutions because the buffer characteristics of the medium concentration solution are best at this particular value (see Fig. 2). This curve represents data

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[3] Macnaughtan and Hammond, "The influence of acidity of the electrolyte on the structure and hardness of electrodeposited nickel." Trans. Faraday Soc., **27**, 635 (1931).

obtained by adding 4 *N* sulfuric acid to one liter of the 300-H nickel bath and then determining the pH by the colorimetric method.

Determination of pH.

The acidity of the original solutions was measured by means of the quinhydrone electrode. Duplicate tests were also made by the colorimetric method using the Hellige comparator. In testing these concentrated nickel solutions by the colorimetric method, it was necessary to use a much thinner cell than those furnished with the comparator. Cells were made of thin sheet celluloid of such dimensions that the thickness of solution was about $\frac{3}{16}$ in. (19 mm.). The intense green color of the most concentrated solution made color comparison difficult even with these thin cells. Since only 1 cc. samples of the solutions were required for a pH test, it was possible to run a number of checks of the pH of the solutions during the course of the experimental work without seriously changing the concentration of the solution under test. The conditions of running the experiments were finally adjusted so that no change of pH could be detected by the colorimetric method.

TABLE I.

Nickel Plating Baths: Composition of Component and of Plating Solutions.

	300-H	450-H	300-L	450-L
$NiSO_4.7H_2O$				
g./liter	300	450	300	450
oz./gallon	40.1	60.2	40.1	60.2
$NiCl_2.6H_2O$				
g./liter	30	30	30	30
oz./gallon	4.01	4.01	4.01	4.01
H_3BO_3				
g./liter	20	20	20	20
oz./gallon	2.68	2.68	2.68	2.68
NORMALITY				
Ni	2.4	3.9	2.4	3.9
Cl	.252	.252	.252	.252
H_3BO_3	.97	.97	.97	.97
pH				
Colorimetric	6.4	6.0	2.0	2.0
Quinhydrone	5.7	5.4	1.7	1.8

Current Efficiency.

Current efficiencies were determined with one liter of solution in round porcelain-lined jars, 12 cm. (4¾ in.) diam. and 17 cm. (6¾ in.)

high. The nickel anodes for these tests were Harshaw's "99 plus" containing carbon. The cathodes were one inch (2.54 cm.) strip copper extending the entire depth of the solution and placed flush against the side of the container, so that most of the plating deposited on the front of the strip. Current densities were calculated on the basis of the area of one side. Two such cells were placed in a water thermostat and connected in series. This method was used in order that the high and low pH solutions could be tested under identical conditions of temperature and current density. The current was measured by means of a copper coulometer assuming its efficiency to be 99.58 per cent.[4]

Throwing Power.

The method of measuring throwing power was essentially that developed at the Bureau of Standards by Haring and Blum.[5] According to their definition, throwing power is "the deviation (in per cent) of the metal distribution ratios from the primary current distribution ratio."

$$\text{T.P.} = \frac{K - (M_n/M_f)}{K}$$

$$K = \frac{D_f}{D_n}$$

D_f = distance to far cathode.

D_n = distance to near cathode.

M_f = weight of metal deposited on far cathode.

M_n = weight of metal deposited on near cathode (see Fig. 1.).

A change was made by substituting a small wire cathode for the usual sheet metal cathode whose area must be the entire area of cross-section of the solution. This condition is very seldom found in regular plating practice and in the case of the test leads to a condition where the results are unnecessarily complicated due to the unequal heating effect (especially at high current densities) of the large and small currents flowing in the near and far cathode compartments respectively. Although it is true that the results may be corrected for the change of resistance of the solution with change of temperature,[6] the corresponding change of polarization at the cathodes with change of temperature should not be ignored. Indeed, this effect probably accounts for

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[4] M. deK. Thompson, Theoretical and Applied Electrochemistry, New York (1925).

[5] Haring and Blum, "Current distribution and throwing power in electrodeposition." Trans. Am. Electrochem. Soc., **43**, 313 (1923).

