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DEPARTMENT OF CHEMICAL ENGINEERING

UNIVERSITY OF WISCONSIN

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[FROM THE TRANSACTIONS OF THE AMERICAN ELECTROCHEMICAL SOCIETY, Volume XXVII, 1915, being the Transactions of the Twenty-seventh General Meeting, at Atlantic City, April 22 and 23, and at Philadelphia, April 24, 1915.

Cleaning and Plating in the Same Solution

BY

O. P. WATTS

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
			Current Density		Efficiency			
	C.	F.	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 cane 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.

[FROM THE TRANSACTIONS OF THE AMERICAN ELECTROCHEMICAL SOCIETY, Volume XXVII, 1915, being the Transactions of the Twenty-seventh General Meeting, at Atlantic City, April 22 and 23, and at Philadelphia, April 24, 1915.

The Temperature of Reaction Between Acheson Graphite and Magnesia

BY

O. L. KOWALKE and D. S. GRENFELL

A paper presented at the Twenty-seventh General Meeting of the American Electrochemical Society, at Atlantic City, N. J., April 22, 1915, President F. A. Lidbury in the Chair.

ON THE TEMPERATURE OF REACTION BETWEEN ACHESON GRAPHITE AND MAGNESIA.

By O. L. KOWALKE and D. S. GRENFELL.

Among the refractory materials for electric furnace construction, magnesium oxide, with a melting point of 2,800° C.,[1] and carbon, with melting point above 3,500° C., have been found satisfactory and quite indispensable. In the construction, however, they must frequently be in contact with one another, and at high temperatures several investigators have observed a reaction between these two materials.

In August, 1905, while melting some iron alloys in a granular carbon resistor furnace with walls made of magnesia brick, O. P. Watts[2] noticed that the carbon seemed to shrink in volume and that a black, soot-like deposit about one-half inch thick appeared on the interior walls of the furnace. This crust was first thought to be due to impurities in the resistor, but the substitution of other forms of carbon did not decrease the loss. He decided that the reaction was a simple reduction of the magnesia by the carbon and that it was reversible, basing his conclusions upon a chemical examination of the condensed product.

The same phenomenon was observed later by H. M. Goodwin and R. D. Mailey[3] when attempting to fuse magnesia in a carbon tube. They found that a black product condensed on the cooler part of the tube and determined that it was not a carbide, but did not fix its identity.

A study of this phenomenon was made by P. Lebeau[4] in an attempt to determine the nature of the reaction and to confirm

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[1] Melting Point of Some Refractory Oxides. Bur. Stand. Bull., **10**, (No. 212), 18.

[2] Action of Carbon on Magnesia at High Temperatures. Trans. Am. Electrochem. Soc., **11**, 279-89 (1907); Chem. Zeits., **31**, 739.

[3] Physical Properties of Fused Magnesia. Trans. Am. Electrochem. Soc., **9**, 90 (1906); Phys. Rev., **23**, 22.

[4] Reduction of Magnesia by Carbon. Compt. Rend., **144**, 799-801; Rev. Electrochem., **1**, 156-7.

the results obtained by the other investigators. His final decision was that a carbide of magnesium was formed.

R. E. Slade,[5] while carrying on an investigation with the same end in view, confirmed the opinion of Watts and of Goodwin and Mailey, and in addition found that the reaction in the case of the materials he used began at 1,700° C.

While determining the temperature of fusion and volatilization of magnesia on a base of carbon, a violent reaction was reported by Ruff, Seiferheld and Suda[6] at 2,000° C. With a graphite base, however, there could be observed no appreciable reaction below the fusion temperature of the magnesia, which they give at 2,500° C.

The present investigation aimed at the determination of the temperature at which carbon, in the form of Acheson graphite, will react violently with magnesia. Some preliminary work was done in 1913, but the present article covers the results of work done during the past year. Two sets of data were in reality obtained—a set made during the spring of 1914, and another, with different apparatus and pyrometer, during the fall of 1914. The data obtained at the two times are an excellent agreement.

Methods.

In the solution of this problem, three distinct methods of attack were pursued. In the first method, weighed samples of the two materials—magnesia and graphite—were heated in contact with each other for about half an hour at various temperatures and the loss in weight determined. It was thought that a decided increase in the loss would result at the temperature of violent reaction. This method failed in its purpose because of the fact that it was almost impossible to maintain the furnace at a constant temperature for more than a few minutes. These runs did indicate, however, that the reaction proceeds according to the equation

$$MgO + C \leftrightarrows Mg + CO$$

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[5] Reduction of Magnesia by Carbon. Proc. Chem. Soc., 24, 29; Chem. Soc. Jour., 93, 327-33.

[6] Researches in the Realm of High Temperatures: I. On the Fusion and Volatilization of Our Most Refractory Oxides in the Electric Vacuum Furnace. Zeits. f. anorg. Chem., 82, 373-400; (Abst.) Silikat. Zeits., 1, 212.

because the ratio of the losses MgO/C was approximately the theoretical, according to this equation, as shown in the accompaying table:

TABLE I.

Run No.	MgO Loss	C Loss	Ratio of MgO/C (Theoretically 3.33)
3	3.68g	1.05g	3.50
4	2.41	0.66	3.65
5	3.35	0.95	3.53
7	4.38	1.16	3.78
8	0.65	0.23	2.83
9	9.43	2.71	3.48

The second method was based on the fact that the reaction from left to right is endothermic. When the substances attain the reaction temperature there will be heat absorbed from the surroundings which will result in a fall of temperature. This method yielded some excellent results, as shown in Figs. 4 and 5.

After the temperature had been determined, some data on the rapidity of the reaction seemed desirable. The materials were heated in a vacuum furnace of the Arsem type, provided with a mercury manometer for determining the pressure inside the furnace. If the gas, carbon monoxide, were formed, the pressure would increase suddenly at the temperature of reaction and would be an indication of the rapidity of the reaction. The experiments with the vacuum furnace indicated no great rise in pressure, and the usual deposition of carbon and magnesia was observed. This provides additional evidence of the reversibility of the reaction; for had it not reversed, the pressure should have increased, due to the formation of carbon monoxide. As soon as the products of the initial reaction reached the outer, cooled portions, the magnesium reduced the carbon monoxide to amorphous carbon and the two solids were as in the beginning.

Apparatus.

The observations of temperature were made with an optical pyrometer of the Holborn-Kurlbaum type, equipped with a series of revolving sectors for high temperature work, as suggested by Mendenhall.[7] In the calibration of this instrument the standard

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[7] Notes on Optical Pyrometry. Phys. Rev., 33, 74.

was a platinum and platinum-rhodium thermocouple certified by the Bureau of Standards. For the calibration of the optical pyrometer a specially constructed "black-body" tube furnace was used. The E.M.F. of the couple was measured on a Leeds and Northrup Type "K" potentiometer, and the current in the pyrometer lamp on a Weston ammeter, calibrated in the State Standards Laboratory.

The calibration was conducted at one known temperature by the method of Prof. C. E. Mendenhall[8] applying Wien's Distribution Law

$$\text{Log } J = K_1 - \frac{K_2}{T} \quad \dots\dots\dots\text{(a)}$$

If a rotating sector be interposed between the source of light and the pyrometer, such that the intensity is reduced by a factor $\frac{1}{S}$, the above equation becomes

$$\text{Log } \frac{J}{S} = K_1 - \frac{K_2}{T_s} \quad \dots\dots\dots\text{(b)}$$

By subtraction (a—b),

$$\text{Log } S = K_2 \left(\frac{1}{T_s} - \frac{1}{T}\right) \dots\dots\dots\text{(c)}$$

By taking a number of discs and obtaining corresponding values of current through the pyrometer lamp filament, a series of values of T_s can be computed which correspond to the temperatures which would be obtained with an open objective.

In this way, values of T_s were obtained for the various sectors, and were plotted on co-ordinate paper. This gave a calibration curve for an open objective. Then, to obtain the calibration curve for a given sector, the proper value of S was substituted in the equation (c); the value of T_s was obtained from the above-mentioned curves for a given current value, and the temperature T corresponding to that current was computed.

For example, on the open-objective calibration curve, a current of 700 milliamperes corresponds to a temperature of 1,253° C. or 1,526° absolute.

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[8] Notes on Optical Pyrometry. Phys. Rev., 33, 74.

Furnace.

The special furnace employed in this work was a resistor furnace constructed of magnesia brick, insulated with air-slaked lime and fire brick, as shown in Fig. 1.

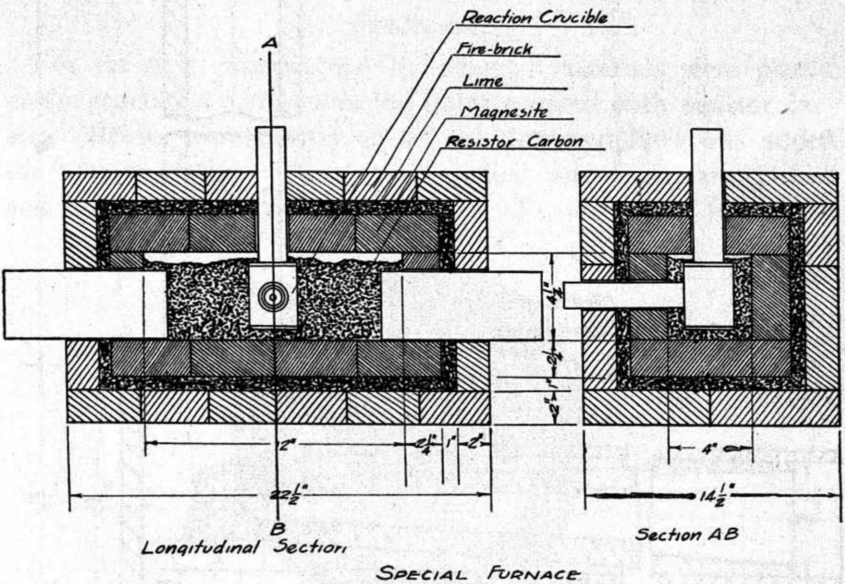


FIG. 1.

Reaction Crucible.

The reaction crucible shown in Fig. 2 was turned from a rod of Acheson graphite, and was provided with a sight tube for the pyrometer observations and a chimney for the escape of the products of the reaction. Various modifications of this idea were tried in the course of the researches, but in the final form the chimney was made very large in comparison with the size of the crucible. The magnesia rested on a slender support, to prevent any large transfer of heat from the crucible to the magnesia by conduction. (See Fig. 2.) It was found that the heat conducted to the magnesia test specimen through the graphite support frequently spoiled the test, so the stem of the support was made small to compel heating by radiation. The materials of the reaction were the purest attainable. The magnesia was some of the electrically fused magnesia made in this laboratory. The graphite specimen was machined from a solid rod of Acheson graphite.

At first the magnesia sample (about 5 g.) was placed inside the reaction chamber on a small graphite support before the end

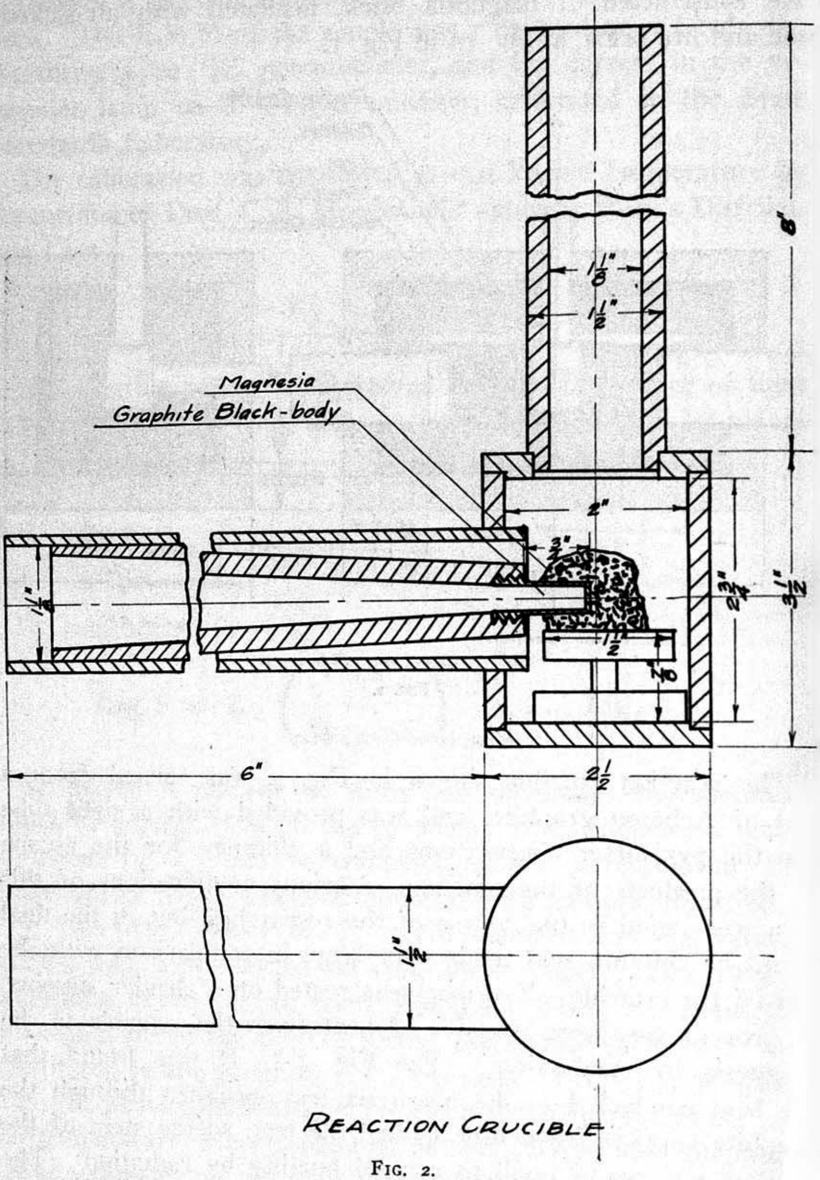


FIG. 2.

of the "black-body" tube. Next, a larger sample (about 15 g.) was used and one side was ground to a plane surface and placed in intimate contact with the end of the black-body tube. Runs

12 and 14 were made in this manner (see Fig. 4). Lastly, the magnesia pulverized to about a 50 mesh and, moistened with water, was molded about the sight tube. The remainder of the runs were all made with this arrangement.

Procedure.

For the first experiments the weighed materials were placed in the reaction crucible and the latter covered with resistor carbon. Bricks were placed on top of this, and lime was added for heat insulation. Power was applied, and temperature, time and current observations were made. No wattmeter was available at first, but later one was installed and the power input could then be measured, each run being made with constant input. After the furnace had cooled, it was opened; the materials were removed from the reaction crucible and reweighed. Curves were plotted showing the relation between temperature and the percentage loss in weight. Due to the removal of the resistor carbon after each run, the resistance of the furnace varied greatly from run to run, and a similar power input did not result in the same rate of heating.

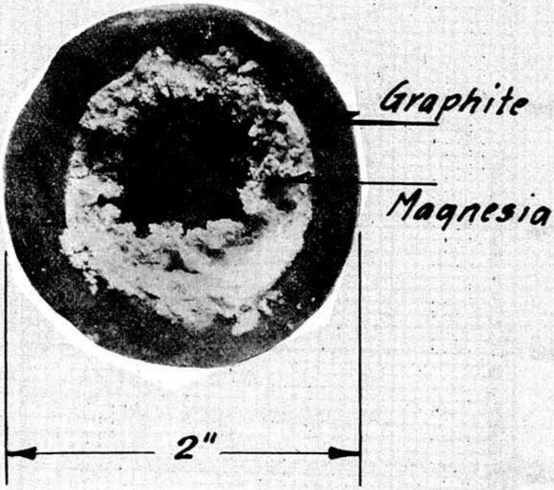
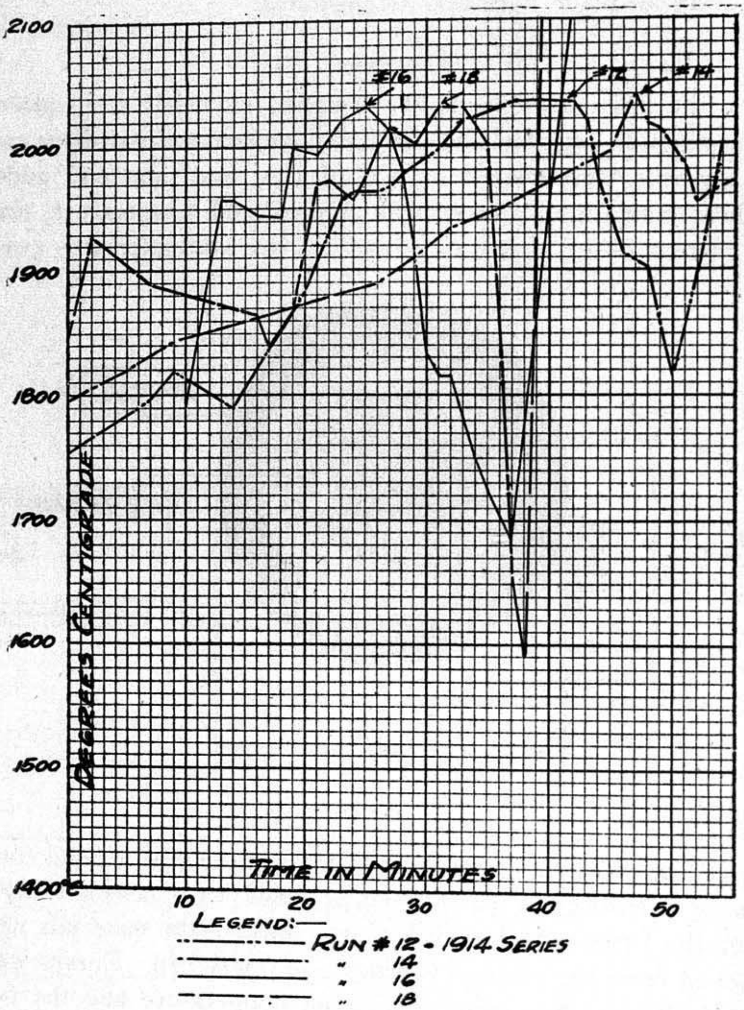


FIG. 3.

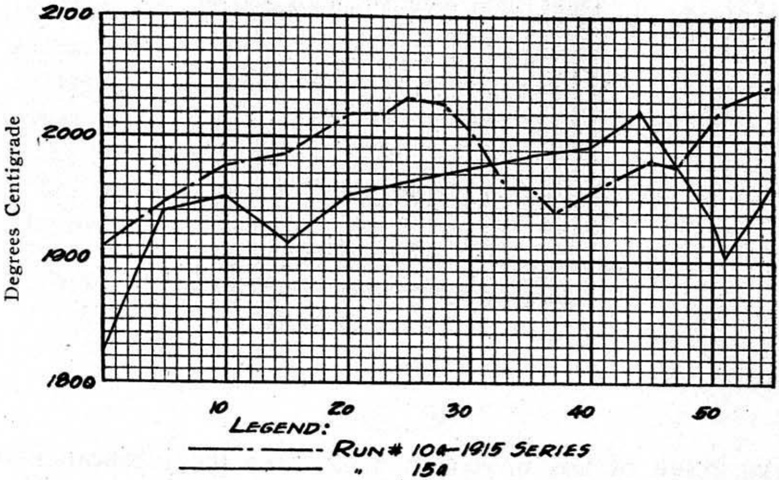
The second method of attack required the same apparatus and manipulation, excepting for the omission of the weight data. The recorded data consisted of time, current or power and temperature, as shown graphically in Figs. 4 and 5. Another obstacle was the fume which resulted from the reversed reaction in the cool portions of the furnace. The products of the reaction condensed in the chimney (see photograph, Fig. 3), and a pressure resulted in the furnace from the stoppage of this exit. As the pressure increased in the crucible, a portion of the magnesium vapor passed through the walls of the pyrometer sight tube, united with oxygen and formed a white fume, reducing the in-



RESULTS OF THE MORE SUCCESSFUL RUNS - 1914

Fig. 4.

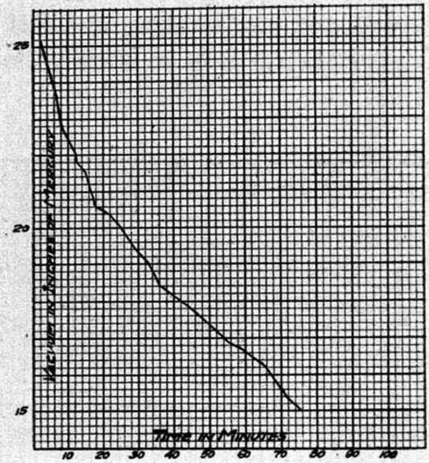
tensity of the light and finally closed the sight tube. It was necessary at frequent intervals to remove the condensed magnesia and amorphous carbon from the chimney by forcing a passage with a carbon rod. At this time an intense bright flame issued from the chimney, showing that the reaction was proceeding with great violence. The fumes from the combustion of the magnesium vapor filled the room with a haze. The chimney was then increased in size to about one-half the diameter of the crucible, but even then it was frequently stopped at the end of the run.



RESULTS OF THE MORE SUCCESSFUL RUNS-1915

FIG. 5.

For the experiments in the vacuum furnace a small crucible of about one and one-half inches diameter and three inches high was turned from graphite and filled with loose, pulverized magnesia. A cover was provided with a sight tube for the pyrometer. Holes were drilled in the sides of the crucible for the escape of the products of reaction. This was placed within the graphite spiral of the Arsem vacuum furnace and the chamber sealed. The suction was applied and the power circuit closed. Preliminary tests showed that the furnace was fairly gas tight, although there was a slight leakage at the joints of the rubber tubing connections. The evacuation was stopped at a temperature of 1,500°-1,600° C., and observations of time, power, temperature and pressure were noted. There was a great deal of difficulty in measuring the temperature within the vacuum furnace because of the fume in the furnace and also because of a deposit of condensed magnesia on the inner side of the mica window. For this reason the temperature data secured are not considered reliable.