[6] B. K. Braund, "Throwing power of plating solutions with particular reference to certain zinc plating solutions." Trans. Faraday Soc., **27**, 662 (1931).

the unexpected change noted in some cases by Flowers and Warner,[7] of positive to negative throwing power due to increase of current density.

The cell used (Fig. 1) for the determination of throwing power was made of 1 cm. (3/8 in.) hard rubber, 50 cm. (20 in.) long, 6 cm. (2.4 in.) wide and 7 cm. (2.8 in.) deep (inside dimensions). 2 mm. (1/16 in.) slots were cut in the sides for supporting the cathodes and anode in the proper relation to each other. The two cathode slots were 1 cm. (3/8 in.) from each end of the box, the anode being 8 cm. (3.2 in.) from one cathode, thus giving the ratio of distance 8 cm. to 40 cm. or 1 to 5. The anode was made by drilling 3/32 in. (2.4 mm.) holes in thin commercial sheet nickel which, prior to use was corroded electrolytically in dilute hydrochloric acid to provide a surface of large area which is favorable for good corrosion. Using this as a base, enough pure nickel was plated on the roughened surface for several runs. The volume of solution used in a test was one liter.

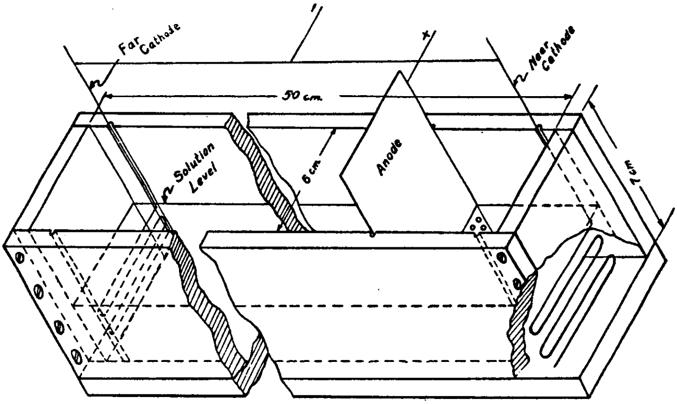

FIG. 1. Throwing power cell.

Since cells of different dimensions usually give different numerical results, a method for comparison of results of different cells was suggested in the original work. The throwing power of a simple easily prepared solution of copper sulfate under particular conditions of temperature and current density[8] was given as a convenient method for comparison. This solution in the original cell of the Bureau of Standards gave 7.4 per cent throwing power at 2 amp./dm.^{2} and 21° C. (18.6 amp./ft.^{2} and 70° F.). Under the same conditions this

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[7] Flowers and Warner, "Properties of low pH nickel plating baths." Trans. Electrochem. Soc., 62, 84 (1932).

[8] Blum and Hogaboom, Principles of Electroplating and Electroforming, p. 115, New York (1930).

solution gave an average value of 6.5 per cent in our cell with sheet metal cathodes.

The new cathodes developed were formed from 0.025 in. (0.635 mm.) copper wire. A 42 cm. (16.8 in.) length of wire was stretched 2 cm. (¾ in.) to stiffen it and thus facilitate handling and forming. Stretching reduces the diameter of the wire an average of 0.0005 in. (0.0127 mm.). The wire was then bent by means of pliers to make five passes 6.3 cm. (2.5 in.) long with each pass 5 mm. ($\frac{3}{16}$ in.) apart. The cathode thus formed has an area of 6.5 cm.^{2} (1 in.^{2}). Small numbered tags were soldered to the stems for purposes of identification. Although the side of the cathode facing the anode receives a somewhat heavier deposit, the difference is small due to the small diameter of the wire compared to the distance from the cathode to the anode.

The cathodes described above were used because results could be obtained which were more reproducible than was possible when sheet metal cathodes were employed. Conditions which may have caused erratic results when sheet metal cathodes were used are, the difference of temperature in the near and far cathode compartments, the change of composition of the solution during a particular test and changes of current density conditions when the box is not perfectly level. More reproducible results were obtained with the small wire cathodes.

Better results can be expected by using small cathodes for the following reasons: the total current flowing through the cell is so small that the unequal distribution of current in the near and far cathode compartments causes a difference of temperature of less than ½° C. even when a current density of 9.3 amp./dm.^{2} (100 amp./ft.^{2}) is used. In the case of sheet metal cathodes differences of temperature were found to be as much as 5° C. (9° F.). The small total current also permits the use of high current densities without seriously changing the composition of the solution during a particular test or for several tests, so that a number of tests may be run under different conditions of temperature and current density without the necessity for "doctoring" the solution either for its metal content or pH. The light weight of the small cathode permits a more accurate determination of the amount of deposit, since the weight of metal deposited is a larger fraction of the total weight in the case of the small cathodes than when sheet metal cathodes are used.

The current density values given in Table V have been calculated on the basis of one cathode because this gives a more correct idea of the conditions of the experiment.

The two cathodes were connected by a ⅛ in. (3.2 mm.) round copper rod. Battery clips were attached to each end of the rod to make connection with the wire stems of the cathodes. The jaws of the clips were plated with silver to provide a low resistance contact and the tension was adjusted to between 1,000 and 1,100 grams.

TABLE II.

Comparison of Throwing Power Results Using Sheet Metal and Formed Wire Cathodes.

Standard Copper Solution. Average current density 2 amp./dm.^{2} or 18.6 amp./ft.^{2} Temperature 21° C. (68° F.).

Sheet Metal Cathodes	Formed Wire Cathodes
7.6	27.2
5.4	22.0
6.5% Ave.	24.6% Ave.
Difference 24.6 — 6.5 = 18.1	

300-H Nickel Bath. Average current density 2.7 amp./dm.^{2} or 25 amp./ft.^{2} Temperature 60° C. (140° F.).

Sheet Metal Cathodes	Formed Wire Cathodes
—2.0	17.4
—2.4	18.7
—2.2% Ave.	19.0% Ave.
Difference 19.0 — (—2.2) = 21.2	

Temperature conditions were maintained uniform by supporting the cell in a water bath, and for the tests run at 60° C. (140° F.). It was necessary to cover the cell with plates of glass to prevent evaporation with consequent lowering of temperature. In most cases the temperature of the solution within the cell was held constant to within 1° C. (2° F.), although in a few cases the fluctuation was as much as 2° C. (3.6° F.) due to the poor conductivity of the hard rubber.

The above results show that the difference in the per cent throwing power due to the substitution of the formed wire cathodes for the sheet metal cathodes is approximately 20.

Determination of Resistivity.

Resistivity was determined in a wax impregnated wood cell 41 cm. (16⅛ in.) long, 2.5 cm. (1 in.) wide and 3.5 cm. (1⅜ in.) deep.

Solid nickel electrodes were placed at each end of the cell and 100 cc. of solution used as the test sample. The source of current was the regular 110 v. 60 cycle alternating current. Voltage was measured by a Weston meter Model 155, No. 455, with full scale deflection of 125 v. Current was measured by means of a Weston milliameter Model 155, No. 14614. Both meters were calibrated after the tests and the corrected values used to calculate resistivity. Values of current and voltage used in the tests were of such value that the meter readings were above the middle of the scale. Due to the small volume of solution the current caused an appreciable heating effect. The solutions were therefore allowed to cool below the temperature at which the readings were made before the current was applied. Then when the temperature passed through the desired values, readings of current and voltage were made.

RESULTS.

See Tables III, IV, V and VI.

TABLE III.

Effect of Temperature and Current Density on Current Efficiency.