RUN #5V ON THE ARSEM VACUUM FURNACE

FIG. 6.

Results.

One result of this investigation has been the justification of the original assumption that the equation of the reaction is expressed thus:

$$MgO + C \leftrightharpoons Mg + CO$$

This is proven by the facts:

(1) The ratio of the combining weights is closely that of the equation.

(2) The products of the reaction have all the appearance of being MgO and C (see photograph, Fig. 3).

(3) The pressure of the vacuum furnace does not rise appreciably at the reaction temperature, showing the reversibility.

(4) The extremely bright flame of magnesium burning to magnesium oxide occurred again and again at the reaction temperature, and the collected magnesia formed is characteristic.

The pyrometric results indicate that the reaction commences slowly at about 1,950° C. (this temperature being somewhat dependent on the rate of heating), and becomes very violent at temperatures above 2,030° C. This agrees well with the results of Ruff, Seiferheld and Suda, who found a violent reaction with amorphous carbon at 2,000°.

Since the reaction temperature has been found many times at about 2,030° C., and that with definiteness, it is suggested that this may be a "fixed point" for the calibration of optical pyrometers. This arrangement has the following advantages: (a) can be carried on in presence of carbon, (b) done at atmospheric pressure, (c) no contamination of materials, (d) cheapness of test materials.

Care must be exercised to provide adequate vents to the reaction chamber to avoid a pressure inside which produces fume in the pyrometer black-body tube.

The power in the furnace should be kept constant for satisfactory results.

Chemical Engineering Department,
University of Wisconsin.

DISCUSSION.

C. W. BENNETT (*Communicated*): There is no doubt but that magnesia is decomposed by carbon or graphite at high temperatures. It would have been of much more interest to practical electrochemists if Mr. Kowalke had studied the point of break-down of commercial magnesia fire-brick instead of chemically pure magnesia, as we all know that the commercial article is less resistant than chemically pure material.

Granting the decomposition of magnesia by carbon and graphite, the mechanism of this break-down is quite a different proposition.

Let us assume that magnesia is reduced by carbon to magnesium. I do not believe it would be possible to distil magnesium through carbon without forming carbide. As a matter of fact we all know that magnesia and carbon react to form magnesium dicarbide at approximately 1,700°. Furthermore, a reaction occurs between magnesia and carbon at 1,500°.

From Fig. 6 it would appear that the pressure in the vacuum furnace does rise at 1,600° at least and that an increase of two-fifths of an atmosphere occurred in a little over an hour. There are no data from which it can be determined whether the temperature at this time was higher than 1,600°. As a matter of fact we know that there is an increase of pressure at 1,500°, 1,600° and 1,700°, and carbon monoxide is formed.

In the third conclusion where it is stated that the pressure in the vacuum furnaces does not rise appreciably at the reaction temperature, I think it will depend upon how long the product has been heated below the so-called reaction temperature and above 1,500°. If the charge is completely transformed to carbide by heating for an appreciable time at, say, 1,600°, then run up to 1,950°, there is no reason why there should be an increase of pressure, because the carbide would distil and condense on the cool parts of the furnace without changing the pressure appreciably. We have not yet determined the composition of these carbides, but it is believed that oxidation of the carbides yields free carbon and magnesia. This fact would not be occasioned by carbon monoxide, but would be caused by oxygen of the air upon opening the Arsem furnace. Whether oxidation is possible or not, we have repeatedly demonstrated that it is impossible to open an Arsem furnace and obtain the product as it was formed in the neutral atmosphere. Oxidation always occurs very rapidly. As a matter of fact I have scraped from the cool parts of the furnace a magnesium compound and caught it in the palm of my hand. The heat from the palm of my hand was sufficient to cause the whole mass to take fire spontaneously.

The magnesium flame would be occasioned by the oxidation of such material as well as the oxidation of pure magnesium. It would therefore appear that the conclusions reached in this paper are largely unwarranted and are open to serious criticism.

E. F. NORTHRUP: This paper has had some interest for me, because I found occasion to study the problem of finding a stable material for electrical insulation between slabs of graphite, and to get the information I made some measurements on magnesium oxide, aluminum oxide, and certain other oxides, and I have a few facts which may be of interest, which I will presently give.

Before doing so, I wish to suggest a possible means of studying the moment at which violent reactions begin. An arrangement which I have already described in Metallurgical and Chemical Engineering, February, 1914, enables one to be sure that one is measuring the conductivity or electrical resistance of the material itself.

I have taken hundreds of observations, and I have not known any case in plotting a resistance curve against temperature where there is not some kind of an inflection when there occurs any chemical or physical change in the material measured.

Suppose you had the arrangement I have described down in a furnace, and had a means of measuring the temperature, and were measuring the electrical resistance. When you got a violent chemical reaction, you would have unquestionably a decided inflection in the curve. Unfortunately, in my work I did not carry my temperatures on magnesium oxide high enough to get the violent reaction, but as far as I went I can assure you that the figures I have put down, for this class of work, are quite accurate, and they have some bearing on the properties of magnesium oxide. I will put the figures down, temperature against resistivity of MgO in ohms per centimeter cube.

C°	Resistivity in ohms per centimeter cube
1060	420,000
1100	320,000
1170	62,000
1230	24,000
1352	510
1386	415

I should say, to be accurate, that there was mixed with the magnesium oxide 10 percent of pure magnesium carbonate. The presence of this amount of magnesium carbonate seemed to slightly cake or sinter the electrically shrunk magnesium oxide, so that the mixture did not drop out from between the slabs of graphite. It is, after heating, about as hard as plaster of paris.

The figures just given by themselves are not so interesting unless you have some comparison figures. I give now some figures obtained for electrically shrunk aluminum oxide. It was in the form of powder, and is as pure as the best made by the

Norton Company. I only list here every fifth one of the figures I obtained:

C°	Ohms per centimeter cube
26	90×10^6
1170	23.8×10^3
1380	16.3×10^3
1458	6.5×10^3

Noting the above figures, we have 16,300 ohms as the resistivity of Al_2O_3 against 415 ohms as the resistivity of MgO at a temperature of 1,380° C. Now why this difference? Perhaps the following fact has some bearing. When I took apart the graphite slabs between which the MgO had been clamped, their surfaces were covered with a thin blackish deposit of what appeared to be amorphous carbon, but when I took apart the graphite slabs between which the Al_2O_3 had been clamped the surfaces were polished, clean, and unaltered in appearance. It seems certain therefore that at a temperature of 1,450° C. there is no reaction between aluminum oxide and graphite, and that there is a slight reaction between magnesium oxide and graphite.

Without making any measurements of resistance or temperature I heated the magnesium oxide considerably higher than 1,450° C. and noted that the resistance went on falling rapidly and that it becomes unfit for an electrical insulator between slabs of graphite when the temperature is very high. By a small increase of voltage an arc is established at these high temperatures, which breaks the insulation down completely.

I think if some one interested in studying chemical reactions at these high temperatures would use the method I have suggested and plot resistivity curves, they would learn from the inflections in the curves where reactions begin and obtain perhaps some idea of their violence. The measurements should be made with low frequency alternating current—low frequency rather than high because there seem to be some strange capacity effects—and an alternating current galvanometer or sensitive electrodynamometer should be used as a detector. An ordinary Wheatstone-bridge connection should be used. It is probable that chemical changes would be shown by marked inflections in the curve. It would not be difficult to arrange for measuring the temperature. A graphite tube closed at the lower end could be inserted in the furnace and the bottom of this tube could then be viewed with an optical pyrometer. No fumes coming from the furnace could enter the tube to obscure the view.

Many ideas are held as to what constitutes high temperature; but I do not call a temperature high until one has passed 1,000° C. I wish more people would get busy on lines of investigation above 1,000° C., as it is the most fruitful field for original research work I know of.

A. T. HINCKLEY: I would like to point out a case in which the temperature of reaction between carbon and magnesia (MgO) is lower than that given in this paper.

Petroleum coke (ash under 0.5 percent and volatile matter under 0.25 percent) was finely ground and mixed with pulverized magnesia. This mixture was bonded with tar, molded and then baked to remove the volatile matter. This test piece was heated in a carbon tube furnace and the temperatures noted by means of Seger cones. At about 1,500° C. a marked decrease occurred in the crushing strength of the test pieces, indicating that the reaction had started, and at 1,600° the vigor of the reaction was marked by deposits on the walls of the tube, as noted by other workers.

The results indicate that the temperature at which this reaction may be termed vigorous depends upon the physical subdivision of the reacting materials and the intimacy of their mixture. On this account it does not seem that the temperature of reaction is well enough fixed to be made a standard for pyrometric measurements.

F. A. J. FITZGERALD: It would be better not to make measurements of "reaction temperatures" until a reaction temperature is defined. As Mr. Hinckley pointed out the so-called reaction temperature depends so closely on the conditions of the experiment that these results have no particular value.

W. R. WHITNEY: I take exception to Mr. Bennett's statement that it would have been better to try this experiment on magnesia fire-brick. A magnesia fire-brick is an indefinite thing, while pure magnesia is definite. We of this Society should stand for the knowledge gained from what we test, and when a man says he has tested a thing, we want to know exactly what he tested.

Moissan, in his book, mentions the fact that plates of magnesia in contact with carbon are stable at arc temperatures, and he used blocks of magnesia against blocks of carbon in the arc furnace. Therefore it must be an important matter to have the magnesia and the carbon in very close contact to produce any very violent reaction at 2,000° C.

J. W. RICHARDS: Whether a reaction between magnesia and carbon will take place at a given temperature will depend on the pressure put upon them. If the two are strongly compressed they will react at a lower temperature than if they are simply lying against each other. It also depends on the intimacy with which the materials are mixed.

What is the "temperature of reaction" is also indefinite, because in these reversible reactions the velocity of the reaction, starting low at a low temperature, increases very rapidly in a certain region of temperature, and it is only that range of temperature which can be indicated, and not any definite temperature, as one of active reaction. The practical temperatures at which endothermic reductions take place are roughly proportional to the amount of heat absorbed in the reaction. This is only another way of saying that the stronger the oxide the higher the temperature necessary to reduce it by carbon. The data to prove this generalization are fragmentary, but may be illustrated by the following approximate figures:

Oxide reduced	Calories absorbed per atom of oxygen	Approx. Temperature for Reduction
PbO	21,500	500° C.
FeO	36,500	750° C.
SnO_2	41,500	900° C.
ZnO	55,500	1050° C.
SiO_2	69,000	1500° C.
TiO_2	80,000	1600° C.
Al_2O_3	101,500	1800° C.
MgO	114,000	1950° C.

This is only a crude statement of a difficult problem, but it has its applications. Another deduction from these principles is that at any given reduction temperature, with several oxides present, the relative amounts of each reduced will be governed by the same considerations, and may be predicted from the calories absorbed in each reduction. An example of this is the presence of considerable silicon, some titanium and sometimes traces of aluminium in pig iron produced in the blast furnace. There are no large or important exceptions to this general principle.

WILLIAM R. MOTT: Referring to what Dr. Whitney said about Moissan's work, it is interesting to recall that Moissan tested several kinds of magnesia. He says that the magnesia purified by the method of Schloesing was not reduced by carbon. (See Moissan's book, The Electric Furnace, Translation by Lenher, page 24. Schloesing, C. R.) Moissan showed that the density of magnesia changed from 3.19 to 3.65 on heating in the electric furnace. Along with this change in density, Horton has found a peculiar change in resistance. (Magnesia decreased rapidly in resistance to about 1,200° C. but at 1,300° C. increases in resistance.) Hence, Prof. Kowalke is asked to discuss the effect of using magnesia of different densities on temperature of reaction, as well as magnesia prepared in different chemical ways.

W. R. WHITNEY: I would ask Prof. Northrup whether the small variation in figures for alumina depends on its purity, because in electrical conductivity the question of impurity is very important. Would impure alumina depart very much from that?

E. F. NORTHRUP: I measured alundum, which has a binder in it, and it has a little less resistance. Your question brings up an extremely important point that must be considered in these high temperature measurements. Suppose you had water between two electrodes in a vessel, and the vessel was filled with sand, and you were to pass current between the electrodes, you would have no idea of the electrical conductivity of the sand, for you would be electrically measuring not the sand but the water. When you bring these oxides to these high temperatures, the pores or interstices of the oxides are filled, in all my measurements, at least, with a mixture of other things; nitrogen, CO and free carbon. When you get over 1,500° C. there is always some free carbon vapor, and you measure the conductance of the oxide itself, in parallel with the conductance of the gas, which is by no means insignificant.

Alumina has a resistivity of 40 at 1,550° C. The same space filled with nothing but CO gas has an electrical resistivity of 8.5 at the same temperature. So a great deal of the conductivity is due to the conductivity of the gas in the interstices of the material, and when one reaches these high temperatures, this has to be taken into consideration. You are not measuring the conductivity of the material itself, you are measuring the conductivity of the material plus the conductivity of the gas. It is not a question of a current which will go through a galvanometer, but it is a question of several milli-amperes which will pass through the gas.

PRESIDENT LIDBURY: These magnesia figures you gave, you stated were not for pure magnesia, but a mixture?

E. F. NORTHRUP: Ten percent admixture of magnesium carbonate.

PRESIDENT LIDBURY: That might have had some influence on the kinks?

E. F. NORTHRUP: I do not think that had any great effect in bringing the resistance down. It was magnesia, plus 10 percent of pure magnesium carbonate.

K. H. HITCHCOCK: A good many years ago I tried the best Greek magnesite brick I could get as retainer for a granular carbon resistor in an electric furnace, of that type where the resistor surrounded the glass bath, and I found that at a temperature in the resistor sufficient to liquify the glass in the bath, the magnesite did react with the carbon.

I am not familiar with the experiments of Moissan to which allusion has been made, but in the ordinary arc furnace the magnesite would not come in direct contact with the incandescent carbon, but with either the vapor of carbon, CO or CO_2, or more accurately a mixture of all these gases, which would greatly affect the reaction to which the magnesite itself would be subjected.

There is another thing about the magnesite brick in connection with the resistor furnace above alluded to: It was noticed when any reaction started at a given point in the resistor, the resistor failed with considerable rapidity, and that these failures were never general, along the whole line of the resistor, but more violent in one particular spot.

FRANCIS C. FRARY: I would like to point out one other point: the possibility of an explanation of the volatilization of MgO. It is suggested this volatilized as magnesia and as carbide. I shall show in a paper which is to be read tomorrow[1] that there is a sub-oxide of magnesium which is formed by the reduction of magnesium oxide at temperatures below 1,000 degrees. It is probable that it would have a different volatility and different properties from either of the other substances, and might account for the phenomena observed.

L. E. SAUNDERS: I think attention should be drawn to the fact that magnesium oxide has a considerable vapor tension below the temperatures which the authors of this paper have described; for instance, at 1,700 or 1,800° C. vapors of magnesium oxide will be given off when there is no contact with carbon at all, and probably carbon also has an appreciable vapor tension at the same temperature. That might account for some of the reaction products which the authors describe, accounting for them in another way.

I would call attention to the fact that the authors of the paper state that the materials used in the reactions were the purest attainable. That is rather a presumptuous statement.

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[1] See page 209.

CLEANING AND PLATING IN THE SAME SOLUTION

By OLIVER P. WATTS

Although the simultaneous cleaning and plating of metals in a single solution is now quite extensively practised, the literature upon this subject is extremely scanty, being limited, so far as the writer has observed, to a few patents and a brief published article by Mr. E. G. Lovering.

In spite of the slight attention paid to this process in the books and periodicals devoted to plating, it is well worth a trial by every plater. After a series of experiments in the University laboratories, the writer believes that the general adoption of the combined cleaning and plating solution will prove almost as revolutionary in plating-room practice as has the electric cleaner. Once adopted, the plater will wonder how he ever did his work without it.

Before considering baths for cleaning and plating in a single operation, it may be well to devote a few minutes to the electric cleaner.

It may be news to many here that electric cleaning of metals for plating by use of the dynamo current was discovered in Wisconsin at the State University, but that such is the case is shown by a report in the *Electrical World* for October 29, 1898, of experiments by C. F. Burgess. Adoption of the process by platers proceeded very slowly, and it is only in recent years that the great value of this method of removing grease from metal has been generally recognized.

The principle of operation is simple. When an electric current is passed through a solution of any sodium or potassium salt hydrogen is liberated and a film of alkali is produced on the cathode. There is therefore a two-fold cleaning effect; the alkali tends to saponify animal and vegetable fats, and the hydrogen which is set free under the grease upon the metallic surface knocks off particles of grease in its escape. The higher the current density, the more rapid and effective the cleaning, because of the more violent evolution of hydrogen, and the greater concentration of the film of alkali produced by the current. If instead of using as electrolyte a neutral salt, such as sodium sulphate, or cyanide, which of itself has no action on grease, sodium carbonate or lye be substituted, the chemical action of these substances is added to the electrochemical cleaning already referred to, and the cleaning process is greatly accelerated. Lye also plays the part of a conducting salt, and greatly lessens the resistance of the solution. Heat is a great accelerator of electric cleaning. The tremendous effect of rise of temperature upon the velocity of chemical action is well known, and the saponification of fats by alkalies is no exception to the general rule. Besides increasing the rate of cleaning by accelerating the action of the alkali present in the solution, heating greatly lessens the resistance and therefore increases the current. This results in an enormous increase in the rate of cleaning by a hot, in comparison with a cold, electric cleaner. The use of cold electric cleaners is not to be encouraged, since 90 per cent. or more of the possible cleaning power is not utilized at low temperature.

That the regular cyanide copper solution possesses some cleaning power has been known for many years. The reason is easily seen. When in use hydrogen is always evolved at the cathode and a corresponding amount of lye is produced there. This dissolving action of cyanide baths on grease, under the influence of the current, combined with their solvent power for many metallic oxides was probably the reason for the addition of cyanide to many of the earlier electric cleaners. Now that it is recognized that cyanide does not help the electric cleaner in removing grease from metals, its use has been generally discontinued.

To secure the greatest cleaning power from the electric cleaner requires a boiling solution strong in lye and, by the use of large electric conductors, the delivery of the full voltage of the dynamo at the cleaning tank. For cleaning metals which are attacked by lye, or where the maximum of cleaning power is not needed, soda ash or sal soda may be substituted for lye, and the bath may be operated below the boiling point.

In order that a plating bath may remove grease one of two things is necessary—there must be a vigorous evolution of gas on the work during plating, or the solution must be used hot and must contain enough lye or other saponifier of grease to clean by chemical action. Most effective cleaning requires a vigorous evolution of gas in a hot, strongly alkaline plating bath.

Many of the plating baths now in use evolve hydrogen vigorously only when strongly acid, or so weak in metal as to produce a burnt deposit. Many metals are precipitated by alkalies, so that a strongly alkaline solution of them cannot be made. It is therefore evident that cleaning and plating in a single solution will be somewhat limited in its application.

Lovering's formula, previously referred to, for cleaning and depositing brass, is as follows:

Lye	8 oz.
Copper carbonate	2 oz.
Zinc carbonate	2 oz.
Ammonium carbonate	4 oz.
Potassium cyanide	4 oz.
Water	1 gallon

For a copper solution he recommends the same without the zinc carbonate. Both solutions are used at the boiling point and are claimed to work with great rapidity.

Starting with Lovering's solution as a basis, many experiments have been tried in the University laboratories. It was soon found that the bath needed more cyanide than given in the formula, but even with a great increase of cyanide anode corrosion was not satisfactory. The presence of lye caused a coating of copper oxide to form on the anodes. It was discovered that the addition of Rochelle salt dissolved this film and caused excellent anode corrosion, even at extremely high current densities.

The following is recommended as a good solution for cleaning and depositing copper:

English		*Metric*
8 oz.	Lye	60 grams
4 oz.	Copper carbonate	30 grams
8 oz.	Sodium cyanide	60 grams
12 oz.	Rochelle salt	90 grams
1 gal.	Water	1000 c.c.

The addition of 4 oz. of ammonium carbonate will cause a brighter deposit from a freshly made bath, but since ammonium salts are expelled by boiling lye, this addition is not recommended. Experiments with this and other solutions have already been described in a paper presented at the April meeting of the American Electrochemical Society, and therefore will not be repeated here. The solution should be used between 158 deg. F. (70 deg. C.) and the boiling point at current densities of 60 to 250 amperes per square foot.

The fraction of the total current devoted to cleaning may be controlled by regulating the amount of free cyanide. An increase of cyanide causes more vigorous cleaning, and increasing the current density has the same effect. Current efficiencies vary from 55 to 90 per cent., depending on the amount of free cyanide, the current density and the temperature. The less the current density and the higher the temperature, the greater will be the current efficiency. Lye is without effect on the current efficiency.

In comparing rapidity of deposition of copper from this and other solutions, it should be noted that a cyanide solution at 50 per cent. efficiency deposits as much metal as the sulphate solution at 100 per cent. This fact, together with the low resistance due to the lye, and the very high current density which may be used without causing a burnt deposit, all combine to yield a more rapid deposition of metal than from any other bath in use to-day.

If a maximum of cleaning and a minimum of plating is desired, this can be obtained by diminishing the amount of copper and Rochelle salt, and increasing the amount of cyanide and lye. When it is desired to have a low current efficiency at the cathode, the composition of the solution should be altered in such a way as to keep the rate of solution of metal from the anode equal to deposition at the cathode, and thus maintain the original composition of the bath—which, in this case, means to diminish the amount of Rochelle salt—the material, which in the presence of free cyanide, promotes anode corrosion.

Experiments with this solution in plating sheets of copper, brass, zinc and iron, just as they came from the polishing wheels, showed perfect adhesion of the deposit without the formation of a single blister. The remarkable power which this solution possesses of penetrating surface coatings of grease and rust, and depositing firmly adherent copper upon the metal beneath, is strikingly illustrated by the illustration here presented.