High pH		Low pH	
300-H	450-H	300-L	450-L
0.93 amp./dm.^{2} (10 amp./ft.^{2}) — 30° C. (86° F.).			
99.38 98.55	98.81 98.78	65.83 66.05	81.98 81.78
98.96% Ave.	98.79% Ave.	65.94% Ave.	81.88% Ave.
5.4 amp./dm.^{2} (50 amp./ft.^{2}) — 30° C. (86° F.).			
99.14 99.43	99.70 100.32	86.26 87.31	91.82 91.69
99.28% Ave.	100.00% Ave.	86.78% Ave.	91.75% Ave.
5.4 amp./dm.^{2} (50 amp./ft.^{2}) — 60° C. (140° F.).			
99.92 100.4	99.36 99.33	96.65 91.45	90.66 91.46
100.16% Ave.	99.35% Ave.	91.05% Ave.	91.06% Ave.
9.3 amp./dm.^{2} (100 amp./ft.^{2}) — 60° C. (140° F.).			
100.15 100.05	99.81 99.50	93.94 92.82	93.96 92.84
100.10% Ave.	99.65% Ave.	93.36% Ave.	93.40% Ave.

TABLE IV.

Effect of Temperature on Resistivity.

Solution	Ohms/cm.^{3}		Reciprocal Ohms/cm.^{3}	
	30° C. (86° F.)	60° C. (140° F.)	30° C. (86° F.)	60° C. (140° F.)
300-H	17.4	11.2	0.0574	0.0893
300-L	15.9	10.7	0.0628	0.0935
450-H	15.9	10.3	0.0628	0.0971
450-L	15.3	9.7	0.0653	0.1030

TABLE V.

The Effect of Temperature and Current Density on Throwing Power.

High pH		Low pH	
300-H	450-H	300-L	450-L
5.4 amp./dm.^{2} (50 amp./ft.^{2}) — 30° C. (86° F.).			
9.6	7.4	—26.0	—19.4
9.0	3.8	—30.6	—19.8
7.6	4.4	—27.0	—24.4
8.7% Ave.	5.2% Ave.	—27.9% Ave.	—21.2% Ave.
5.4 amp./dm.^{2} (50 amp./ft.^{2}) — 60° C. (140° F.).			
17.4	10.0	—3.0	3.6
18.7	11.0	—1.4	2.8
20.8	13.0	—3.0	—0.4
19.0% Ave.	11.3% Ave.	—2.5% Ave.	2.0% Ave.
9.3 amp./dm.^{2} (100 amp./ft.^{2}) — 60° C. (140° F.).			
13.4	5.6	4.2	4.4
15.4	8.2	5.2	4.2
14.2	5.0	5.0	0.8
14.3% Ave.	5.7% Ave.	4.5% Ave.	3.1% Ave.

TABLE VI.

Summary of Average Throwing Power Results.

	300-H	300-L	450-H	450-L
5.4 amp./dm.^{2}— 30° C. 50 amp./ft.^{2} — 86° F.	8.7	—27.9	5.2	—21.2
5.4 amp./dm.^{2}— 60° C. 50 amp./ft.^{2} —140° F.	19.0	—2.5	11.3	2.0
9.3 amp./dm.^{2}— 60° C. 100 amp./ft.^{2} —140° F.	14.3	4.5	5.7	3.1

DISCUSSION OF RESULTS.

Flowers and Warner[9] claimed that their results were reproducible within a certain per cent. The formula set up from the Haring and Blum proposal is effective for calculating throwing power. It seemed desirable to express reproducibility in terms of deviation from an average of the results obtained on the basis of the formula of the Haring and Blum proposal. Thus from the data in Table V the deviation of the individual results from their average was 1.3 units; in only one case in that table there was a deviation of 2 units.

As an alternative consider the case where according to the above formula the following individual results were obtained: plus 2, minus 1, and minus 1. The average is zero. Now assume the first individual result, plus 2. The per cent deviation is 2 divided by zero and multiplied by 100 which equals infinity.

Thus it is clear that the proposal to express the deviation in units instead of per cent is more defensible. The mean deviation from average values of throwing power as given in Table V is 1.3 units, and in only one case was the average deviation more than 2 units.

Current Efficiency.

Table III gives values of current efficiencies for nickel solutions of medium and high nickel concentration. Each solution was tested at high and low pH, high and low temperature and at high and low current density. The principal object of these tests is to serve as a check for the throwing power tests since it has been pointed out in earlier work[10] that cathode efficiency is the most important factor in determining throwing power in nickel plating. It will be noticed that high pH solutions have practically a constant cathode efficiency of about 99 per cent which is not appreciably affected by concentration of nickel, or by change of temperature or current density. Thus it may be said that throwing power will not be poor and that change of temperature and current density will not have a large influence in changing the throwing power of high pH solutions.

Low pH solutions present an entirely different condition. Relatively large changes of current efficiency were obtained by changing each one of the three variables—concentration, temperature, and current density. The solution containing a high concentration of nickel

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[9] Flowers and Warner, "Properties of low pH nickel plating baths." Trans. Electrochem. Soc., 62, 84 (1932).

[10] H. E. Haring, "Throwing power, cathode potentials and efficiencies in nickel deposition." Trans. Am. Electrochem. Soc., 46, 107 (1924).

gives a smaller increase of current efficiency with increase of current density, at low temperature. This indicates that the high concentration solution will probably have the better throwing power. At the high temperature the change of efficiency with current density is about the same for both solutions, thus indicating that efficiency will not be the ruling factor if there is a difference of throwing power.

The effect of temperature on throwing power can be seen by comparing the extent to which the efficiency is changed at the high and low temperature by change of current density. In the case of both concentrations of nickel the efficiency is increased much less at the high temperature. It can therefore be predicted that the throwing power will be better at the high temperature for both solutions.

Table IV gives a comparison of the resistivity and conductance of the nickel solutions under the same conditions of temperature as were used in the current efficiency and throwing power tests. It may be rather surprising that the resistivity should show such a small decrease due to the addition of acid. The decrease is even less for the high concentration of nickel than for the medium concentration. The decrease of resistivity with increase of temperature was approximately the same for all solutions and was about 30 per cent for the temperature difference of 30° C. to 60° C. (86° F. to 140° F.). Since low resistivity makes a given value of polarization more effective in determining the distribution of current, it may be predicted that increased temperature will give better throwing power due to the decreased resistivity of the solution.

Very good agreement is noted for the resistivity of the "300" solutions when compared with the values given by Flowers and Warner using the Kohlrausch method for similar solutions.

Throwing Power.

Haring and Blum have shown that throwing power depends on the rate of change of cathode current efficiency and polarization with change of current density and the resistivity of the plating solution. When the current efficiency improves with increase of current density, poor throwing power may be expected. Polarization usually increases with increase of current density. The effect of polarization on throwing power will depend on the magnitude of the increase, and its relative value compared to the IR drop through the solution. The influence of any given voltage of polarization will be greatest in a solution having the lowest resistivity, other things being equal.

Table VI gives a summary of average throwing power results showing the effect of four variables, concentration, pH, temperature, and current density. The effect of concentration at high pH will be seen by comparing solutions 300-H and 450-H. Under all conditions of temperature and current density, the medium concentration (300-H) solution has the better throwing power. This result is not due to changes of current efficiencies as has already been pointed out in the discussion of Table III, the efficiencies of both series of solutions being very nearly the same. It should also be noticed in Table IV that the resistivity is not greatly changed by the concentration of nickel sulfate. Since, in general, polarization voltages are greater in the more dilute of two similar solutions, it is quite likely that the better throwing power observed in the more dilute solution is due to its greater change of polarization with increase of current density. The effect of concentration on throwing power at low pH is shown by comparing solutions 300-L and 450-L. In this case the high concentration solution has the better throwing power, except at the high current density. These results agree with deductions made while considering Table III, namely that at low temperatures and current densities, there is less change of efficiency with change of current density in the concentrated solution. At high current density the efficiencies are equal, and since the medium concentration solution has the best throwing power, it is probably due to the higher cathode polarization.

The effect of pH on throwing power will now be considered. First of all, observe that the influence of pH on resistivity is small (Table IV). We may state, therefore, that the effect of change of pH on throwing power will not be due to the change of resistivity. It is found that for both concentrations of nickel, the throwing power is much less for the low pH solutions, but that the difference is not so great at high temperature and high current density. These results are in excellent agreement with predictions made on the basis of changes of efficiencies with changes of temperature and current density.