This is the raw material for plating—a bar of heavily rusted steel picked from a scrap pile where it had been exposed to the weather all winter.

Has any plater a solution which he will guarantee to deposit a thick, firm, adherent coating of metal on this bar with no preliminary cleaning?

This bar, plated five minutes at 25 amperes, and scratch-brushed. The iron rust had been forced off of the part immersed in the bath.

A piece was cut with a hack saw after plating to test the adhesion of the deposit, which proved entirely satisfactory.

Brass

Experiments with Lovering's brass solution resulted in several changes in composition. One of the first solutions used had the following composition:

2 oz.	zinc carbonate	15 grams
4 oz.	copper carbonate	30 grams
8 oz.	lye	60 grams
7 oz.	ammonium carbonate	50 grams
10 oz.	Rochelle salt	75 grams
17 oz.	potassium cyanide	120 grams
1 gal.	water	1000 c.c.

At 176 deg. F. (80 deg. C.) this solution deposited good yellow brass between current densities of 50 and 150 amperes per square foot.

Copper plate directly on rusty iron. Current, 25 amperes. Time, five minutes. Amperes per square foot, 240. Both ends of rod similar when immersed in plating solution.

This cleaning and plating solution is more difficult to control than the regular brass bath since the presence of lye is a disturbing factor. Lye, like cyanide, causes an increase in the proportion of zinc in the deposit, and since the presence of both of these substances is necessary for vigorous cleaning, this solution, unlike the regular brass bath, should contain much more copper than zinc.

The large amount of cyanide required by this bath in order to obtain a satisfactory color constitutes a serious objection to its use, and other combinations were tried. One of these, which gave an excellent deposit between 30 and 90 amperes per square foot consisted of—

4 oz.	copper carbonate	30 grams
1½ oz.	zinc carbonate	12 grams
8 oz.	ammonium carbonate	60 grams
7 oz.	lye	50 grams
13¼ oz.	potassium cyanide	100 grams
13¼ oz.	Rochelle salt	100 grams
1 gal.	water	1000 c c

A half-hour's operation at 176 deg. F. and 62 amperes per square foot gave current efficiencies of 64 per cent. at the cathode and 47 per cent. at the anode, while a similar bath, except for the omission of the Rochelle salt, showed the same efficiency of deposition, but an anode corrosion of only 2½ per cent. In these brass solutions Rochelle salt has the same beneficial effect upon anode corrosion as was previously noted for the copper solution. Its use in a hot bath solves the troublesome problem of the corrosion of brass anodes. The remarks concerning ammonium salts in the copper solution apply here, and they should be left out of the solutions containing lye, which are to be operated continuously at or near the boiling point.

The solutions above mentioned are only two out of many possible combinations of copper carbonate, zinc carbonate, cyanide and lye, which will operate at high current densities and yield good brass deposits.

The best method for the plater to use to obtain a cleaning and plating solution for brass,* suited to his particular needs, is to make up a cyanide copper solution containing lye, heat it at the temperature at which he intends to use it, and add zinc carbonate in very small quantities until the desired quality of brass is obtained. Increasing the quantity of lye in the original copper solution will lower the amount of cyanide and of zinc needed to yield a good yellow brass. Too little free cyanide will result in poor anode corrosion, even in the presence of Rochelle salt.

This procedure resulted in a good solution of the following composition:

2⅝ oz.	copper carbonate	20 grams
8 oz.	lye	60 grams
7 oz.	sodium cyanide	50 grams
¼ oz.	zinc carbonate	2 grams
1 gal.	water	1000 c.c.

At 176 deg. F. and 36 to 56 amperes per square foot, this solution gave an excellent

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*For the facts concerning the brass solutions the writer is indebted to Mr. R. E. Baker, scholar in chemical engineering during this year in the university.

deposit. Like the copper bath, it has remarkable cleaning power and in 8 minutes at 370 amperes per square foot produced a fine deposit through heavy rust.

Nickel

For a year past many experiments have been tried in the University laboratories in the hope of discovering a solution for cleaning and plating with nickel. At the outset this looked like an easy task, for it appeared only necessary to add lye to a hot solution of nickel sodium cyanide. On trial this solution cleaned effectively but deposited a mere color of nickel, too thin to be useful.

Glucose is one of several substances other than cyanide which prevent the precipitation of nickel solutions by alkalies. A hot nickel solution containing glucose and lye proved to be an effective electric cleaner, and gave a nickel deposit of a fine color, but like that from the alkaline cyanide solution, it was too thin to be of service. A half-hour's deposition at 52 amperes per square foot gave a current efficiency of only one-tenth of one per cent. The substitution of sodium carbonate for the lye did not change the result.

Failure to succeed with alkaline solutions directed attention to acid baths, and some degree of success has been achieved with the following solution:

13 oz.	nickel ammonium sulphate	100 grams
2½ oz.	sodium chloride	20 grams
1½ oz.	sodium citrate	10 grams
¾ to 1 oz.	citric acid	5 to 7 grams
1 gal.	water	1000 c.c.

Exact proportions are not necessary, the only need being enough acid to cause a violent evolution of hydrogen on the cathode. The bath must be boiling, and current densities of 40 to 250 amperes per square foot may be used. This solution has no solvent power for grease, and for cleaning depends entirely upon the mechanical action of hydrogen. Although its cleaning power is far less than that of the copper and brass solutions, it has been possible to give a sheet brass twelve successive coats of nickel, each deposit being polished on a muslin buff with tripoli and immediately returned to the bath for the next coat. This solution may have some value for re-plating nickeled articles without stripping the original deposit. It is at present the only solution which the writer can offer as a combined cleaner and plater for nickel.

As containers for the copper and brass solutions iron or steel tanks should be used, with an exhaust hood over each to carry off the poisonous spray thrown up by the escaping hydrogen. Ample current should be provided in cables, tank rods, and sling wires. On account of the great evaporation from boiling solutions, it will probably prove most satisfactory to sacrifice something in rapidity of action by operating the baths below the boiling point.

There is a very general opinion that combined cleaning and plating solutions are only suited to thin deposits. This is a natural, though mistaken view. The combined solutions for brass and copper can be made to deposit metal more rapidly than is possible in any of the regular plating baths, and are particularly suitable for heavy deposits. Blistering of deposits on iron, which is a common complaint of platers using the regular brass and copper solutions, has never occurred with the combined baths.

The only question as to their general adoption would seem to be in regard to the more rapid fouling of the solution by the dirt, which in the old method was removed in the cleaning tank and so kept out of the plating bath. Whether this will outweigh the saving in time and labor made by the single bath is for the practical plater to decide. Should this fouling of the solutions prove a serious matter, the bulk of the dirt may be removed by a few seconds' immersion in a hot electric cleaner, and the cleaning-and-plating bath may then be regarded as only an extra-rapid plating solution that is guaranteed to give a deposit which, like that oft-quoted smile, will not come off.

As an addenda to the foregoing, I ought to state that in discussion with two members of the Chicago Branch I was informed that the combined cleaning and plating solution had been tried, but its use abandoned because of excessive consumption of cyanide. In view of these statements, it will be well for those who try this process to note carefully the cyanide consumption of this bath in comparison with that of the number of regular copper or brass baths required to do the same amount of work. Lowering the temperature will probably lessen cyanide consumption.

It may be well to call the attention of platers to the conditions under which most experimental work in plating must be performed in the laboratories of educational institutions. In most cases research is not regularly provided for on the program, but must be done at such hours of the day or night as are left after all other demands upon one's time and energy have been met. Although an investigation may extend over many months before the final results are announced, the actual number of hours that the successful solution has been operated is rarely equivalent to a week's use under plating-room conditions. The college experimenter can rarely afford either the time or the material to give his supposed discovery the test of eight hours' operation daily for a period of six or eight months. It is not surprising then that laboratory processes often fail when put to the test of long-continued operation in the plating shop.

Yet it will never do for the plater to become discouraged and cease trying the processes and methods announced from the laboratory. Progress is possible only through the substitution of better methods, processes and solutions for those now in use. The chaff must be sifted from the wheat, and the plater is the man who must do the sifting. Having done this, it is his duty to report his results in print, not only to call attention to valuable processes, but to save scores of others from wasting their time in trying that which has proved useless. A single report of failure should not, however, be regarded as final. There are those in whose hands nothing new ever succeeds.

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When aluminum was first introduced in brass foundry practice it was tried in all kinds of mixtures, to the sorrow of the founder, and it ultimately earned the title of the brass founders' curse.

And in later years, even after the foundryman had become wary, he was frequently careless, and in melting and casting aluminum would get it into the brass, where a very little would cause a vast amount of trouble; and it was considered a difficult matter to remove it, in fact almost impossible, and such spoiled brass became quite a problem to use up.

◆

Summarizing conditions that have been created by war orders, *The Iron Age* says the great war business is gradually expanding.

Magnesium Made Electrolytically

Metallic magnesium is to be manufactured electrolytically by the Aviation Materials Corporation, 99 Cedar Street, New York, which has been incorporated under the laws of New York State. The plant will be located at Niagara Falls, N. Y., and it is expected it will be completed in June. It will operate under the patents of George O. Seward and F. von Kügelgen, who developed the process at the Virginia plant of the Virginia Electrolytic Company, Holcombs Rock, Va. The output is expected to be 10 tons of metallic magnesium per month. Besides being a constituent of some important alloys, magnesium is a beneficial addition to aluminum castings, as much as 2 per cent. often being used. An alloy containing 98 per cent. magnesium has been made by the inventors mentioned, which is lighter than aluminum and stronger. The average market price of metallic magnesium is $1.50 per lb.

◆

A Cheaper Substitute for Fuel Gas

The gases commonly employed in autogenous welding and cutting are oxygen, acetylene and hydrogen, all of which are expensive products. The average cost of oxygen throughout the United States is probably not less than $0.025 per cubic foot measured at atmospheric pressure; the average cost of acetylene probably ranges from $0.0075 to $0.01 per cubic foot, and the cost of hydrogen may safely be placed at about the same figure. These figures are compiled by J. F. Springer in *Machinery*. Apparently no one has yet devised a system of oxygen manufacture that will enable this gas to be inexpensively produced. However, there appears to be a likelihood of heavy reduction in the cost of the fuel gas used in autogenous welding—not through a reduction in the cost of acetylene or hydrogen, but through the discovery of an adequate substitute for these gases. This substitute is a semi-natural gas obtained from the waste gas from oil wells, and is known as "gasol." It can be produced at about $0.001 per cubic foot, and its heating capacity is even greater than that of acetylene. Other things being equal, this gas selling for $0.0008 to $0.001 per cubic foot should have a considerable market.

QUESTIONS AND ANSWERS

All communications under this head should be addressed to the "Questions and Answers Editor"

Nickel Solution For Nickel Bath

QUESTION No. 46.—Please state ingredients and quantity for good nickel solution for nickel bath; also a good trisalyt of copper solution for depositing on wood plaster, plaster of paris and galvanic work.

ANSWER.—

1.	Water	1 gal.
	Double ni. salt	8 oz.
	Single ni. salt	1 oz.
	Sal ammoniac	1 oz.
	Boracic acid	6 oz.

Use hot water in making up solution, but solution must be cold when plating.

2. The manufacturers of trisalyt, The Roessler & Hasslacher Chemical Co., will supply you with formulæ for using trisalyt on application.

Brands of Spelter and Analyses

QUESTION No. 47.—We would be very glad to have information regarding the different brands of spelter, with approximate analysis of each.

ANSWER.—The American Society for Testing Materials divides commercial spelter into four grades, the specifications for each grade being as follows:

High grade spelter shall not contain over

Lead	0.07 per cent
Iron	0.03 per cent
Cadmium	0.05 per cent

The sum of these impurities shall not exceed 0.10 per cent.

Intermediate spelter shall not contain over

Lead	0.20 per cent
Iron	0.03 per cent
Cadmium	0.50 per cent

The sum of these impurities not to exceed 0.50 per cent.

Brass special spelter shall not contain over

Lead	0.75 per cent
Iron	0.04 per cent
Cadmium	0.75 per cent

The sum of these impurities shall not exceed 1.2 per cent, and no aluminum is allowable in any of the above spelters.

Prime western spelter shall not contain over

Lead	1.50 per cent
Iron	0.08 per cent

All the various brands of spelter on the market fall under some one of the above grades. High grade brands are very difficult to obtain at present. Such brands as Horsehead, Bertha, and Golden Rod, formerly used in the manufacture of high grade manganese bronze are now unattainable, while even Franklin, which runs as high as 0.50 per cent lead occasionally, is very difficult to obtain at present.

Formula Does Not Have Claimed Properties

QUESTION No. 48.—I have a formula that is said to be a malleable and non-corrosive metal when properly melted. I have tried several times and have been burned almost as often. The zinc or antimony is what apparently causes the trouble. It flares up.

Can you give me any idea as to how I should proceed to make this alloy? I have at my shop a small cupola, also crucible coke as well as tilting oil furnace.

This alloy calls for pig iron, 50 lb.; sodium, ½ lb.; copper, ¼ lb.; antimony, ¼ lb.; zinc, 2½ lb.

The directions state that by omitting the sodium and decreasing the quantity of zinc a softer iron is obtained. Also tell me what this formula means by sodium. There are so many kinds.

ANSWER.—We fail to see how the formula in question can possess any of the properties ascribed to it, and we strongly advise that no further attempts to make it be tried. It is dangerous to attempt to alloy zinc and cast iron, as they combine with explosive violence, and are of no value when alloyed. It is a mistake to assume there are many kinds of sodium; there is only one "sodium," and this is a metal very dangerous to handle by the uninitiated. It is probably very fortunate that the metal

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Rapid Nickel Plating

BY

O. P. WATTS

A paper presented at the Twenty-ninth General Meeting of the American Electrochemical Society, in Washington, D. C., April 27-29, 1916.

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.

Exp.	Temperature		Time	Amperes per		Ampere-Hours per	Deposit
	C°	F°	Min.	Sq. Dm.	Sq. Ft.	Sq. Ft.	
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.

Exp.	Temperature C°	Temperature F°	Time Min.	Amperes per Sq. Dm.	Amperes per Sq. Ft.	Ampere-Hours per Sq. Ft.	Cathode Eff. Percent
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°	F°	Time Min.	Amperes per Sq. Dm.	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?

[FROM THE TRANSACTIONS OF THE AMERICAN ELECTROCHEMICAL SOCIETY, Volume XXX, 1916, being the Transactions of the Thirtieth General Meeting, at New York City, September 28, 29, 30, 1916.]

The Protection of Iron by Electroplating

BY

O. P. WATTS and P. L. DeVERTER

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.

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 Inches	Thickness m.m.	Amp. Hrs./dm.^{2}	Cur. Eff. Percent
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 Inches	Thickness m.m.	Amp. Hrs./dm.^{2}	Cur. Eff. Percent
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 Inches	Thickness m.m.	Amp. Hrs./dm.^{2}	Cur. Eff. Percent
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 Inches	Thickness m.m.	Amp. Hrs./dm.^{2}	Cur. Eff. Percent
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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University of Wisconsin.

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.

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Acid Resisting Properties of Some Iron-Silicon Alloys

BY

O. L. KOWALKE

A paper presented at the Thirty-first General Meeting of the American Electrochemical Society, held in Detroit, May 4, 1917, President FitzGerald in the Chair.

ACID RESISTING PROPERTIES OF SOME IRON-SILICON ALLOYS.

By O. L. Kowalke.

[*Abstract.*]

Eighteen low-carbon iron-silicon alloys, containing 1.2 to 19.8 percent of silicon, were immersed from periods of 51 hours to 29 days in ten percent solutions of sulphuric, hydrochloric, nitric, acetic and citric acids, and the losses determined. With a few irregularities the resistance to acid attack was a minimum at 1.2 to 3.3 percent silicon, and a maximum at 16 to 18 percent. The latter alloys are very hard and brittle. Attempts are being made to find an addition element which will decrease these undesirable qualities while not impairing the resistance to acids.

Various acid-resisting alloys of commercial importance have been produced within recent years, and among these the iron-silicon alloys seem to give satisfactory service in many operations. There seems to be, however, but little published information on the acid-resisting properties of the iron-silicon alloys, and it was the purpose of this investigation to determine the resistance to several common acids. This paper is offered as a progress report with the hope that suggestions may be made which will be of assistance in the subsequent tests.

The assistance of Mr. Stanton Umbreit in obtaining these data is hereby gratefully acknowledged.

W. Guertler and G. Tamman[1] worked out the equilibrium diagram for these alloys. The curve shows mixed crystals or a solid solution of Fe and FeSi between 0 and 20 percent silicon. At 20 and at 33.7 percent silicon there are two compounds, Fe_2Si and FeSi respectively, which combine to form a eutectic at about 21.4 percent silicon. The compound FeSi and free silicon form a eutectic at 60.6 percent silicon, which corresponds to the formula $FeSi_3$. The melting point of Fe_2Si is about 1,250° C. and that of FeSi about 1,443° C. The alloys made for this investi-

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[1] Zeit. Anorg. Chem., 47, 163-179.

gation lay in the region of mixed crystals, and did not contain over 20 percent silicon.

Preparation of the Alloys.

The alloys were made from electrolytic iron and ferro-silicon which analyzed 49.5 percent silicon; no test was made for carbon. Acheson graphite crucibles lined with magnesium oxide were used to melt the alloys. Each charge was made up to a total weight of 200 grams and the amount of ferro-silicon for each alloy was computed from the amount of silicon to be added. The charges were melted in the covered crucibles in a granular carbon resistor furnace.

The mold for casting the alloys was made from Acheson graphite. Recesses 4 x 1¼ x $\frac{1}{16}$ in. (10.15 x 3.2 x 0.15 cm.) were cut into a slab of graphite and a cover clamped onto the slab; pouring cups were also cut at the mouths of the recesses. This provided means for making a specimen about 3 x 1¼ x $\frac{1}{16}$ in. (7.62 x 3.2 x 0.15 cm.).

The alloys were not stirred while in the furnace, but as the crucibles containing the fluid alloys were removed from the furnace they were given a gyratory motion so as to mix the molten charge thoroughly. The melted alloys were then poured from the crucibles into the molds. As soon as the alloys solidified in the mold, the cover clamped over the recess was removed, and the alloy taken out.

Since the alloys cooled very rapidly upon being poured into the mold, there was undoubtedly a negligible amount of carbon absorbed, but no chemical analyses were made to prove this point.

The alloys of low silicon content made good soft castings. Above 3.5 percent silicon the alloys were brittle. In alloys of 7.5 percent silicon and above there were such severe strains developed on casting that they would frequently break into small pieces in the mold. Some alloys with more than 11 percent silicon would fly apart with great violence. Two castings with 16 percent and 17 percent silicon broke in the acid during corrosion tests the second week after casting the same.

Acid Corrosion Tests.

The acids used were ten percent solutions by weight of sulphuric, hydrochloric, nitric, acetic, and citric acids, made to this strength by using a hydrometer. The temperatures of the acids when made and when used in the tests were between 20° and 25° C.

Owing to the great brittleness of the alloys, the specimens thereof used for the tests were very irregular in shape. The faces and edges of the specimens were therefore ground to fairly smooth surfaces.

The specimens were placed on edge in hard-rubber racks, which held the specimens rigidly and prevented them from touching one another. From thirteen to eighteen specimens could be placed on the various sized racks. The specimens on the racks were then placed in crystallizing dishes about 2 inches (5.1 cm.) deep and covered with the acid. A glass cover was placed over the dish to prevent evaporation.

From time to time the specimens were removed from the acid to be weighed. They were first washed in distilled water, then rinsed in denatured alcohol, and dried quickly in a current of hot air, after which they were weighed on an analytical balance.

Results.

The results of these tests are shown in Tables I to V. The percent loss is cumulative.

Sulphuric Acid: Tests given in Table I show that the loss is greatest at about 3.7 percent silicon, then the resistance increases to a maximum with a silicon content of 16 percent. Beyond this content of silicon the resistance seems to decrease.

Hydrochloric Acid: Tests given in Table II show that the loss is greatest at about 3.7 percent silicon, and least at about 18 percent silicon. Beyond this content of silicon there is a decrease in the resistance.

Nitric Acid: The loss diminishes quite steadily until the silicon content reaches 16 percent, after which it increased. The results are given in Table III.

Acetic Acid: The loss as shown in Table IV increases up to a content of silicon of about 5 percent, beyond this point it decreases steadily to 16 percent silicon, beyond which it again increases.

Citric Acid: From Table V it is seen that the corrosion increases up to a content of 3.3 percent silicon, beyond which it gradually decreases to the point where the silicon is 17 percent.

TABLE I: LOSS IN 10 PERCENT SULPHURIC ACID.

Cumulative Loss, Percent.

Composition Percent Si	Area sq. cm.	51 hrs.	75 hrs.	141 hrs.	15 days	22 days	29 days
1.2	14.6	0.99	3.7	9.4	100	....	....
1.7	12.8	3.2	7.8	11.8	46.5	59.1	100
2.5	14.7	1.6	4.1	6.5	31.9	39.2	65.3
3.3	21.9	64.9	87.5	92.8	....	....	....
3.7	11.0	51.3	66.8	100.0	....	....	....
4.9	12.7	5.3	11.2	18.0	....	....	....
6.2	11.6	11.6	27.7	38.9	....	....	....
6.6	13.0	13.8	23.9	30.2	....	....	....
7.4	11.5	31.0	48.9	62.0	....	....	....
8.7	14.1	15.0	37.9	40.6	....	....	....
9.9	12.7	10.7	19.8	23.1	....	....	....
11.1	13.0	5.0	8.8	13.1	34.3	42.5	73.1
12.4	9.2	1.2	2.1	2.4	4.4	4.6	14.2
13.6	16.6	0.2	0.6	0.9	1.9	2.0	3.4
14.8	18.0	0.03	0.05	0.05	0.05	0.05	0.05
16.1	10.2	0.03	0.04	0.04	0.04	0.04	0.04
17.3	11.9	0.03	0.03	0.03	0.03	0.03	0.03
19.8	9.6	0.13	0.2	0.25	0.5	0.6	0.7

TABLE II: LOSS IN 10 PERCENT HYDROCHLORIC ACID.

Cumulative Loss, Percent.

Composition Percent Si	Area sq. cm.	7 days	16 days	21 days	28 days
1.2	12.7	12.8	....	....	....
1.7	11.2	2.4	7.9	10.9	14.5
2.5	8.4	2.4	10.0	15.7	20.4
3.3	11.8	9.71	38.7	60.8	74.5
4.9	11.4	2.3	8.6	10.0	14.0
6.2	16.1	3.5	9.7	15.5	21.2
6.6	18.3	5.8	14.7	20.5	28.1
7.4	11.2	5.5	19.0	27.3	33.8
8.7	10.1	12.9	26.0	30.4	35.2
9.9	7.3	7.1	16.4	21.1	25.9
11.1	10.4	4.9	8.1	9.4	11.0
12.4	13.1	1.4	2.7	4.0	4.6
13.6	11.7	0.18	0.51	0.67	0.93
14.8	6.3	0.12	0.31	0.42	0.56
16.1	11.4	0.12	0.27	0.36	0.48
17.3	11.2	0.31	0.40	0.41	0.40
18.5	8.9	0.03	0.03	0.04	0.04
19.8	10.8	0.1	0.28	0.28	0.52

TABLE III: LOSS IN 10 PERCENT NITRIC ACID.

Cumulative Loss, Percent.

Composition Percent Si	Area sq. cm.	115 hrs.	166 hrs.	14 days
1.2	12.7	21.5	53.8	60.3
1.6	11.2	20.9	55.0	60.9
2.5	8.4	20.8	48.0	53.5
3.3	11.8	13.3	21.6	22.1
4.9	11.4	12.3	18.8	19.5
6.2	16.1	11.6	15.6	16.2
6.6	18.3	10.7	13.1	13.5
7.4	11.2	8.9	11.1	11.4
8.7	10.1	7.4	9.7	10.7
9.9	7.3	5.9	8.7	8.9
11.1	10.4	2.4	3.5	3.6
12.4	13.1	2.3	4.6	4.6
13.6	11.7	0.05	0.1	0.1
14.8	6.3	0.013	0.02	0.02
16.1	11.4	0.006	0.003	0.0015
17,3	11.2	0.006	0.007	0.007
18.5	8.9	0.037	0.044	0.046
19.8	13.8	0.01	0.01	0.01

TABLE IV: LOSS IN 10 PERCENT ACETIC ACID.

Cumulative Loss, Percent.

Composition Percent Si	Area sq. cm.	7 days	14 days	20 days	27 days
1.2	10.6	0.5	2.9	4.4	6.3
1.6	7.3	0.5	1.0	1.4	2.2
2.5	7.5	0.5	1.0	1.4	1.8
3.3	6.9	1.3	3.6	5.8	9.8
4.9	9.0	1.4	3.7	5.5	8.10
6.2	13.5	0.4	0.9	1.3	1.9
6.6	10.9	0.3	0.9	1.5	2.2
7.4	10.0	0.26	0.7	1.0	1.8
8.7	12.0	0.2	0.5	0.8	1.6
9.9	6.5	0.2	0.4	0.5	0.8
11.1	10.4	0.1	0.6	0.7	1.0
12.4	10.4	0.1	0.24	0.3	0.4
13.6	5.8	0.08	0.2	0.3	0.3
14.8	8.1	0.03	0.03	0.03	0.03
16.1	7.0	0.006	0.008	0.01	0.013
17.3	10.4	0.006	0.008	0.009	0.009
18.5	8.3	0.014	0.014	0.015	0.016
19.8	8.5	0.07	0.08	0.08	0.08

TABLE V: LOSS IN 10 PERCENT CITRIC ACID.

Cumulative Loss, Percent.

Composition Percent Si	Area sq. cm.	7 days	14 days	21 days
1.2	13.9	5.3	16.3	20.0
1.7	11.9	10.0	19.3	21.0
2.5	12.3	6.8	14.9	16.9
3.3	11.6	54.6	95.1	95.6
6.2	9.5	4.6	9.5	9.8
7.4	7.8	3.4	7.6	....
8.7	13.6	2.8	7.4	....
11.1	9.1	2.5	4.2	4.4
12.4	10.6	1.8	2.8	3.1
13.6	17.0	0.4	0.4	0.4
14.8	8.9	0.07	0.07	....
16.1	8.1	0.04	0.04	0.5
17.3	12.8	0.006	0.009	0.009

Conclusions.

Silicon-iron alloys of about 3 to 5 percent silicon are attacked very readily by sulphuric, hydrochloric, acetic, and citric acids. These alloys are not excessively brittle.

Silicon-iron alloys of about 16 to 18 percent are exceedingly resistant to action of sulphuric, hydrochloric, nitric, acetic, and citric acids. These alloys are so brittle that they must be ground; they can not be machined.

A solid solution of FeSi in iron near 20 percent silicon is resistant to mineral acids.

Search is in progress for a third metal which can be added to the iron-silicon alloys to improve their strength and still retain the resistance to the action of acids.

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University of Wisconsin.

DISCUSSION.

O. P. WATTS[1]: This paper was prompted by the commercial use of acid-resisting irons, with which many of you are familiar. This was an attempt to determine the action of some of the com-

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[1] Asst. Professor of Applied Electrochemistry, University of Wisconsin.

mon acids upon iron alloyed with silicon, through the range in which these various commercial alloys are used.

C. F. **Burgess**[2]: As far as I know, the manufacturers of these irons are not guaranteeing them as to their durability against these acids, especially hydrochloric acid. It seems to me that these tests, while interesting, are made under certain limitations, the conclusions of which cannot be accepted without reservation; that is, the temperatures are comparatively low, and there is no agitation. It is my impression that where you have boiling solutions and agitation, that you still have trouble when handling hydrochloric acid. I am wondering whether we may not have some statement from the producers of these irons along that line.

O. P. **Watts**: While I agree with Prof. Burgess' statement that the matter of temperature is highly important, and that although these alloys will stand these acids at ordinary temperatures they might very well fail at higher temperatures, it seems to me the other point emphasized, that of circulation, is not particularly important. Where there is no chemical action the circulation, so it seems to me, can have no effect. Where there is chemical action, circulation is highly important. As far as the effect of circulation is concerned in these tests, at room temperature, it seems to me it is unimportant.

J. W. **Richards**[3]: I believe that the copper depositing plant at Chuquicamata, Chile, in using duriron for anodes, had some trouble through the action of the sulphuric acid. They used up one pound of duriron for every five pounds of copper deposited.

Prof. Kowalke sent me specimens of his alloys recently, with which we intend to experiment to see how resistant they are as anodes in sulphuric acid solution.

W. C. **Brooks**[4]: In commercial work experience has shown that the limitation of the alloy is not particularly in its resistance to chemical action, but to mechanical stresses.

If we could get a silicon-iron alloy with greater tensile strength or greater elasticity than some of the alloys produced at present, it would be much more useful.

[2] C. F. Burgess Laboratories, Madison, Wis.

[3] Professor of Metallurgy, Lehigh University.

[4] Chemical Engineer, National Carbon Co., Cleveland.

If these alloys were entirely resistant to sulphuric acid, so that we could with safety store a tank of acid, and know that it would dissolve practically no iron, it would be very important.

J. W. RICHARDS: In using the alloy as an anode these mechanical properties would be of only slight importance, but they are especially valuable for chemical apparatus. When they are used as anodes they simply hang on a hook, and have to resist very little mechanical stress.

W. C. BROOKS: I had particularly in mind the use of the material for pipes, plugs, cocks, etc.

W. R. MOTT[5]: These alloys, we know, are being used to a very large extent in nitric acid plants and other chemical works. I understand that in the present war it would have been impossible for Great Britain to have gotten along as well if it had not been for the application of the iron-silicon alloys, which are now used in the production of nitric acid on a scale never before practiced.

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[5] Research Laboratory, National Carbon Co., Cleveland.

[FROM THE TRANSACTIONS OF THE AMERICAN ELECTROCHEMICAL SOCIETY, Volume XXXI, 1917, being the Transactions of the Thirty-first General Meeting, at Detroit, Mich., May 2, 3, 4, 5, 1917.]

The Evolution of Hydrogen from Cyanide Plating Solutions

BY

O. P. WATTS and A. BRANN

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.

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.

[FROM THE TRANSACTIONS OF THE AMERICAN ELECTROCHEMICAL SOCIETY, Volume XXXII, 1917, being the Transactions of the Thirty-second General Meeting, at Pittsburgh, Pa., October 3, 4, 5, 6, 1917.]

Calorized Iron as an Element for Thermocouples

BY

O. L. KOWALKE

A paper presented at the Thirty-second General Meeting of the American Electrochemical Society, held in Pittsburgh, October 4, 1917, President Fink in the Chair.

CALORIZED IRON AS AN ELEMENT FOR THERMOCOUPLES

By O. L. KOWALKE.*

[*Abstract.*]

The author compares the thermo-electromotive force of couples of "calorized" iron-constantan with that of "uncalorized" iron-constantan. A sample of "calorized" iron wire from the General Electric Company gave the same thermo-electric potentials as "uncalorized" iron, up to 1,000° C., on repeated calibrations. A sample from the Brown Instrument Company gave slightly different potentials until after it had been heat treated at 800° C., after which it gave similar results to the other "calorized" wire. The author concludes that a heavy wire, lightly calorized, gives as constant results as uncalorized iron, and has a much longer life.

There are in the market several thermocouples, having iron as one of the elements, which have high electromotive forces and are fairly constant, but have the disadvantage that the iron element oxidizes rapidly above 500° C. If iron could be protected from oxidation by some sort of a coating which would not greatly change the electromotive force, its usefulness as an element for thermocouples would be much extended.

It has been shown by W. E. Ruder[1] that "calorizing" iron, "which consists in producing a rich aluminum alloy upon the surface of the metal," practically prevents oxidation below 1,000° C. It was therefore of interest to determine whether "calorized" iron wire was suitable for thermocouples and whether its electromotive force was as high and as constant as the uncalorized wire. One piece of "calorized" iron wire was donated by the Research Laboratory, General Electric Company, through the courtesy of Mr. F. W. Gillette, of the Diamond Power Specialty Company;

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* Professor of Chemical Engineering, University of Wisconsin.

[1] Trans. Am. Electrochem. Soc., 27, 253 (1915).

another piece of "calorized" iron wire was purchased from the Brown Instrument Company. The wire from the General Electric Company was 0.174 inch (0.44 c.m.) diameter and straight; the wire from the Brown Instrument Company was 0.137 inch (0.34 c.m.) diameter and was bent double on itself so that in straightening it out some of the alloy chipped off.

Grateful acknowledgment is hereby made to the General Electric Company for donating the wire and to Mr. M. A. Powers for assistance in obtaining these data.

Couples Used: Three sets of couples were made, each being 12 inches (30.5 c.m.) long. The wires in each couple were fused together at one end in an electric arc after filing off the "calorized" coating at the point of fusion. The wires were insulated from one another by porcelain bushings, and flexible copper lamp cord was soldered to the elements for leads. The wires used in all the couples were annealed by heating to a bright red with electric current.

Constantan wire, purchased from Leeds & Northrup, was used in all the couples as one element. The combinations used in these tests were:

Couple No. *10B* = constantan *vs.* "calorized" iron (Gen. Elec. Co.)
" " *32B* = " *vs.* " " (Brown Instr. Co.)
" " *81B* = " *vs.* "uncalorized" iron (Leeds & Northrup)

At the conclusion of the tests on the above couples, about 1½ inches (3.8 c.m.) was cut from the fused ends of the couples and remaining long portions fused together again. The couples so made were designated by the letter "C." Thus

Couple *10C* was made from Couple *10B*
" *32C* " " " " *32B*
" *81C* " " " " *81B*

Equipment Used: All electromotive force measurements were made on Leeds & Northrup portable potentiometers. A platinum vs. platinum-10 percent rhodium thermocouple calibrated by the Reichsanstalt in Berlin served as a standard for comparison. An electrically heated tube furnace, such as used in previous tests,[2] served for making the calibrations.

Procedure: Discs of asbestos were drawn over each couple to keep it in the axis of the furnace, and the ends of the furnaces

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[2] Trans. Am. Electrochem. Soc., 29, 561 (1916).

were closed with loose magnesia-asbestos. The couples were all inserted to a length of about 5 inches (12.7 c.m.) into the furnace for all calibrations and heat treatments.

In all tests only one couple at a time was compared with the standard platinum couple. The temperature intervals of the points of comparison were about 100° C., and at each point the temperature was maintained constant for a period of two minutes to insure equilibrium. The couples were calibrated as annealed, then they were heated in an electric tube furnace for 24 hours at 800° C., and given a second calibration, then heated again for 24 hours at 900° C. and calibrated a third time.

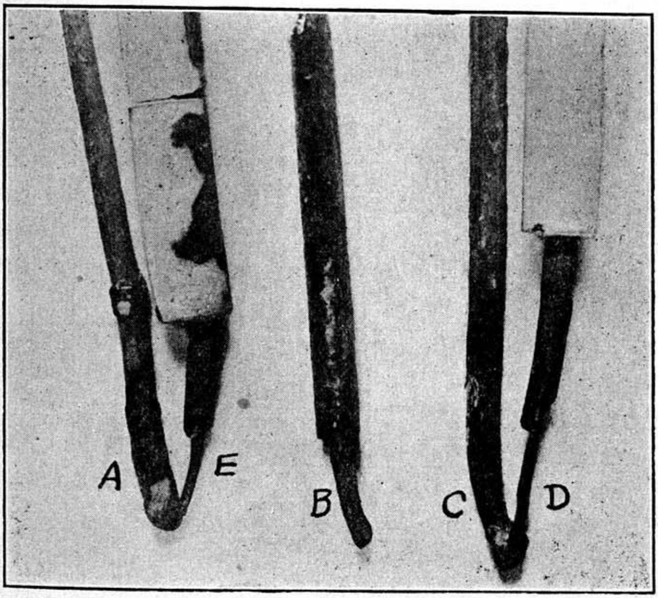

Fig. 1.

After the third calibration about 1½ inches (3.8 c.m.) was cut from the hot junction end of each couple and the remainder fused together again. The remaining couple was called *C*, and was calibrated only at three points to see whether any change in calibration had taken place due to changes in the wires or method of fusion.

Results and Observations: As shown in Fig. 1 above, the constantan wires *E* and *D* and the uncalorized iron wire *B* have oxidized badly. The "calorized" wires *A* from Brown Instrument

Company (couple *32B*), and *C* from General Electric Company (couple *10B*) have not oxidized to any extent as a result of three calibrations and two heat treatments.

On the General Electric Company wire *C*, Fig. 1, there were narrow ridges of iron oxide running longitudinally with the wire. On the whole, the wire was in good condition at the end of the tests.

The wire from the Brown Instrument Company, *A*, Fig. 1, had spots of iron oxide in various places where the wire had been bent and the aluminum alloy chipped off. Owing to the chipping the wire *A* was not in such good condition as wire *B*.

A microscopic examination of the wires as received showed that the coating on the General Electric Company wire was very much thinner than that on the Brown Instrument Company wire. As a result of prolonged heating, the coating of iron aluminum alloy penetrated into the wire. In the wire from the Brown Instrument Company the alloy had penetrated about one-half the radius of the wire; in the wire of the General Electric Co. the alloy did not penetrate so deeply. The observations on microstructure were identical with those of W. E. Ruder.[3]

In Fig. 2 is shown the comparison of the first calibrations of all the samples. It will be noted that couple *32B* on the first calibration gives a higher electromotive force for a given temperature than the other two couples. On repeated calibrations, the latter couples also gave concordant results, but *32B* discordant results. After heat treatment of *32B* at 800° C., however, its calibrations became concordant, and the same as the other couples, showing that it was probably not sufficiently annealed at the beginning.

These tests have not, of course, shown what would happen when the core of iron was all changed to the alloy of iron and aluminum. Before such thing would take place the companion wire, constantan, would be used up.

CONCLUSIONS.

1. "Calorized" iron may be a suitable material to replace iron in the iron-constantan combination, because it has the same electromotive force and constancy as uncalorized iron, but has a much longer life.

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[3] *Loc. cit.*

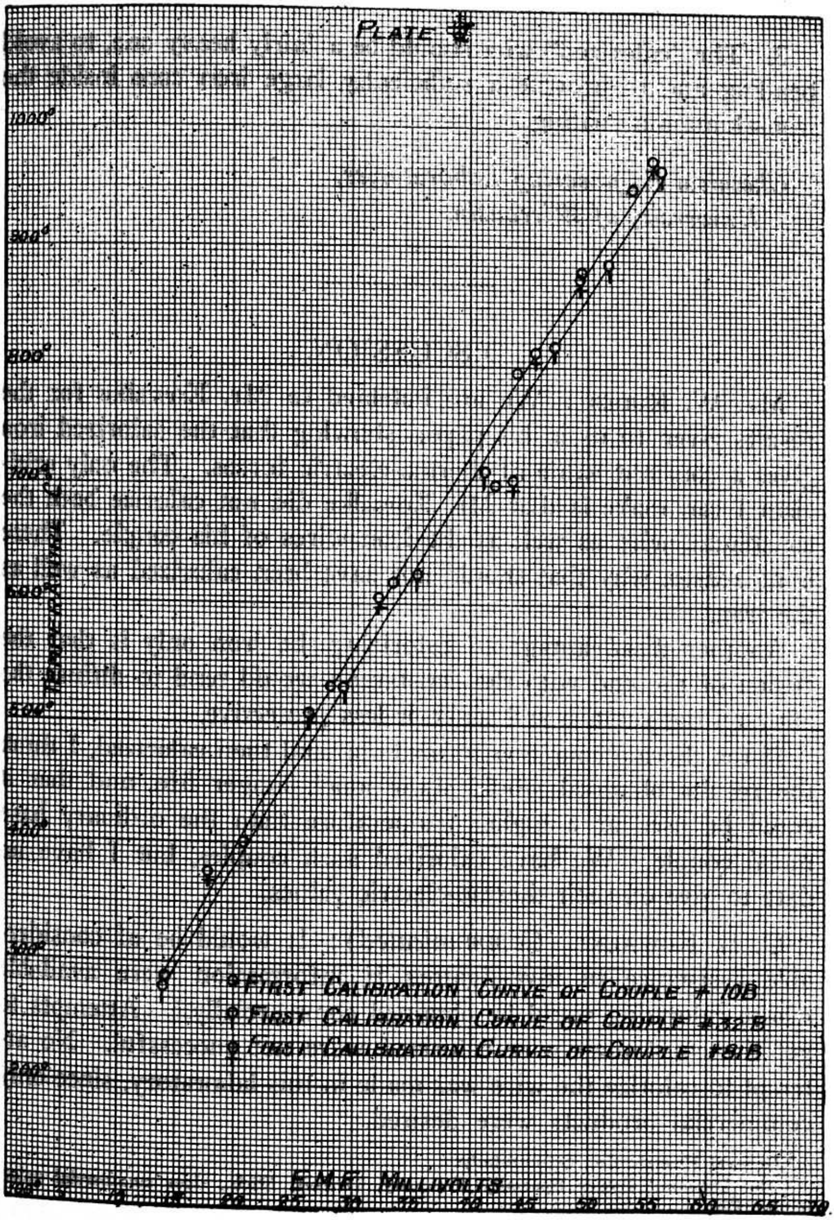

FIG. 2.

2. A thin coating of "calorizing" is effective, and is to be preferred over a thick coating because of the greater liability for a thick coating to flake off on bending.

3. The "calorized" wire should be a fairly heavy one, to avoid bending and to provide a sufficiently large iron core inside the iron-aluminum coating.

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DISCUSSION.

MR. W. RUDER[1]: We are indebted to Mr. Kowalke for the results given to us in his paper, showing that the calorized iron gives a constant value of thermo-electric forces. The only criticism I can make is that Mr. Kowalke did not calorize both the constantan wire as well as the iron wires of his couple. There is no reason why that should not have been calorized as well as the iron.

Another disadvantage of calorizing the iron only is that the fusion of the end with the constantan would tend to diffuse the alloy on the surface and make it less protective.

If the thermo-couple were made up and then calorized, I think the results obtained would show much longer life, and that it could be used at a higher temperature than the ordinary base metal couple. We have calorized such couples, but I have no data to give on their thermo-electric values.

O. L. KOWALKE (*Communicated*): It would be of considerable assistance to investigators if information were available where calorizing could be obtained commercially.[2] Attempts to get the constantan wire calorized were not successful. No attempt to calorize the wire was made in this laboratory, since only commercial products were desired.

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[1] General Electric Co., Schenectady.

[2] The Diamond Power Specialty Company, Detroit, Mich., does commercial calorizing.—ED.

[FROM THE TRANSACTIONS OF THE AMERICAN ELECTROCHEMICAL SOCIETY, Volume XXXII, 1917, being the Transactions of the Thirty-second General Meeting, at Pittsburgh, Pa., October 3, 4, 5, 6, 1917.]

The Corrosion of Metals by Acids

BY

O. P. WATTS and N. D. WHIPPLE

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		Disch. Potential of Hydrogen		Potential minus Dis. Potential of Hydrogen		Heats of formation of chlorides		
	SO_4	Cl						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	0.062	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	—0.080	Fe,Cl_2	82050	99950
Pb	....	—0.095	Cd	0.248	Sn	—0.377	Sn,Cl_2	80790	81140
H	—0.238	—0.249	As	0.158	Pb	—0.497	H_2,Cl_2	......	78630
Cu	—0.515	....	Cu	—0.002	Cu	—0.507	Pb,Cl_2	82770	75970
As	....	—0.550	Ni	—0.022	As	—0.702	Cu,Cl_2	51630	63710
Hg	—0.980	....	Ag	—0.082	Ag	—0.759	Hg,Cl_2	54490	51190
Ag	—0.974	....	Pt	—0.112	Pt	—1.022	Ag_2,Cl_2	58760	......
Pt	....	—1.140	Au	—0.212	Au	—1.138	H_2,Cl_2	44000	......
Au	....	—1.356	PtPt	—0.232	Hg	—1.522	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

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* 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

[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.