Since it has become customary to express the acidity of nickel plating solutions in terms of the pH scale rather than as the actual concentration of acid, it was considered of interest to determine whether throwing power was affected more directly by a change of pH or by the change of concentration of acid. Accordingly, throwing power results were obtained for the medium concentration nickel solution for several additions of acid and the pH was determined by the colori-

Try gluconic acid

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A NEW BATH FOR THE DIRECT NICKELING OF ZINC.[1]

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ABSTRACT.

Methods of direct nickeling of zinc are briefly reviewed. It is shown that several agents, notably lactates, retard displacement of nickel by zinc, thereby permitting direct nickeling of zinc. It is also shown that these agents affect the rate at which the potential of zinc in nickel solutions changes with time.

INTRODUCTION.

An early investigation of the problem of direct nickeling of zinc was made by Hammond.[3] He showed that the addition of sodium citrate to dilute nickel baths makes it possible to deposit nickel direct on zinc. Pfannhauser[4] had previously advocated the use of citrates in the direct nickeling of zinc, but Hammond showed the possibilities of the method.

The use of a separate striking bath was proposed by Graham.[5] He showed that the problem of directly nickeling zinc is greatly simplified by covering the zinc with a layer of nickel *quickly,* thereby minmizing the possibility of streaking.

In the past, various investigators[6] have advocated the use of aluminum magnesium or alkali sulfates in nickel baths. Thompson[7] showed that the use of a high concentration of alkali sulfate in dilute nickel baths permits nickel to be directly deposited on zinc.

Hammond ascribed the beneficial effect of citrates to their ability to retard the rate of deposition by immersion of nickel on zinc. This paper

[1] Manuscript received June 29, 1933.

[2] Graduate student, University of Wisconsin.

[3] Hammond, Trans. Am. Electrochem. Soc., 30, 103 (1916).

[4] Pfannhauser, Die Elektrochemie (1900).

[5] Graham, Trans. Am. Electrochem. Soc., 44, 347 (1923).

[6] Watts, *ibid,* 23, 99 (1913).

[7] Thompson, *ibid,* 47, 163 (1925).

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shows that many other substances, notably lactates possess the property to a marked degree.

EXPERIMENTAL METHODS.

In testing the effect of the various agents on the rate of deposition, strips of zinc were uniformly polished, cleaned cathodically in the alkali cleaner, rinsed in dilute sulfuric acid, and immersed in the various nickel baths (at room temperatures) for the same lengths of time (varying from one-half to five minutes). The zinc strips were then compared with each other.

In measuring the rate of change of potential of zinc in the various baths, the metal was scoured with No. 0 emery paper and wiped with a clean cloth immediately before starting the tests. The potentials were taken with a student type L. & N. potentiometer. Preliminary trials were resorted to in order to obtain the first readings in as close to zero time as possible.

Sheet zinc cathodes, 2 x 5 cm. (0.79 in. x 1.97 in.), flanked by nickel anodes were used in testing the plating properties of the baths. Both flat and bent specimens were used, the latter being crimped at 90 degrees along the long axis.

TABLE I.

Stock Solutions.

Bath No.	1		2		3	
	g./L.	oz./gal.	g./L.	oz./gal.	g./L.	oz./gal.
Nickel ammonium sulfate	75	10	..	..	..	..
Nickel sulfate	..	..	54	7	70	9
Ammonium chloride	..	..	..	..	15	2
Sodium chloride	38	5	38	5	..	..
Boric acid	15	2	15	2	15	2
Sodium sulfate (anhyd.)	..	..	..	..	100	13

The concentrations are given in terms of the hydrated salts.

To the above solutions, varying amounts of citrates, malates, lactates, alcohols (menthanol, ethanol, glycerol), and dextrose were added. The effect of the added agents on deposition by immersion of nickel on zinc, and their effect on the plating properties (on zinc) were investigated. The baths were also tested at increased nickel concentrations and over a wide range of pH.

RESULTS.

The most effective agents found for retarding the rate of displacement of nickel by zinc are lactates. Bright, soft and adherent deposits of nickel may be obtained on zinc from baths containing lactates.

Five g./L. (0.7 oz./gal.) of ammonium lactate added to solution No. 1 permits good deposits on zinc. Further additions up to 10 g./L. (1.3 oz./gal) have little or no effect; but excessive amounts of lactate are injurious, causing treeing at points of high current density.

Solution No. 1 is more suitable than No. 2 as a stock solution, the deposits being more adherent. The appearance of the deposits is very much the same from either bath.

Raising the nickel content of the bath increases the lactate-nickel ratio necessary to prevent streaking. Thus, increasing the nickel content of bath No. 2 from 54 to 70 g. of nickel sulfate per L. makes it necessary to double the lactate content. If the nickel sulfate concentration is increased to as much as 140 g./L., 50 g./L. of ammonium lactate must be added to prevent streaking. Moreover, under such conditions, the deposits are marred by numerous fine cracks. Hence, it is advisable to use a bath low in nickel.

The optimum current density in bath No. 1 to which five g./L. ammonium lactate has been added is 1.5 amp./dm.^{2} (14 amp./ft.^{2}), preceded by a strike for one minute at 2.0 amp./dm.^{2} (19 amp./ft.^{2}). Lower current densities tend toward streaking and higher current densities cause embrittlement and peeling. After four to six minutes plating, the deposit is impervious and the object may be transferred to a rapid plating bath if desired.

Streak-free deposits may be obtained from bath No. 1 to which has been added 10 g./L. of dextrose or sodium citrate or malate. The matte deposits are easily polished, but have a yellowish tone even when highly polished. On the other hand, the addition of 20 cc./L. of methyl alcohol permits very bright, smooth deposits; but such baths have a greater tendency to produce streaks.

The addition of ammonia to lactate bearing baths lessens the tendency to streak, but it also lowers the adhesion of the nickel to the zinc markedly. The addition of sulfuric acid increases the adhesion, but increases gassing, thus lowering the current efficiency, increasing the time necessary to cover the zinc, and increasing the possibility of streaks. Very bright deposits are obtained from acidified baths. Variations in acidity caused by unequal anode and cathode efficiencies may be controlled by pH measurements, since the buffering action of the ammonium lactate *in the concentration used* (5 g./L.) is slight. The best results are obtained at a pH between 3.7 and 4.3, determined colorimetrically with bromphenol blue.

The pH of the lactate bearing baths without the addition of acid or ammonia is from 4.0 to 4.2. The addition of large amounts of lactate buffers highly acid baths (pH below 2.0) or ammoniacal baths (pH above 6.0) toward a pH of 4.0. But the character of the deposits is not changed by the addition of the buffer to such baths. In other words, the acid or ammonia concentration is the controlling factor in highly buffered baths, rather than the pH.

The addition of lactate to high sodium sulfate baths (No. 3) increases the tendency to streak instead of lowering it. Presumably this is due to a lowering of the cathode polarization by the lactate since Thompson[8] points out that the effectiveness of such baths is probably due mainly to high polarization. Deposition by immersion from such baths is retarded by the addition of lactate.

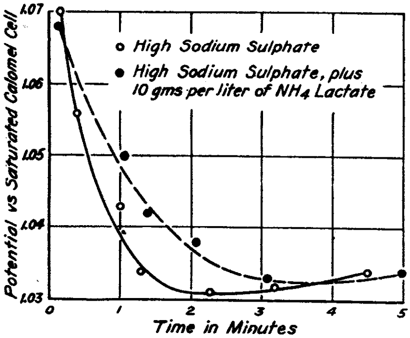

FIG. 1. Potential of zinc in nickel solutions, Bath No. 3.