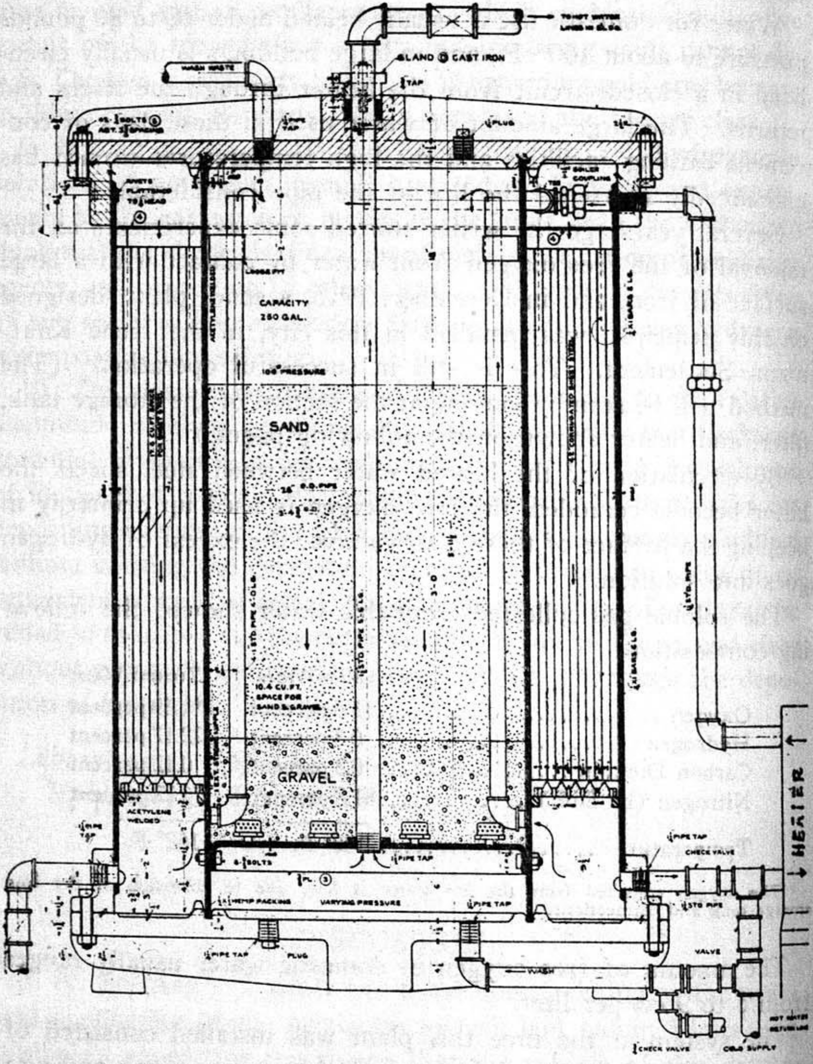

FIG. 1. System for Removing Dissolved Oxygen from Hot Water.

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

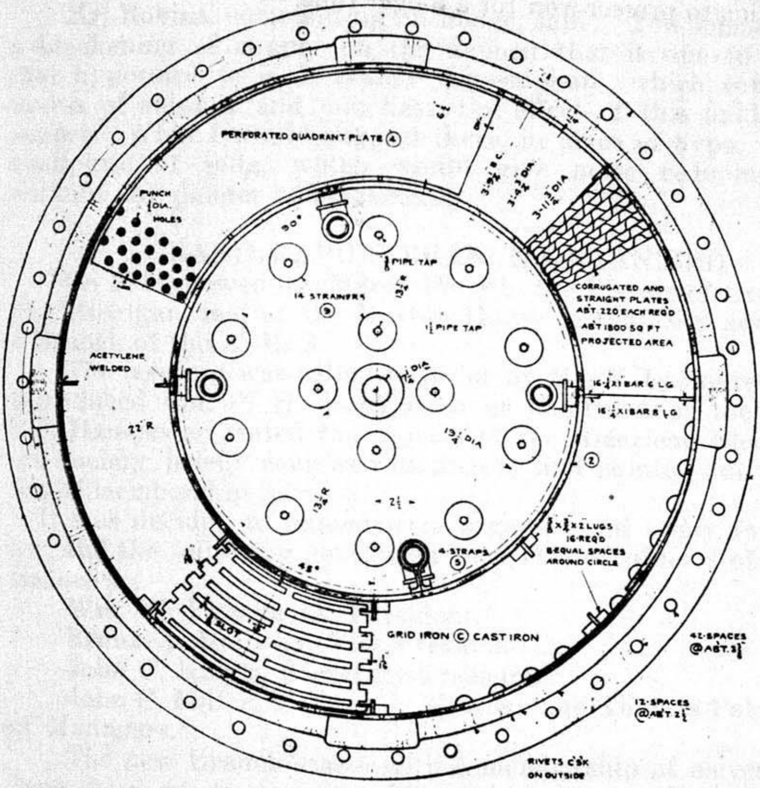

Fig. 2. Cross-Section of Fig. 1.

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.

SOME PRINCIPLES OF ELECTRO DEPOSITION.

By Dr. Oliver P. Watts, Wisconsin University.

This communication is in response to the request for discussion of the questions on page 18 of the February number.

"(d) Why is there a greater evolution of hydrogen gas in an alkali solution with the same current density than in an acid solution?

"(e) Why does not this greater evolution of hydrogen gas in an alkali solution practically ruin the deposit as it would in an acid solution?"

In the first place it is necessary, in discussing question (d), to limit the discussion to particular cases, for there are alkaline solutions in use by the plater from which gas is not evolved any more readily than from acid solutions; for example, the silver bath. If we confine ourselves to the acid sulphate and cyanide baths for depositing copper, which are probably the solutions had in mind by the questioner, the answer to (d) is as follows:

An acid solution may be considered as containing a salt of hydrogen, and whether or not this gas will be deposited along with the metal is controlled by the same principle that determines whether or not, when two metals are in solution, only one, or both of them, will be deposited at the cathode on passing current. The best way of predicting this is from the electrochemical series or from a table of potentials of the metals, such as was given by Mr. H. E. Wilmore on page 8 of the Review for January, 1916. If the solution contains two metals that are far apart in the series, only the one that is of lower potential is deposited at low or moderate current densities, i. e., so long as any of this metal is in contact with the cathode. If deposition is so rapid that the metal of low potential cannot diffuse from the main body of the solution to the cathode as fast as called for by the current, enough of the second metal will be deposited to make up for the deficiency; but before this occurs the current density has become so high that the deposit is "burned." The rough, dark, poorly-adherent metal called a "burned" deposit results from using a current density too high for the strength of solution in the film that actually touches the cathode; and although in certain solutions this condition is accompanied by an evolution of hydrogen, the presence of this gas has nothing to do with the "burning" of the deposit.

This is illustrated by attempting to deposit zinc and copper from a mixture of their sulphates, in which the potentials of the two metals are a volt apart. At low current densities a good deposit of pure copper is obtained; increase of current does not yield brass, that is, the deposition of some zinc along with the copper, until the current has been raised to such a degree that the deposit is spoiled by burning. If the potentials of the metals are close together, some of the second metal begins to be deposited along with the metal of lower potential before the current has become so high as to exhaust the supply of the first metal from the film of solution at the cathode, and an alloy of the two is produced without burning. Nickel and iron, with a difference of

0.003 volt in sulphate solution, are examples of metals that yield alloys by electrolysis. The choice of the cyanide solution for brass plating is because the potentials of zinc and copper are very close together in that electrolyte.

It has been said that acids act like salts of hydrogen, and hence when acid is added to the solution of some metallic salt, for example copper sulphate, there are three possibilities: First, that hydrogen may be deposited alone in place of copper; second, that both hydrogen and copper will plate out; and third, that electrolysis will proceed just as before the acid was added, and copper alone will be deposited. What takes place depends on the relative "discharge potentials" of hydrogen and of the metal, in this case copper. The discharge potential of any element is the potential required at an electrode (in this case we are considering only the cathode) in order that that particular element shall be deposited. Unfortunately the discharge potential of hydrogen is not a constant for a particular solution, as is the case with each metal, but is affected by the metal on which it plates out, so that the discharge potential of hydrogen must be known for the particular cathode employed. The discharge potential of a metal is the same as the potential set up by dipping the metal in that solution, i. e., it is the ordinary value of potential given for that metal.

The discharge potential of copper from sulphate solutions is about 0.5 volt higher than that of hydrogen deposited on copper from the same electrolyte, hence copper deposits in preference to hydrogen, and large amounts of sulphuric acid may be added to a copper sulphate solution without causing hydrogen to be deposited along with the copper. If, however, sulphuric acid be added to a nickel bath a deposition of hydrogen results, and only a moderate amount of acid is required to cause a complete substitute of hydrogen deposition in place of nickel.

In an alkaline solution of the double cyanide of copper and potassium or sodium (the active material of the plater's cyanide copper solution) without any free cyanide, the potential of copper is slightly below the discharge potential of hydrogen on copper, and it is possible to deposit copper at low current density without visible evolution of hydrogen; but the potential of copper rises rapidly with increase of free cyanide so that only a little free cyanide is required to raise the potential of copper above the discharge potential of hydrogen; when hydrogen is deposited in preference to copper. The amount of free cyanide necessary to secure good anode corrosion and a good color to the deposit is sufficient to bring about the deposition of some hydrogen along with the copper. The amount of free cyanide can be made so great that only hydrogen and no copper is deposited, just as one can take a solution of zinc sulphate which is giving a good deposit of zinc, and by adding copper sulphate to it in increasing amounts, lessen and finally prevent entirely the deposition of zinc. The reason for the change in deposit is the same in each case—the addition of a compound which is capable of yielding at the cathode an element whose discharge potential is much less than that of the metal which was being deposited at the outset.

When, because of a considerable difference in discharge potentials, there is a decided tendency toward the deposition of one of two elements in preference to the other, the addition of any considerable amount of a salt of the first element will prevent deposition of the second by supplying at the cathode enough of the first to carry all the current; but adding a compound of the second element to a solution from which the first is being deposited does not, as a rule, cause a change in the deposit. Much acid may be added to solutions of the chlorides, sulphates, or acetates of copper, silver, mercury, gold and platinum without seriously diminishing the current efficiency through the deposition of hydrogen, because the potentials of these metals are less than the discharge potential of hydrogen on them; but the addition of a strong acid (a salt of hydrogen) to a solution from which iron, cobalt, nickel, or zinc is being deposited causes hydrogen to be evolved at the cathode instead of much or all of the metal, depending on how much the discharge potential of hydrogen is below the potential of the metal, on the amount of acid added, and on the current density.

Although many details could not be explained within the compass of a short letter, it is hoped that the general principle governing the simultaneous deposition of two elements, or the deposition of one in preference to the other, has been made clear.

DON'T BE LIKE A LOBSTER.

The lobster, when left high and dry among the rocks, has not sense or energy enough to work his way back to the sea, but waits for the sea to come to him. If it does not come, he remains where he is, and dies, although a little effort would enable him to reach the waves, which are, perhaps, tossing and tumbling within a few feet of him.

"ENGLISH AS SHE IS SPOKE."

They sometimes say, "It's cold as ——"
Sometimes they say, "It's hot as ——"
And when it rains "It's ——" they cry.
It's also —— when it's dry.
They "hate like ——" to see it snow,
"It's a —— of wind" when it starts to blow.
Now "How in ——" can anyone tell,
"What in ——" they mean by the word of ——?

Appreciation is valued because it is the testimony to an accomplishment. There is no joy comparable with that given by the realization of a work well done.

He who thinks only of himself hasn't any too much to think about.

SOME CHARACTERISTICS OF FIRE CLAY AND SILICA REFRACTORIES

O. L. KOWALKE

Chemical Engineering Laboratories, University of Wisconsin.

As read at the Seventeenth Annual Convention of the Wisconsin Gas Association at Milwaukee, March 26 and 27, 1918.

The answer to the question "What is the best refractory?" is not simple. The use for which a refractory is intended will determine its composition and characteristics. Because of the wide variation in quality of the raw materials and the indeterminate reactions in the process of burning the ware, the finished products will vary between wide limits. Some of these products will have the property of being infusible at the highest temperatures attained in combustion operations and of being resistant to cracking through sudden changes in temperatures. Some will resist the corrosive action of slags and fluxes and the cutting action of flames; others will resist abrasive actions. The principal refractory materials of importance to the gas industries are fire clay and silica; they have quite different properties and can not be used interchangeably for all purposes.

Fire bricks are made by moulding into the desired shapes a mixture of moist fire clay and grog, which after being dried is fired to about 1300°C. Fire clay is a most complex material, the principal ingredient being a hydrous silicate of alumina (Al_2O_3, 2 $Si\ O_2$, $2H_2O$), and in addition there may be many other elements present. The elements in clay other than the silicate of alumina have a decided influence on the way the clay behaves when heated. Clay does not possess a sharp melting point like copper or iron; it sinters together, becomes less porous, contracts in volume, and softens gradually until finally it will flow. The sintering of clay is accompanied by contraction and is due to the melting of some of the more fusible constituents which dissolve the less fusible and bind the whole into a compact mass. This contraction is increased by raising the temperature or extending the time of exposure. To avoid subsequent shrinkage, it is important that the brick be fired at a temperature higher than that obtained in the furnace where it is used.

The greatest portion of the material used in brick is grog. Grog is a term applied to burnt fire clay or ground fire brick which serves as the framework. Mellor has called grog the skeleton and the clay bond the flesh of the refractory. When a brick is burned the clay bond sinters and part of its own more fusible constitutents dissolve portions of the clay and of the grog. This plastic mass binds the skeleton together into a solid brick. Each clay has its own capacity for dissolving grog and upon this fact depends to some extent the refractoriness of a brick. If grog is made of the same material as the bond clay the tendency toward mutual solution is increased. The character of the grog controls the contraction of the brick during burning because of its solubility in the bond clay. Some grogs are sparingly soluble in the clay and the refractoriness of that brick is apt to be high.

The grog should be so graded as to size that the voids between the larger particles are filled with smaller particles and the whole cemented together by the clay. If only coarse particles of uniform size are used, shrinkage cracks in clay develop on drying and firing which are sources of weakness. Coarse ground grog produces brick which are more resistant to cracking due to sudden changes in temperature than fine grained brick. Brick made with a coarse grog have a lower crushing strength cold they do not resist wear and abrasion so well; they will in general resist a high temperature before softening; they do not resist corrosive slags and the cutting action of flames so well as brick made with a fine grog. Thus it is apparent that all conditions in furnace operations are not met by any one fire brick. Each condition must be served by a brick made with a combination of clay and grog that is best suited for the purpose.

Fine-grained texture gives brick the property of resisting the corrosive action of slags, dust, fluxes, etc. The slag or flux first attacks the bond clay and very soon eats out a small pocket. Should the grain be coarse, the particle of grog may fall or be scraped out and thus new surfaces of clay be exposed; with fine-grain texture there is not the danger of dislodgment of particles but the slag or flux must eat its way in. For retorts and similar devices a fine texture material is superior to a coarse one, other things being equal, because of the lower porosity of fine textured material, there will evidently be less gas loss. On the other hand a fine textured refractory will crack easier with sudden changes of temperature. Hence for retorts the size of grog and its proportion to clay bond must be carefully determined. The preceding discussion has touched on only a few of the complex problems in fire clay ware. The problem with silica is somewhat simpler.

Silica brick consists of crushed quartzite mixed with a suitable binder of slaked lime, moulded into desired shapes, dried and then fired to convert the mixture into a mineral complex which possesses desirable properties for furnace construction. The desirable properties are:

(1) Ability to withstand sudden changes of temperature without cracking or disintegration;

(2) Refractoriness at the highest temperature employed in the furnace;

(3) Resistance to the attack of products of combustion;

(4) A regular and not excessive co-efficient of expansion.

The silica is the skeleton and the lime is the binder. Upon firing a lime silicate is formed which is more fusible than silica, and which binds the particles together. The more lime that is used, the more readily will the brick fuse at a lower temperature. Since the formation of lime silicate is aided by intimate contact of lime and silica, hence the smaller the particles the larger will be the surface exposed per unit volume and the greater the amount of lime silicate formed. One method of obtaining a minimum of voids and surface of silica is to mix two sizes of silica, one about one-half the size of the other. Such a procedure also reduces the lime bond necessary.

Fenner of the Geophysical Laboratory at Washington has investigated the transformations occurring in silica at elevated temperatures and found that:

(1) The change from alpha to beta quartz occurs at 575°C and is rapid and reversible.

(2) The change from beta quartz to tridymite occurs at 870°C and is very sluggish and also reversible.

(3) The change from tridymite to cristobalite occurs at 1470°C and is very sluggish and also reversible.

The specific gravity of quartz is about 2.66, that of tridymite and cristobalite 2.27 and 2.33 respectively. Thus the tridymite and cristobalite are lighter than quartz from which they originate. This explains why a silica brick expands upon being fired. In firing silica brick the change that occurs is from quartz to cristobalite mainly, but this change takes place very slowly. When all the quartz has been changed to cristobalite the change in volume is complete and no further expansion takes place.

Seaver* has shown that brick made from Baraboo quartzite and burned for forty hours at 1540°C had about 77 per cent of the quartz changed to cristobalite. A second and third reburning at the same temperature for 40 hours, extended the change from quartz to cristobalite to about 83 per cent and 84 per cent respectively. The expansion in the brick intended for by-product coke oven silica is $\frac{3}{8}$ to $\frac{7}{16}$ inch per foot which is somewhat better than 13 per cent by volume which is the change from pure quartz to wholly cristobalite.

Ross** cut two-inch tubes from silica brick made from the principal quartzites in this country and fired them at 1400°C, 1450°C and 1500°C. He found that the porosites decreased, the volume expansions increased, and the specific gravities decreased

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*Seaver—"Manufacture of Silica Brick"—Met. & Chem. Eng. 1915.

**Ross—Volume Changes in Silica Brick—Trans. Am. Ceram. Society 1917.

with treatments at the temperatures noted above. The Pennsylvania and Wisconsin quartzites that had reached equilibrium upon firing at 1500°C showed very small changes as compared to the same materials fired at 1450°C.

Thus it is clear that unless silica brick are fired above 1470°C to complete the change from quartz to cristobalite, there will always be a residual expansion in the brick when subsequently heated in furnace operations. Such expansion will result in the formation of cracks in the walls of the furnace or retort that may be very serious.

From the results of the tests on the volume changes in silica brick, Ross* believes that a fairly accurate and rapid determination of the completeness of the volume change and the firing temperature can be made by taking the specific gravity of the brick.

The methods proposed by Ross for volume, porosity and specific gravity changes are as follows:

$$\text{Volume} = \text{Wet Weight} - \text{Suspended Weight.}$$

$$\text{Porosity} = \frac{\text{Wet Weight} - \text{Dry Weight}}{\text{Wet Weight} - \text{Suspended Weight}}$$

$$\text{Specific Gravity} = \frac{\text{Dry Weight}}{(\text{Wet Wt.} - \text{Susp. Wt.}) - (\text{Wet Wt.} - \text{Dry Wt.})}$$

"The range of pórosities observed are between 22.64 per cent and 31.96 per cent and indicate what is likely to be found in industrial practice." The specific gravities of all bricks tested by him lay within the limits of 2.66 and 2.27 which are also the limits between raw quartz and tridymites. Since the specific gravities of tridymite and cristobalite are 2.27 and 2.33 respectively, there is ample range to designate those bricks which have been fired at a high enough temperature, and to fix the quality of the material. The tests proposed by Ross are simple and may be made rather rapidly.

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*Ross—Volume Changes in Silica Brick—Trans. Am. Ceram. Soc. 1917.

[FROM THE TRANSACTIONS OF THE AMERICAN ELECTROCHEMICAL SOCIETY, Volume XXXIII, 1918, being the Transactions of the Thirty-third General Meeting, on a trip through the Appalachian South, April 28 to May 5, 1918.]

WHY BUSY RAILS DO NOT RUST

BY

O. P. WATTS

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:

	1st Exp.	2d Exp.	3d Exp.
Time in Days.	303	730	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

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

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Brittleness Produced in Steel Springs by Electroplating

BY

O. P. WATTS and C. T. FLECKENSTEIN

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.

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 use 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 reports entire freedom from brittleness; Fuller[5] secures the same result when copper-plating steel from a cyanide solution by first

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[1] Assoc. Prof. of Chemical Engineering, University of Wisconsin.
[2] Student, University of Wisconsin.
[3] Met. & Chem. Eng., 1917, 16, 83.
[4] Tr. Amer. Electrochem. S., 1917, 32, 237.
[5] Tr. Amer. Electrochem. S., 1917, 32, 247.

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 mm. 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 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

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

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

Chemical Engineering Laboratories,
University of Wisconsin.

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

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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[*Advance Copy. Printed; Not Published. Discussion Invited. For Release May 5, 1918.*]

CRUSHING STRENGTH OF MAGNESIA-SILICA MIXTURES AT HIGH TEMPERATURES.[1]

By O. L. KOWALKE[2] AND O. A. HOUGEN.[3]

ABSTRACT.

Magnesia was mixed with varying proportions of silica, baked at various temperatures, and cylinders of the mixture subjected to pressure in an electrically heated furnace, the pressure being applied by a carbon rod, at carefully measured temperatures. The various mixtures were compared by noting the temperatures at which they were crushed by a given applied pressure. Maximum strength was found in mixtures with 7½ percent silica. The apparatus used is described, and microphotographs shown which explain the theory of the formation of compounds between magnesia and silica at the various temperatures. [J. W. R.]

Magnesia, because of its high melting temperature and strong basic qualities, is one of the most important refractories for electric furnace operation. It has served for crucibles used for melting alloys at high temperatures, especially where it was desired to keep the metal or alloy free from contamination with carbon. Although magnesia melts at 2,800° C.,[4] it becomes mechanically weak and somewhat plastic much below this temperature, so that when used for crucibles it must be backed up by some stronger material. At temperatures above about 1,600° C. a charge of molten iron in a crucible 3 inches by 5 inches high (7.6 cm. by 12.7 cm.) will break through the magnesia, owing to its low mechanical strength.

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[1] Manuscript received March 2, 1918.

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

[3] Instructor in Chemical Engineering, University of Wisconsin.

[4] Kanolt: Bull. Bureau Standards, 10, 295.

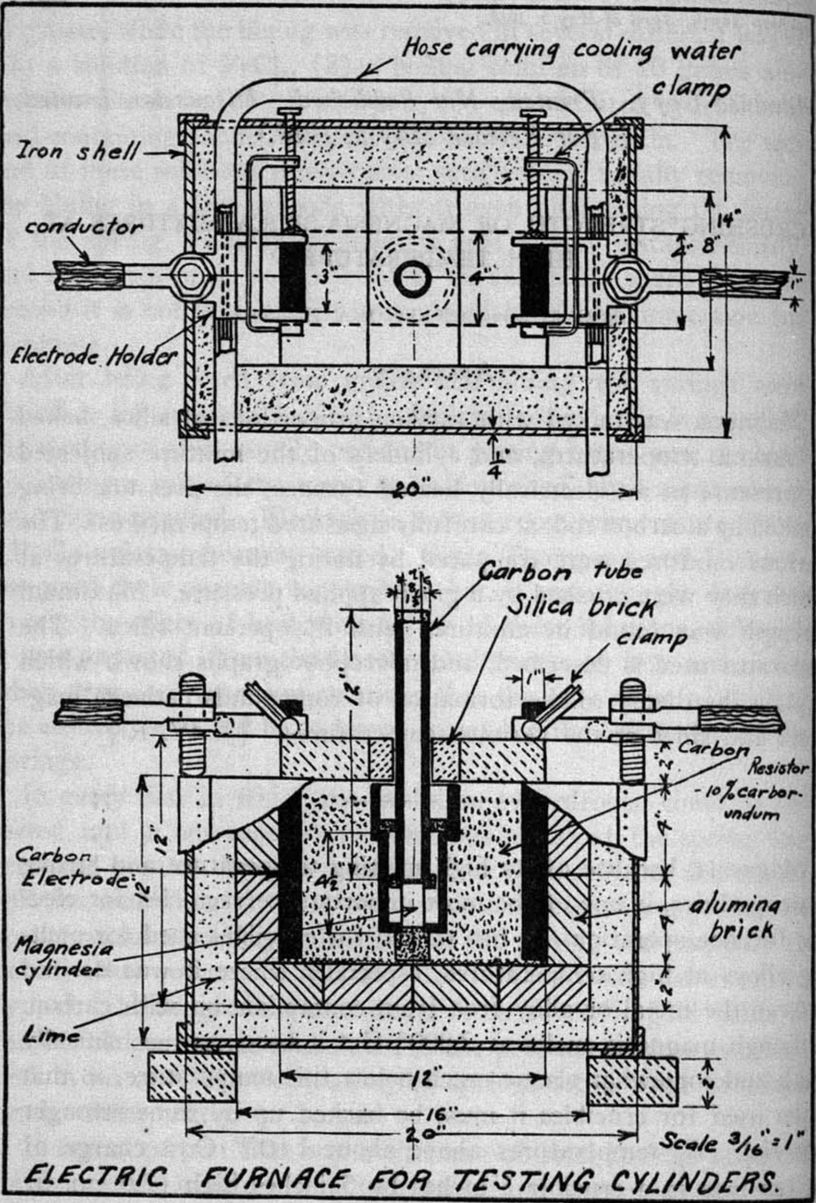

PLATE I.

An investigation was made by one of us to determine whether the addition of various metallic oxides, such as Al_2O_3, Cr_2O_3, TiO_2, SiO_2, ZrO_2, to magnesia would give a mechanical strength at high temperatures greater than magnesia itself. This preliminary investigation showed that in general there was an increase in mechanical strength. Of all the materials tried, silica gave the best results.

The purpose of this investigation was to determine more closely the influence of silica upon the crushing-strength capacities of silica-magnesia mixtures at high temperatures.

PROCEDURE.

A pure grade of magnesia was prepared from Merck's "Magnesium Oxydatum" by calcining the same in a gas furnace at about 1,500° C. The analysis of the calcined product was: MgO 99.92, Fe_2O_3 0.08, H_2O 0.02. The silica used was obtained from a rather good grade of quartz, which analyzed: SiO_2 97.66, CaO 0.86, Fe_2O_3 0.80, H_2O 0.08.

Both materials were ground to 40-mesh (16 per cm.) in a porcelain ball-mill. After grinding, the two were mixed in the various proportions desired and tumbled again in a porcelain ball-mill to insure intimate mixture. From the mixtures of silica and magnesia test cylinders were made.

The mixtures of silica and magnesia were moistened with 10 percent (an amount found most effective) of their weights of water, and then formed into cylinders in a hydraulic press under a pressure of 1,500 lb. per sq. inch (105 kg. per sq. cm.). They were dried at 100° C., and then baked in a granular carbon resistor furnace to about 2,100° C. After the cylinders had cooled in the furnace, they were ground to a uniform cylindrical form, 1 inch diameter by 2 5/32 inch long (2.54 cm. diameter by 5.5 cm. long), with the ends parallel.

The test cylinders were then put under a uniform static load of 66.5 lb. per sq. in. (4.65 kg. per sq. cm.) and heated at a uniform rate until they failed. The rise in temperature and the temperature at which failure occurred were measured by means of a Holborn-Kurlbaum optical pyrometer.

APPARATUS.

The furnace used for testing the cylinders is shown in Plate I. The resistor consists of carbon plus ten percent of carborundum. The magnesia-silica cylinder under test (*D*, Plate II) rested upon a graphite block *A* which was held in place by a graphite crucible *B*. The pressure was transmitted to the magnesia cylinder *D* through the carbon tube *C* and the graphite disc *E*. Recesses were turned in the disc *E* so that the test cylinder *D* and the carbon tube *C* were held in place. A cover ring of graphite *F* was

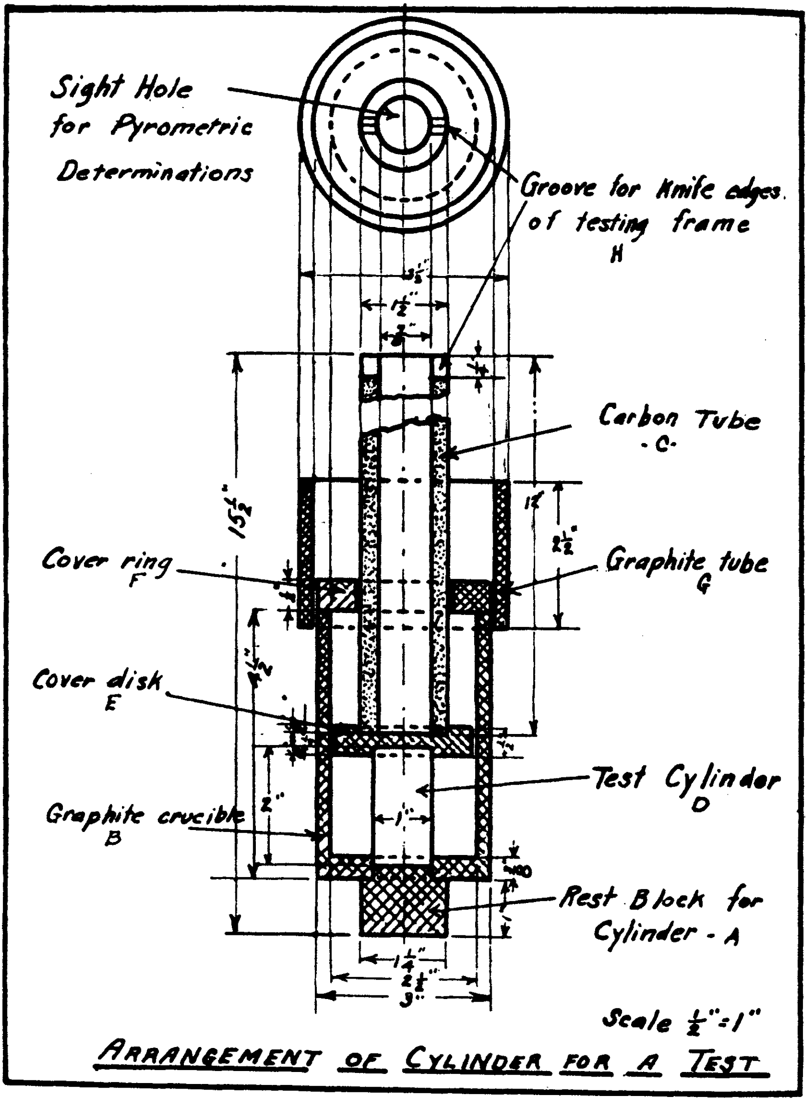

PLATE II.

placed on top, and another graphite tube *G* was fitted around the crucible *B* to prevent the resistor from falling in.

Pressure was applied to the carbon tube by means of a lever and weight, so arranged that eccentric loading was minimized. The lever was kept as horizontal as possible, and the motion sideways was also restricted, yet freedom of motion in a vertical plane was possible.

The Holborn-Kurlbaum optical pyrometer was mounted on a platform so that the line of sight in the telescope coincided with the axis of the carbon tube *C*, Plate II. The tube *C* served as a "black body" for observing the temperature of the test cylinder. The brightness of the lamp filament in the pyrometer was matched against the brightness of the disc *E* which was ¼ inch (6.5 mm.) thick at the section covering the test cylinder. All carbon and graphite parts used in the temperature measurements were first thoroughly heated to above 2,100° C. to distill off any volatile materials or such as would produce fume. Since the rise in temperature of the furnace was very slow, it was assumed that observations for temperature on the graphite disc would also give the temperature of the test cylinder. The pyrometer was provided with a rotating sectored disc to permit extension of the range without overheating the lamp, and it was calibrated against a carefully calibrated platinum thermo-couple according to the method proposed by Prof. C. E. Mendenhall.[5]

PRELIMINARY TESTS.

After a few tests had been made it was recognized that the rate of heating the cylinders under test had a big influence on the result. The preliminary tests were made in the apparatus just described, but the cylinders were heated rapidly to 1,000° C. and then beyond that to the point of failure at rates varying from 10° to 20° C. per minute But it soon was clear that the rate of heating *below* 1,000° C. affected the results obtained. All temperatures were measured by the optical pyrometer, and since this is not sensitive below 800° C., the results were not satisfactory. The following table shows the irregularity of the results from this procedure.

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[5] Mendenhall and Forsythe: Phys. Rev., 1911, 33, 74.

Crushing Temperature of MgO / SiO_2 Mixtures Under Load.

Percent Silica	Temp. of Failure	Rate of Heating deg./min.	Temp. of Failure	Rate of Heating deg./min.
0	1,682	19	1,684	10
3	1,752	16	....	..
5	2,708	15	....	..
7	1,756	22	1,924	8
9	1,736	20	1,902	12
11	....	..	1,800	13

The manner in which the test specimens failed was quite uniform; it usually occurred by the cylinders bursting out at the middle, with ends telescoping each other.

While the rate of heating affected the results obtained on the magnesia-silica cylinders, it did not affect the results in a similar manner when pure magnesia cylinders were tested. A change in the rate of heating pure magnesia had but little effect on the temperature at which failure occurred. Failure in the magnesia cylinders came on gradually and slowly; in the magnesia-silica cylinders the failure was always abrupt.

FINAL TESTS.

From the preliminary tests it was evident that the addition of six to eight percent silica to magnesia gave a product whose strength at high temperatures was greater than pure magnesia. Owing to irregularity in the baking and testing, the results were open to question. A series of cylinders having amounts of silica varying from zero to twelve percent was made and baked at the same temperature—about 2,100° C. In the load-carrying tests, the temperature for each specimen was raised at a uniform rate of 10° C. per minute, from room temperature to the point of failure. A thermo-couple was used to measure temperatures below 1,000° C., and the optical pyrometer above that point.

The results of these tests are given in the table below. It is apparent that there is a distinct maximum at about seven to eight percent silica. The increase of strength up to eight percent silica

Plate III.

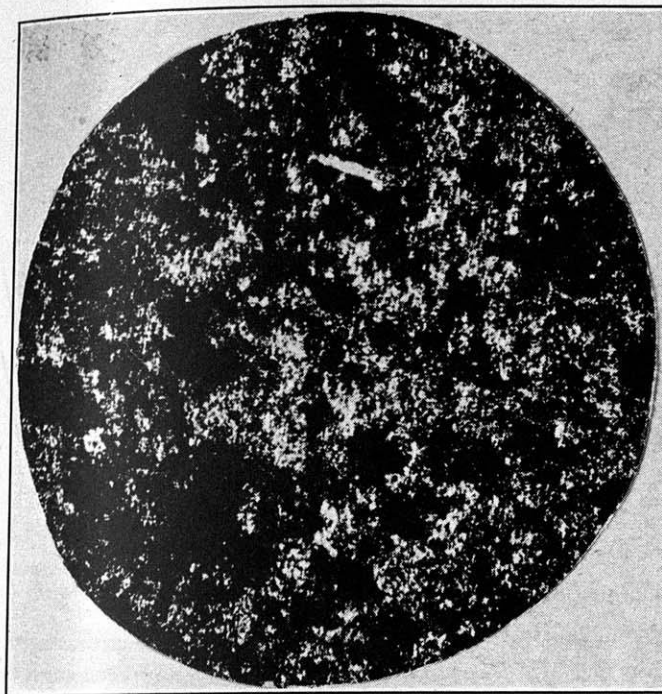

Fig. 1. *c* —baked at 1,900° C.; cooled in furnace.

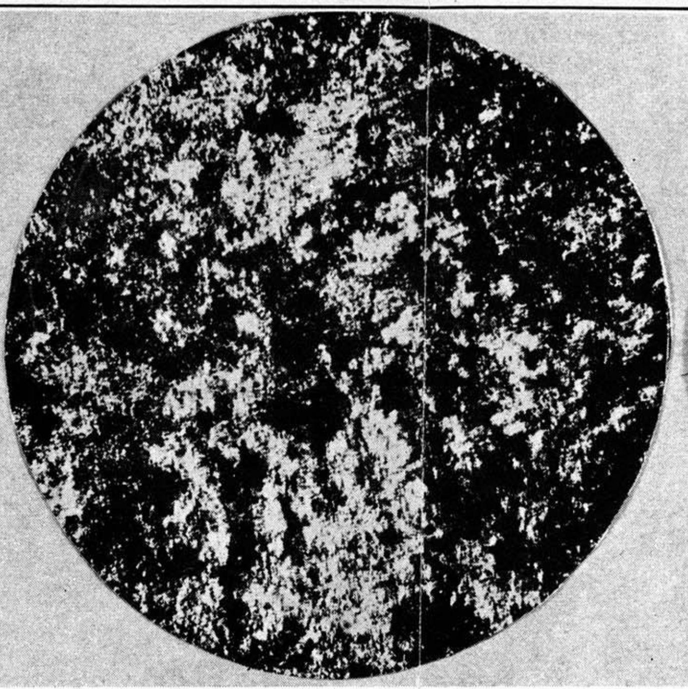

Fig. 2. *e*—baked at 2,000° C.; held 1 hour above 1,950° C.; cooled in furnace.

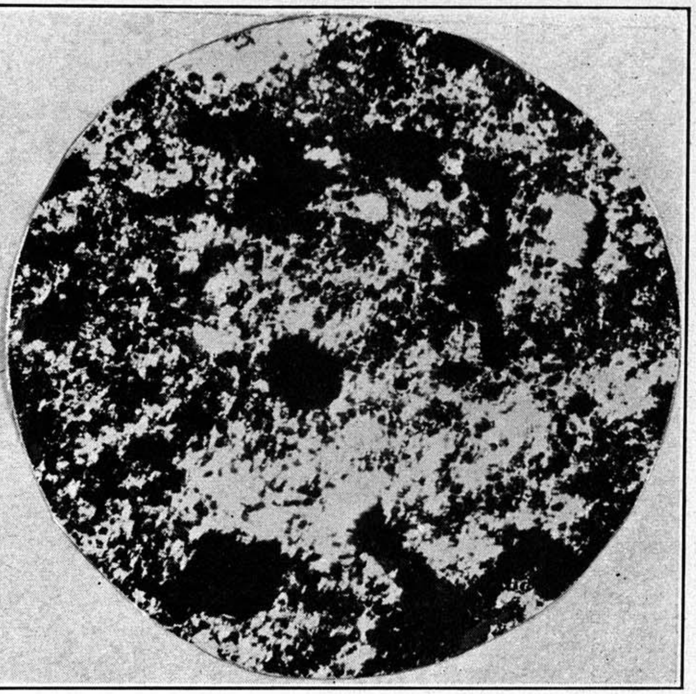

Fig. 3. *f*—baked at 2,100° C.; held 1½ hours above 1,950° C.; cooled in furnace.

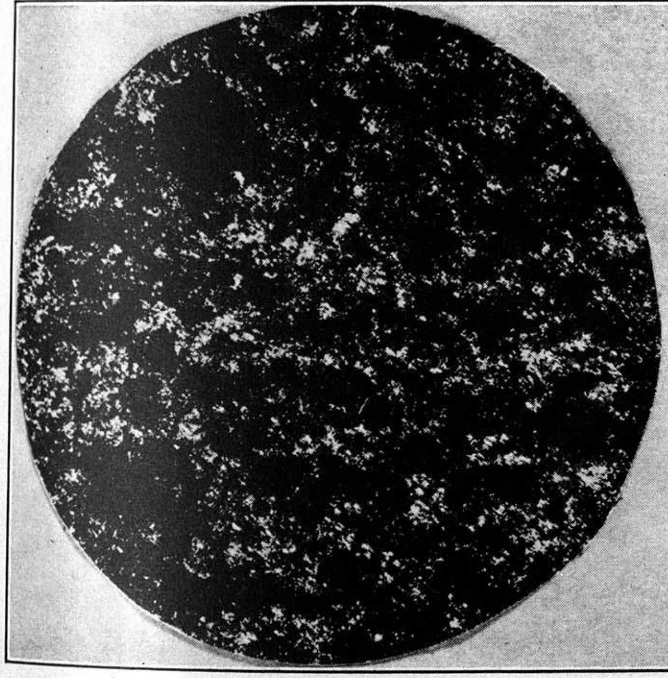

Fig. 4. *A*—baked at 1,800° C.; quenched in cold water.

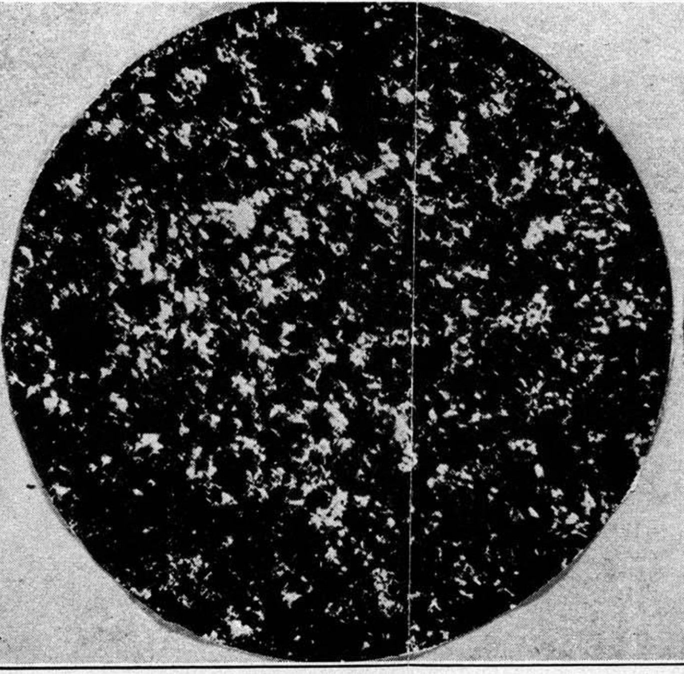

Fig. 5. *E*—baked at 2,000° C.; held 1 hour above 1,950° C.; quenched in cold water.

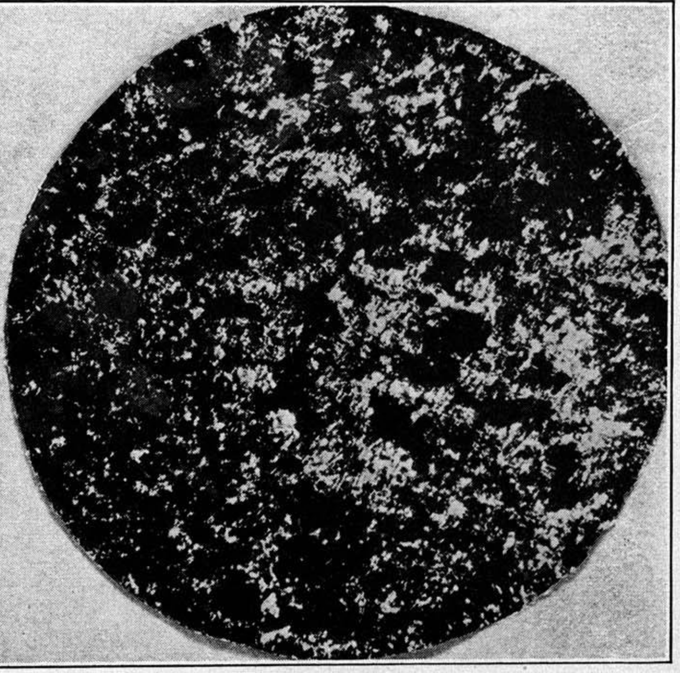

Fig. 6. *F*—baked at 2,000° C.; held 1½ hours above 1,950° C.; quenched in cold water.