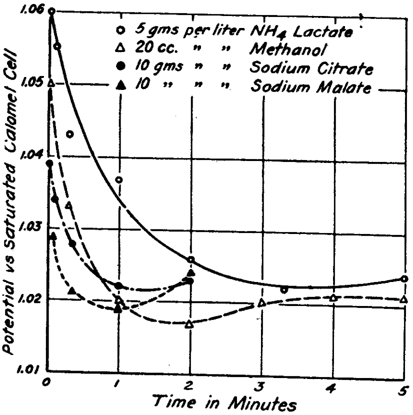

FIG. 2. Potential of zinc in nickel solutions, Bath No. 1.

Visual examination of zinc strips immersed in the various solutions show that many substances are capable of retarding the rate of chemical deposition of nickel. This property is possessed by hydroxy acids such as citric, malic and lactic; by certain alcohols, methanol and ethanol, but not by glycerol; and by at least one sugar, dextrose.

Visual examination and comparison of immersed specimens is unsatisfactory. Measurement of the change of potential (with time) of zinc in nickel solutions offers some advantages. The potential of a metal against a given solution depends partly on the concentration of that metal in the solution immediately adjacent to the surface of the metal. When zinc is immersed in nickel solutions, it displaces nickel

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[8] *loc. cit.*

in the solution and accumulates in the film surrounding the metal, since the process of diffusion requires time. Assuming the rate of diffusion to be substantially the same in all cases, the rate of change of potential corresponds to the rate at which zinc accumulates in the solution which in turn is roughly equal to the rate at which nickel is displaced by zinc. The attached curves show that the various added agents have characteristic effects on the reactions taking place, and consequently on the rate of change of potential. The curve for citrates is similar to that for malates. The curve for lactates differs materially from that for citrates or malates (Fig. 2). The curve for the high sodium sulfate bath (Fig. 1) is at higher potentials than for the other baths. Apparently the sodium sulfate affects the rate of change of potential. The effect of the lactate is still perceptible in the solution high in sodium sulfate. Acids lower the potential and ammonia raises it (Fig. 3).

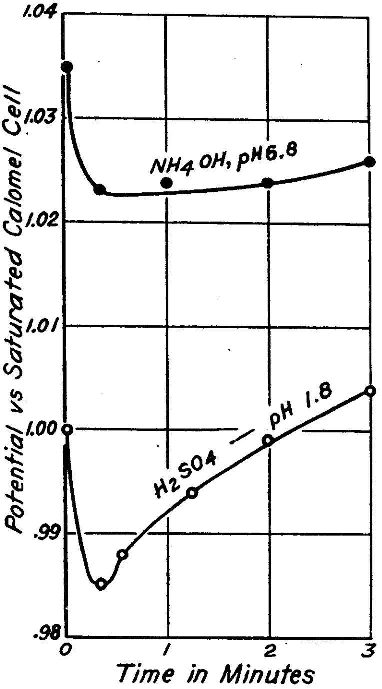

FIG. 3. Potential of zinc in nickel solutions, Bath No. 1.

Fig. 1 shows the effect of adding 10 g./L. of ammonium lactate to the high sodium sulfate bath, pH 4.0 to 4.3.

Fig. 2 shows the effect of 20 cc. methanol, 5 g. ammonium lactate, and 10 g. sodium citrate and malate per L., pH 4.0 to 4.3.

Fig. 3 shows the effect of adding ammonia or sulfuric acid.

CONCLUSIONS.

1. Displacement of nickel from its solutions by zinc is retarded by salts of hydroxy acids, alcohols and dextrose.
2. Lactates are especially effective in retarding deposition by immersion.
3. Good deposits of nickel on zinc can be obtained from solutions containing lactates. The yellow tone of deposits from citrate bearing baths is not met with.
4. The best deposits are obtained at a pH between 3.7 and 4.3. More acid baths increase the possibility of streaking; more basic baths decrease the adhesion.
5. Highly acid or ammoniacal baths may be buffered to the optimum pH by the addition of excessive amounts of ammonium lactate, but the plating characteristics of such baths are not altered by the buffering.
6. The ratio of lactate to nickel in the baths must be increased as the concentration of nickel is increased.

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University of Wisconsin.

Written discussion, preferably typewritten and in triplicate, of this paper is invited and should be sent to The Electrochemical Society, Columbia University, New York City.