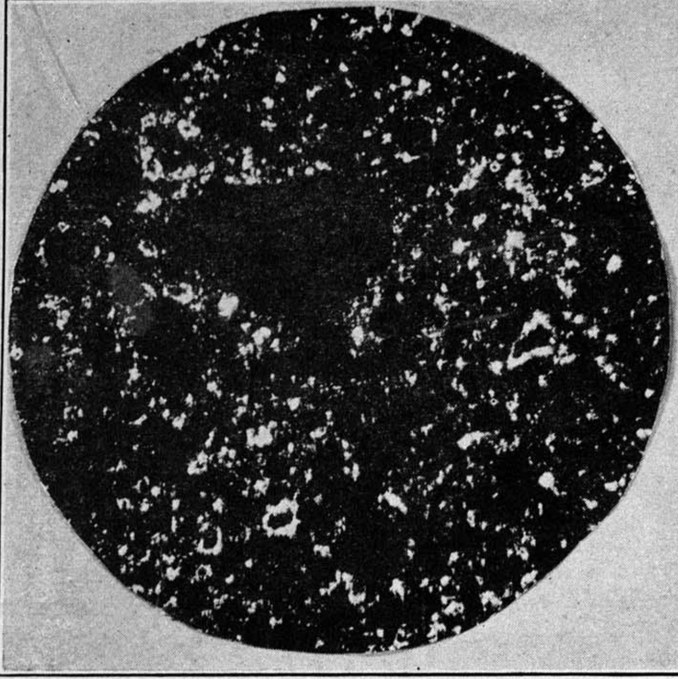

FIG. 7. *g*—baked at 1500° C. for 1 hour.

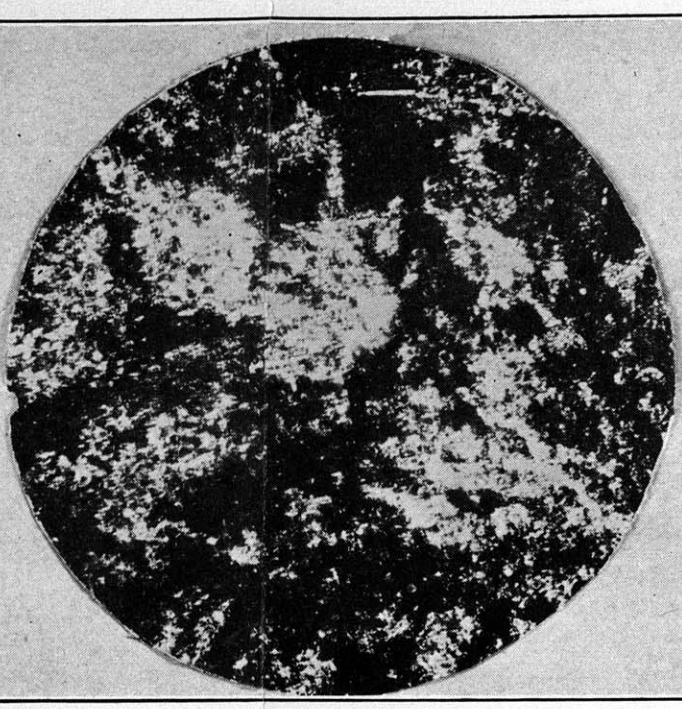

FIG. 8. *h*—baked at 1,800° C. for 1 hour .

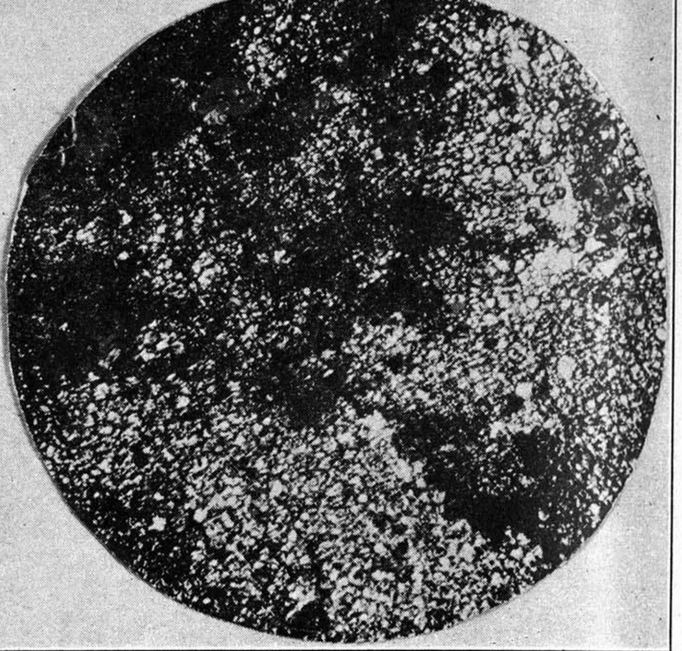

FIG. 9. *i*—baked at 1,960° C. for 1 hour.

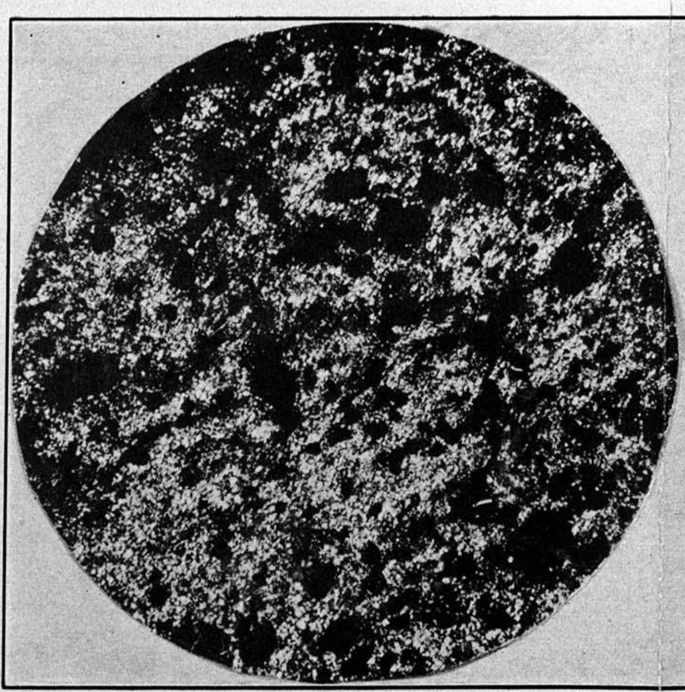

FIG. 10. *j*—baked at 2,200° C. for 1 hour.

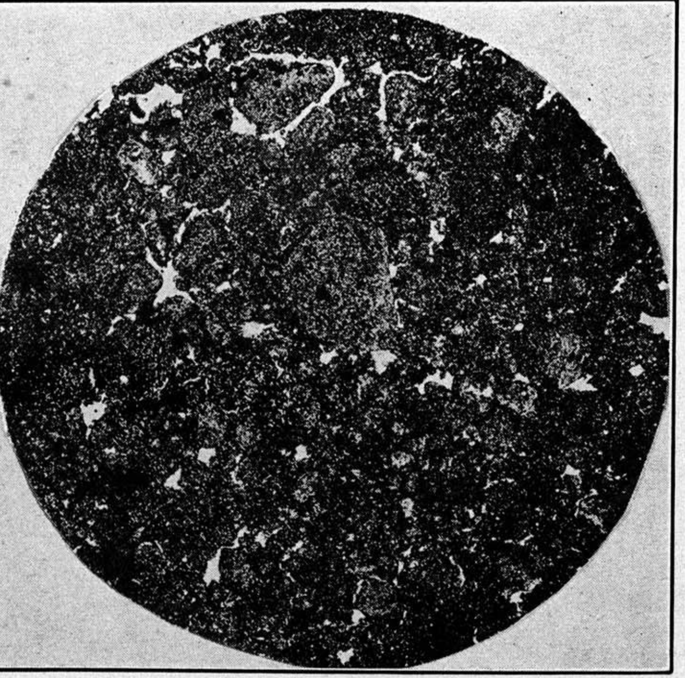

FIG. 11. PURE MAGNESIA—baked at 2,120° C.
[40 Diameters—*Unpolarized light.*]

is somewhat more rapid than the decrease in strength beyond that amount. The specimens having 7½ percent silica failed at a temperature 190° C. higher than that for pure magnesia.

Silica Content Percent	Temperature at Failure
0	1,680° C.
3	1,800
6	1,850
7	1,860
7½	1,870
8	1,845
8	1,860
12	1,830
12	1,845

Heat treatment during baking was recognized as an important factor in determining the subsequent strength of the cylinders. A series of cylinders containing 7.5 percent silica was made in the regular manner. The temperature of each cylinder in baking was raised uniformly at the rate of 20° per minute from room temperature to the maximum, and then the maximum was maintained for an hour. Then cooling proceeded slowly in the furnace. Cylinders so treated were baked respectively at 1,500°, 1,800°, 1,950°, and 2,200° C. The cylinders heated to 1,950° C. and 2,200° C. were badly pitted and corroded and showed a low temperature of failure.

Temperature of Baking	Temperature at Failure Under Load
1,500° C.	1,570° C.
1,800	1,820
1,950	1,720
2,200	1,790

The corrosion and pitting noted in the above tests above 1,900° C. made it desirable to study the effect of prolonged heating on the loss in weight. A series of cylinders having approximately 7.3 percent of silica were baked at various temperatures for varying lengths of time and allowed to cool in the furnace. Each cylinder was weighed before and after baking to determine the loss. The results are given in the following table:

Maximum Temperature of Baking	Percent Loss in Weight	Heat Treatment
1,500° C	3.7	1 hour at maximum temp.
1,800	6.1	10 min, " " "
1,800	7.4	1 hour " " "
1,800	8.5	10 min " " "
1,850	7.5	10 " " " "
1,900	9.8	10 " " " "
2,000	14.6	1 hour at 1,950° C.
2,000	17.1	1½ hours above 1,950° C.
2,000	11.0	1 hour at 1,950° C.
2,100	31.7	1½ hours at maximum temp.
2,200	27.0	1 hour at maximum temp.

From this data it will be seen that prolonged heating above 1,900° C. produces a great loss in weight, and that for temperatures above 2,000° C. the loss increases rapidly. In one case of prolonged heating at 2,100° C. complete volatilization of a magnesia-silica mixture resulted, due to the violent action of carbon upon both magnesia and silica. Cylinders baked at 2,100° C. and suddenly quenched in cold water produced a distinct acetylene odor.

Since the above heat treatment proved to be too severe, another set of 7½ percent silica cylinders was baked under less severe treatment. In this baking all cylinders to be heated at 1,800° or above were maintained at 1,800° C. for one hour and then heated at the usual rate, 20° per minute, until the maximum temperature was reached. Data obtained is given herewith.

Maximum Temperature of Baking	Crushing Temperature
1,500° C.	1,570° C.
1,800	1,820
1,850	1,870
2,100	1,900

This data shows that increased temperature and duration of baking increases the subsequent strength of the cylinders, but prolonged heating above 1,900° C. must be avoided, because of the destructive action of carbon upon magnesia.

MICROSCOPIC EXAMINATION.

Thin sections of various cylinders, baked at various temperatures and cooled in various ways, were made, to permit a microscopic examination of the crystallographic structures produced.

The specimens from which the thin sections were taken were all made with 7.5 percent silica. As shown in the table below some were heated to a predetermined maximum temperature, held there for a given period of time, and then quenched in cold water; other cylinders were allowed to cool slowly in the furnace after being brought to the maximum temperatures.

Mark	Maximum Temp. of Baking ° C.	Rate of Heating per Min.	Period of Heating at Max. Temp.	Cooling
A	1,800°	20°	10 min.	Quenched in cold water
B	1,850	“	10 “	“ “ “ “
C	1,900	“	10 “	“ “ “ “
D	1,950	“	10 “	“ “ “ “
E	2,000	“	1 hr. at 1,950° C.	“ “ “ “
F	2,000	“	1½ hrs. above 1,950° C.	“ “ “ “
a	1,800	“	10 min.	Cooled slowly in furnace
b	1,850	“	10 “	“ “ “ “
c	1,950	“	10 “	“ “ “ “
d	1,950	“	10 “	“ “ “ “
e	2,000	“	1 hr. at 1,950° C.	“ “ “ “
f	2,100	“	1½ hrs. above 1,950° C.	“ “ “ “
g	1,500	“	1 hr.	“ “ “ “
h	1,800	“	1 “	“ “ “ “
i	1,960	“	1 “	“ “ “ “
j	2,200	“	1 “	“ “ “ “
k	2,120	40°	(Pure magnesia)	“ “ “ “

In these specimens the minerals Periclase and Forsterite were identified. Below 1,500° C. there is only a slight formation of Forsterite. This mineral is formed first in minute crystals in the grain boundaries of Periclase. As the temperature is raised to between 1,700° C. and 1,800° C. the crystals grow rapidly in number and size, and finally unite to form a complete envelope about the Periclase. Above 2,000° C. this envelope of Forsterite, due to surface tension, collects into separate crystals. Specimens in which the Forsterite had collected into separate crystals failed under load at a lower temperature than those specimens where the envelope remained intact. This would appear to show that the Forsterite acts as a binder to hold the Periclase together, and that failure comes at a temperature when Forsterite softens.

The microphotographs shown in Plates III and IV were made with polarized light and crossed Nicols. The Periclase is represented by the black areas and the Forsterite by the white; the magnification being about 40 diameters. From Plate IV it is apparent that the Forsterite growth is progressive with a rise in temperature. The quenching operation serves to repress the formation of Forsterite, as shown in Plate III.

Pure magnesia, whose melting point is 2,800° C., has the proberty of bonding itself at temperatures 1,000° degrees below its melting point, into a hard mass. As shown in Plate IV, made in unpolarized light, the grain boundaries are fairly distinct. This specimen was thicker than the ordinary run of thin rock sections, but the material did not permit of thinner grinding without breaking. This specimen was baked at 2,100° C.; no other specimens of magnesia baked at lower temperatures were examined microscopically.

ACKNOWLEDGMENT.

Grateful acknowledgment is here made to Professors A. N. Winchell and W. J. Mead, of the Department of Geology of the University of Wisconsin, for many suggestions and assistance in identifying the minerals, the use of equipment, and the making of the microphotographs.

CONCLUSIONS.

1. Pure magnesia failed under a load of 66.5 lb. per sq. in. (4.65 kg. per sq. cm.) at a temperature of 1,680° C.
2. The addition of silica to magnesia, with seven to eight percent silica as a maximum, increased the mechanical load-carrying capacity, so that failure occurred only at about 1,870° C., which is approximately 190 degrees higher than magnesia supported.
3. The failure of magnesia cylinders is slow and gradual; that of magnesia-silica cylinders is abrupt.
4. The superiority of magnesia-silica mixtures with 7½ percent silica, over pure magnesia, in mechanical load-carrying capa-

city, appears to be due to the envelope of Forsterite, which cements the grains of Periclase.

5. Above 2,000° C. carbon attacks magnesia-silica mixtures very rapidly.

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University of Wisconsin.

[*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.*]

[FROM THE TRANSACTIONS OF THE AMERICAN ELECTROCHEMICAL SOCIETY, Volume XXXIV, 1918, being the Transactions of the Thirty-fourth General Meeting, at Atlantic City, N. J., Sept. 30, Oct. 1 and 2, 1918.]

The Sign of the Potential

BY

O. P. WATTS

A paper presented at the Thirty-fourth General Meeting of the American Electrochemical Society at Atlantic City, N. J., Sept. 30, 1918, President Tone in the Chair.

THE SIGN OF POTENTIALS.[1]

By Oliver P. Watts.[2]

Abstract.

A historical retrospect is given concerning the usage of electrochemists in designating the signs of potentials, and the plea made for continuing the present conventions. It is pointed out that if the present conceptions of electric current being a flow of (so-called) negative electrons be correct, that negative electrons would flow only to material of relatively higher (more positive) potential, and that the present usage of designating potentials would fit the facts in this case, while the proposed inversion of signs would contradict the facts. [J. W. R.]

At the meeting of this Society held at Detroit in May, 1917, a committee was appointed, of which the writer is a member, to consider and report upon the sign of the potentials of the metals, concerning which there are two different usages. The committee has held several meetings, has indulged in a voluminous correspondence, and has circulated among its members several tentative reports, but no definite recommendation has yet been made to the Society so far as the writer is aware,[3] although at the last meeting a member of the committee presented a paper on "the Sign of the Zinc Electrode." In this paper Dr. Bancroft distinguishes two kinds of potential, chemical and electrical, and concludes that the minus sign should be used for the electrical potential of zinc.

It may seem at first sight a matter of purely academic interest whether the positive or negative sign be prefixed to the potential

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[1] Manuscript received August 8, 1918.

[2] Associate Professor of Applied Electrochemistry, University of Wisconsin.

[3] Notice of the presentation of reports by the committee at the last meeting came after this paper had been sent in for publication.

of zinc; it is the purpose of this paper to show that the sign adopted for the potential of a metal is of importance to the progress of electrochemistry, and to present reasons for continuing the long-established use of the plus sign for the potential of zinc.

A phenomenon which attracted much attention from the early electrochemists was the displacement of metals from solution by other metals. The relative displacing power of many of the elements was thus measured, and when they were arranged in the order of their power of precipitating other metals, this constituted the electrochemical series. In the early electrochemical series the list began with oxygen, sulphur, etc., and ended with sodium and potassium, but later the order was reversed, potassium, sodium, etc., being placed at the beginning or positive end of the series, while chlorine, oxygen, etc., constituted the rear-guard, and were called electro-negative. The sequence was the same in both arrangements, and if this series were an isolated thing to be considered only by itself, it would make little difference which order were adopted, provided that one arrangement were adhered to by all. Electrochemists, however, have not been satisfied with a mere order, but have measured and expressed in volts the distances between different metals, so that the old electrochemical series has been converted into the modern table of potentials.

For many years such tables of potentials have been available, and in spite of their inaccuracy and the very limited number of electrolytes in which the potentials of metallic conductors are as yet known, these tables have proved of the greatest value in explaining the phenomena encountered in electrolysis, and in successfully predicting what will happen when certain electrodes are employed in a particular electrolyte. With the single exception of the table of electrochemical equivalents based on Faraday's law, the writer has found even the present incomplete tables of potentials to constitute the most valuable and most frequently consulted data in the whole field of electrochemistry. The complete and more accurate tables which will some day be available should prove of far greater value.

Some of the practical uses of tables of potentials are as follows:

1. They give the relative stability of compounds of the metals in solution.

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[1] Manuscript received August 8, 1918.

[2] Associate Professor of Applied Electrochemistry, University of Wisconsin.

[3] Notice of the presentation of reports by the committee at the last meeting came after this paper had been sent in for publication.

According to this table magnesium, zinc, etc., are electro-positive metals, while platinum and gold are highly negative. If a voltaic cell be formed by using two of the above metals as electrodes in a chloride solution the flow of current through the electrolyte will be from the metal of higher to that of lower potential, and the E. M. F. of the cell will be equal to the difference of potential between the metals.

For many years the above convention regarding the use of signs was unanimous. A few of many references are appended, in which writers on electrochemical subjects either give a table similar to that above, or refer to sodium, zinc, etc., as electro-positive, thus indicating their adherence to this method of designating potentials:

1890. Gore. Electrolytic Separation of Metals, p. 51.
1894. Neumann. Z. f. phys. Chem., **14**, 193-230.
1902. S. B. Christy. Amer. Chem. J., **21**, 354-420.
1904. Kahlenberg. Trans. Am. Electrochem. Soc, **6**, 57.
1905. Neuberger. Kalender f. Elektrochemiker, p. 250-254.
1905. G. McP. Smith. J. Amer. Chem. S., **27**, 541.
1908. C. F. Burgess. Trans. Am. Electrochem. Soc., **13**, 21.
1910. Cushman & Gardner. Corrosion and Preservation of Iron and Steel, p. 122.
1911. Friend. Corrosion of Iron and Steel, p. 265.
1915. McGraw-Hill. Handbook for Electrical Eng., p. 1565, 1567.
1915. Kahlenberg. Outlines of Chemistry, p. 457.
1916. Liddell. Metallurgists and Chemists Handbook, p. 299, 300.

In reading recently several thousand pages on the corrosion of iron, in books dating from 1822 to 1918, wherever stimulation of rusting by local action was mentioned, the iron was said to be positive to the copper, graphite, or whatever constituted the other electrode of the cell. Similarly the protective action of zinc was ascribed to its being electro-positive to iron.

In the gravity cell, shown in Fig. 1, we consider that mysterious something, which for want of a better name, is called an electric current, as passing from the positive zinc plate through the electrolyte to the negative copper; and, because electricity flows only in closed circuits, it must return to the zinc through the wires, etc., which constitute the remainder of the circuit. That terminal of an ammeter, voltmeter, or other D. C. electrical instrument, by which current should enter is marked by a plus sign, and therefore must be connected to the copper plate to receive the current that passes through the electrolyte to this electrode. The futility of attempting to represent completely the electrical conditions in a voltaic circuit by attaching a single sign to either electrode was recognized by the early electrochemists when they spoke of the zinc as "the positive plate (we should now say electrode), but the negative pole of the cell." There is yet to be found a simpler way of designating the relation of the zinc electrode to the whole electrical circuit; for current will flow from the zinc into the electrolyte provided that it be permitted to return to the zinc again from that portion of the circuit which lies outside of the cell; yet the driving force resides within the cell.

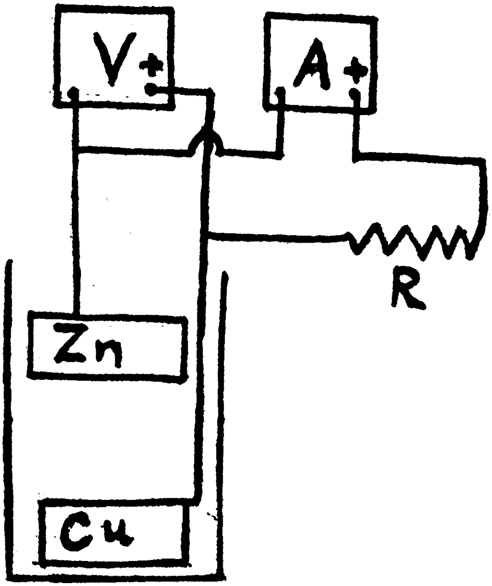

Fig. 1.

Faraday gives us the terms anode (up or entering way) and cathode (down or leaving way), and we designate the anode of the electrolytic cell, from which current enters the solution, by a plus sign, and the cathode by which it leaves by the minus sign. The use of signs is the same in the electrolytic as in the voltaic cell—a simple and easily understood arrangement, which is in harmony with the use of the minus sign on thermometers, and as applied to the flow of heat between bodies of unequal temperatures, the flow always being from the place or body of higher to that of lower temperature. If, however, zinc be considered as electro-negative and copper as positive there will no longer be harmony in the use of signs in the voltaic and electrolytic cells, but we will be compelled to say that current flows in the electrolyte from the positive to the negative electrode in the electrolytic cell, but from the negative to the positive electrode in the voltaic cell—in the latter case outraging our fundamental conception of the terms positive and negative as used everywhere else in science and industry. This is indicated in Fig. 2.

The table of potentials as previously quoted consists, in accordance with the ionic theory, of "the potential of the solution minus the potentials of the metals"; the table as re-written by those who contend for a change of sign consists of "the potentials of the metals minus the potential of the solution." So far as the phraseology goes there is little to choose between them. Since ions of the metals are usually considered to be charged positively, when a strip of zinc, for example, is thrust into an electrolyte, zinc ions go into solution carrying positive charges, therefore lowering the potential of the zinc and raising that of the solution, so that the zinc should be negative to the solution. It would thus appear that the advocates of the minus sign for the potential of zinc are contending for the truth, as opposed to error; but the physicists, who have been the most ardent advocates of this change of sign, tell us that we have the whole matter of sign wrong in electricity, that what we call a positively charged ion has less than the normal number of electrons, and that our negatively charged ions have an excess of electrons, and that the "flow of electric current" is really in the opposite direction to that which is now accepted.

It follows that if the proposed change of sign in potentials be adopted, carrying with it all the confusion which will result in electrochemical literature and the inconsistencies which have been pointed out, we shall still fail to express the truth regarding the potentials of metals, for the latest theory of the nature of electricity leads us to believe that the zinc electrode is really at a higher potential than the electrolyte, and consequently the plus and not the minus sign correctly indicates its potential. It therefore seems for the best interests of electrochemistry, that until such time as the scientific world is ready to revise the entire terminology of the electric circuit, the time-honored custom in regard to writing the electrochemical series and tables of potentials should be followed. The writer hopes that the members of the world's greatest electrochemical society will throw the weight of their influence, individually and collectively, toward the use of that sign for the potentials of the metals which is in harmony

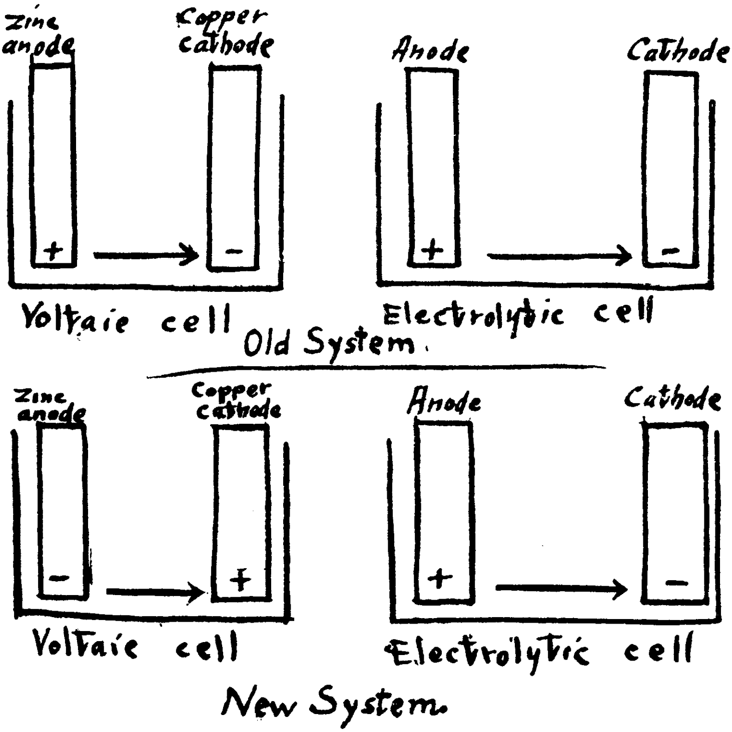

FIG. 2.

with electrochemical literature for a century past, and which will tend to promote the widest understanding and most extended use of tables of potentials by practical workers in electrochemistry, for by this means the advancement of electrochemistry will be best assured.

Chemical Engineering Laboratories,
University of Wisconsin.

DISCUSSION.

F. C. FRARY[1]: The society has heard about this matter before. I am very sorry that Dr. Hering, the chairman of the committee to which Dr. Watts referred, was not able to be present at this meeting and explain what appears to be a misunderstanding on the part of Dr. Watts. My understanding is that the paper by Dr. Bancroft, to which Dr. Hering refers, is the majority report of the committee, signed by all the members of that committee with the exception of Dr. Watts, and that this paper is a minority report, which is of course always in order. The only point I would like to make in this connection is that on page 194 Dr. Watts agrees to our saying that in the electrolytic cells, by which I judge he means a cell like a chlorine cell or storage battery into which we are putting energy, current flows from the positive, or anode, to the negative electrode; that is, he is defining the flow of current as the direction of the flow of positive charges in the solution. But in the voltaic cell, he objects to our saying that the current flows from the negative pole (zinc) to the positive pole (copper), which of course is exactly what it does do, because the positive charges are given off, as he himself states, from the zinc pole. The thing that seems to worry him is that we are trying to get something out of nothing, we are trying to get a positive charge out of a negative pole, but he forgets that in the first case we are doing work upon the solution and in the second case the work is being done by the solution, the case being exactly analo-

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[1] Director of Research, Aluminum Co. of America, New Kensington, Pa.

gous to the motor and dynamo. In direct-current practice we know that if a machine is running as a motor, the current in the armature is from the direction of the positive brush to the negative brush. If, on the other hand, we speed up and make it function as a dynamo, the armature current is reversed but the polarity of the machine does not change. The same thing of course holds here in the distinction between the voltaic and the electrolytic cell. As far as the phraseology of the potential of the solution minus the potential of the metals, and *vice versa,* is concerned, the committee felt that if we talk about electrode potentials, we necessarily talk about the potential of the electrode as the positive thing, and therefore talked about the potential of the electrode minus the potential of the solution, and not the reverse. The confusion of which he speaks I think is largely confined to a very narrow circle, because, as the committee found, and its report showed, the recommendations of the committee are in harmony with the practice of most of the electrochemists of this country and of practically all foreign societies.

F. A. J. FITZGERALD[2]: There is a rather interesting historical parallel to this dispute about the sign of potentials which occurred to me the other day, and sometimes these historical parallels are of some use in arriving at decisions about these matters. You will remember that when Dr. Lemuel Gulliver was released by the Lilliputians he had a long interview with Reldresal, the principal Secretary of Private Affairs. On that occasion Reldresal described a dispute between the two great empires of Lilliput and Blefuscu as to which was the best way of breaking an egg. "It began upon the following occasion: It is allowed on all hands that the primitive way of breaking eggs before we ate them was upon the larger end; but his present Majesty's grandfather while he was a boy going to eat an egg, and breaking it according to the ancient practice, happened to cut one of his fingers. Whereupon the Emperor, his father, published an edict, commanding all his subjects, upon great penalties, to break the smaller end of their eggs. The people so highly resented this law, that our histories tell us there have been six rebellions raised on that account. . . . . . . Many hundred large volumes have been published upon

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[2] Electric Furnace Expert, Niagara Falls, N. Y.

this controversy. The emperors of Blefuscu did frequently expostulate by their ambassadors, accusing us of making a schism in religion by offending against a fundamental doctrine of our great Prophet Lustrog in the fifty-fourth chapter of the Blundecral. . . . This, however, is thought to be a mere strain upon the text; for the words are these: That all true believers break their eggs at the convenient end,—and which is the convenient end seems, in my humble opinion, to be left to every man's conscience, or at least in the power of the chief magistrate to determine."[3]

W. R. MOTT[4]: I would suggest that people who give these single potential measurements by all means state the single potential of zinc in the system used. It is a matter of indifference to many of us which system is used, only we hope that one system will be adopted by everybody, because there is otherwise a great loss of efficiency.

J. W. RICHARDS[5]: I think, seriously, that there are good reasons why we should not quickly or lightly change from the present system of designating the positive and negative electrode, and I should be sorry to see our Society take any action which would tend to force a change upon electrochemists. Speaking from a very general standpoint, we find that metals displace each other chemically from solutions in a certain order. We arrange the metals in this order, with the strongest on top and the weaker beneath, and I think we naturally think of the stronger metals towards the top as the more positive, which coincides with the ordinary use of the sign, such, for instance, as the positive and negative signs on a thermometer scale. Again, we find that the order in which they replace each other is the order of their thermochemical heats of combination, so that the stronger metals have larger heats of combination with other elements, and the weaker metals have smaller. If we arrange the thermochemical constants of these elements in order, putting the strongest at the top, from + 81,240 per chemical equivalent for caesium down to — 30,300 for gold, this series represents the heat which the chemical equivalent gives out when it goes into combination.

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[3] "Gulliver's Travels, Part I, Chap. IV.

[4] Research Laboratory, National Carbon Co., Cleveland, Ohio.

[5] Professor of Metallurgy, Lehigh University.

These are a set of definite quantitative data, which run from large positive amounts of heat down to small positive amounts, and even to the negative. That again is the same order in which they replace each other, but expressed quantitatively from definite positive to definite negative quantities. This is also the order which Prof. Watts pleads for in this paper as the historical order. I feel that until we are very, very certain that the current does run in the opposite direction, or that the signs absolutely must be changed, that we leave them as they are, for practical purposes and for the writing of papers. Where anyone feels that his conscience will not let him use that order and the corresponding signs, let him state the signs which he prefers in connection with his paper.

COLIN G. FINK[6]: I know that I am responsible for a good part of this trouble, because our Mr. Koerner used signs in his paper which were not the same signs which Prof. Watts used; but I do not believe we will ever come to a final decision on this question of signs of the potential by long-winded debating. I would suggest, therefore, that not the Society, but the Transactions of the Society, adopt either one sign or the other. Let it be understood that all papers appearing in the Transactions assume the zinc electrode to be negative or assume it to be positive and have all papers appearing in the Transactions use the same sign. It is very annoying indeed to pick up the Transactions and read one paper in which the sign of the potentials are equivalent to zinc as negative, and the next paper in which all the signs are reversed and zinc is positive. Why not adopt either one or the other as a temporary measure until such time as we can better decide which is the proper sign to use? I think much confusion is caused by allowing both signs to stand in our Transactions.

F. J. TONE[7]: Do I understand that this committee, which was mentioned this morning as a regularly appointed committee of the Society, has reported?

C. G. FINK: The committee has reported in favor of the Society using the negative sign for the zinc electrode; that is in accordance with the majority report.

[6] Head of Laboratories, Chile Exploration Co., New York City.
[7] Works Manager, Carborundum Co., Niagara Falls.

J. W. RICHARDS: I think it would be more practical if we put before the members a statement that now they have had the majority report and the minority report, and ask them to vote, if they wish, as to which one of the three ways they would choose—either to keep the old, to go to the new, or to have the papers state decisively in each case what sign they adopt. I hardly think that the number of members present at a meeting would be competent to decide a thing in which the whole Society is interested.

F. J. TONE: If there is no objection, we will act on that suggestion.

J. W. RICHARDS: I move that the membership be canvassed as to their opinion regarding this matter, as to accepting or rejecting the report of the committee; and that the matter be brought up for action at the next general meeting of the Society.

(The motion was carried.)

O. P. WATTS (*Communicated*): As expressing my views, Mr. Frary says: "But in the voltaic cell, he objects to our saying that the current flows from the negative pole (zinc) to the positive pole (copper), which of course is exactly what it does do." I have never at any time, in any place, or under any circumstances, stated that the direction of flow of current in the primary cell is other than from zinc to copper through the electrolyte; will Mr. Frary cite his authority for the accusation that I object to his saying that the flow of current is from zinc to copper. What I do object to is the designation of the anode of the primary cell, be it made of zinc or any other metal, as the negative electrode. Faraday gave us the term anode for that electrode by which current enters the electrolyte, and neither he nor anyone else has attempted to restrict its use to the electrolytic, in distinction from the volatic cell. Mr. Frary is in agreement with general usage when he says of the electrolytic cell that "current flows from the positive, or anode, to the negative electrode," but is going contrary to long established practice when he calls the anode (zinc) of the voltaic cell the negative electrode. To this designation of the anode as positive in those particular combinations of two electrodes and an electrolyte which function as an electrolytic cell; but as negative in similar combinations of electrodes and electrolyte that constitute a primary cell, I emphatically object.

Given an electrochemical system consisting of two particular electrodes in an electrolyte, the products liberated at anode and cathode, the chemical changes that occur in the electrolyte, the change in temperature, etc., all depend solely upon the current flowing, and are entirely independent of the circumstance that the cell happens at that moment to be functioning as an electrolytic or as a voltaic cell. With a certain current flowing between two electrodes in an electrolyte, the cell shows an utter ignorance of and indifference to the source or magnitude of the E.M.F. which causes current to flow; whether the source of E.M.F. is a dynamo, a storage battery, a thermo-element, or lies within the cell itself. For any particular current a constant weight of metal dissolves from the anode; the amount and kind of substances deposited at the cathode, and the changes in the electrolyte are the same. Nature declares that there is uniformity of action, but Mr. Frary would have us make a distinction between the electrolytic and voltaic cells by calling the anode of the latter negative.

The motor and dynamo, which Mr. Frary cites as "being exactly analogous" to the relations between the electrolytic and voltaic cells, is not at all a parallel case; for, as Mr. Frary himself points out, when a motor acts as a dynamo, "the armature current is reversed," but in both the electrolytic and voltaic cells the direction of flow of current in the cell is always from anode to cathode. Therefore whatever sign is used for the anode of the electrolytic cell should be used for that of the voltaic cell also, if we are to be consistent.

I infer from Mr. FitzGerald's interesting historical(?) parallel that he considers the question of the signs attached to anode and cathode a matter of no importance to electrochemistry. With this view I cannot agree. The basis of science is uniformity: Nature's uniformity of action under like conditions, and man's uniformity in the use of terms. Lacking uniformity, science would become chaos. Any loose, confusing, or contradictory use of electrochemical terms is detrimental to progress, and therefore worthy of serious consideration by our Society.

ON THE COMBUSTION OF CARBURETTED WATER GAS FOR INDUSTRIAL FURNACE HEATING AND THE HEATING OF STEEL

O. L. Kowalke

As read at the Eighteenth Annual Convention of the Wisconsin Gas Association at Milwaukee, March 25 and 26, 1919.

The experimental work of this report was performed by Mr. Howard E. Sweet, holder of the Wisconsin Gas Association Fellowship, as a partial requirement for an advanced degree in Chemical Engineering. This report is on:—(1) A series of tests made to determine the maximum temperature which can be obtained in a given furnace, using three types of mixers with regulated and unregulated air supply, by burning carburetted water gas in a simple Bunsen flame and also under adapted surface combustion conditions. (2) Can a furnace be maintained at a given temperature more easily by using a simple Bunsen combustion or by the surface combustion process? (3) Can the atmosphere in the furnace be regulated so that no scale is formed on steel exposed to the products of combustion? (4) Will a strongly reducing atmosphere affect the quality of the steel when heated?

The furnace used for these tests was an American Gas Furnace Company No. 5 Muffle, shown in perspective in Fig. I and in section in Fig II. The combustion chamber is 12″ high x 15″ inside x 18″ long. As ordinarily used, a hearth is mounted on supports so as to leave a space of about three inches between the bottom of the hearth and the floor of the furnace. The material to be heated is set on the hearth and comes in direct contact with the products of

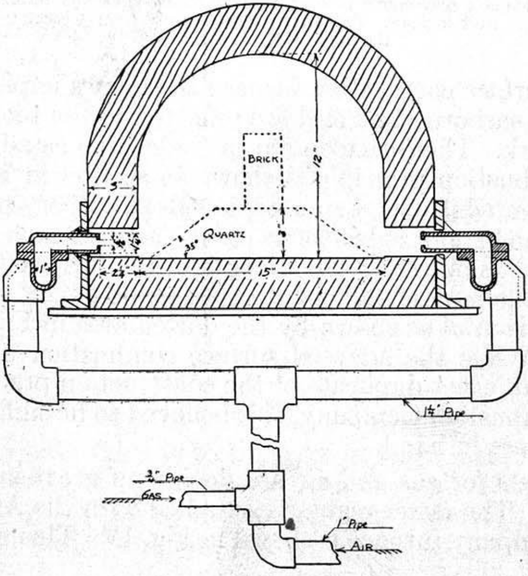


Fig. II.

(Cut for Fig. 1 not available at time of going to press.)

combustion and is also heated by radiant heat from the walls of the furnace. The flames from the eight burners, four on each side, pass under the hearth to the opposite side of the furnace, thence upward and out through the roof.

The furnace was adapted to apply the surface combustion principle as practiced by the Surface Combustion Company of New York. Fig. III shows the section of a furnace as built by the company.

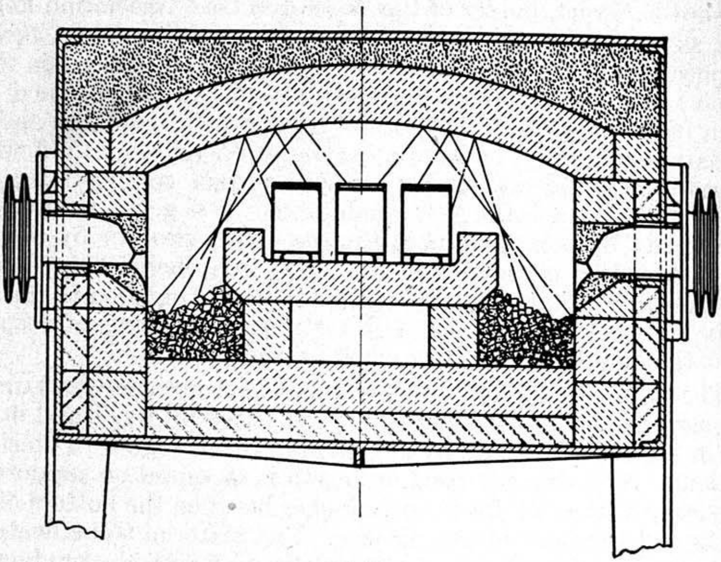


Fig. III.

Cross-section of a semi-muffle or oven type Surface Combustion furnace showing work in place. The straight lines from the bed represent the course of the rays given off.

In the surface combustion furnace the flames impinge on a bed of quartz or carborundum and are reflected to the roof and thence onto the work. The furnace used in these tests as adapted to the surface combustion principle is shown in section in Fig. II. The material upon which the flame impinged was a very pure grade of quartz crushed and sized so as to pass a one-half inch square sieve opening. It was piled the whole length of the furnace to a depth of 3 inches in the middle while the slopes made angles of 35 degrees with the horizontal as shown by the dotted area in Fig. II labelled "quartz." While the adapted surface combustion used in these tests is not an exact duplicate of the construction practiced by the Surface Combustion Company, it is believed to be sufficiently close for the purpose in hand.

The mixers for gas and air are devices of great importance in combustion. The mixer regularly supplied with the American Gas Furnace Company furnace is shown in Fig. IV. This will hereafter be called the "Regular" mixer. The nozzle on the air pipe consists of a piece of tin stamped in the form shown and soldered onto the outlet of the Streater "ELL". The Eclipse Fuel and Engineering Company, Rockford, Illinois, loaned a venturi type of mixer shown in section in Fig. V. This mixer hereafter called the "McKee," was made of a cast iron shell with carefully machined lead and steel cones on the inside. The Surface Combustion Company make a high pressure mixer shown in Fig. VI; this was not used in these tests but is here given to show the care used in construction and

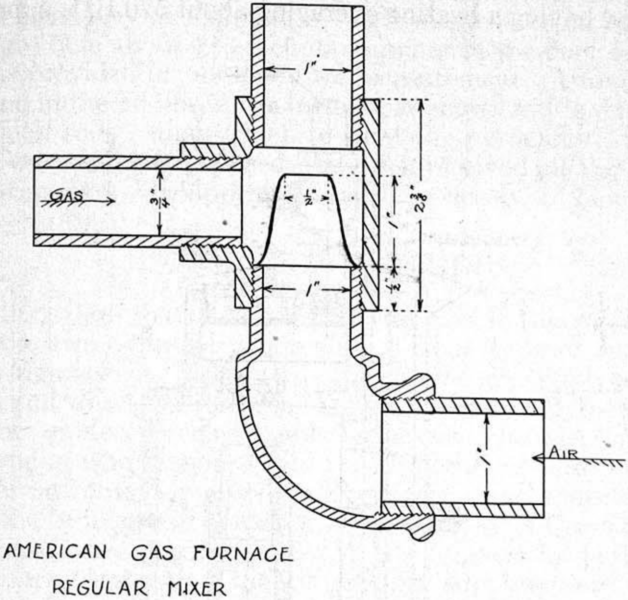


Fig. IV.

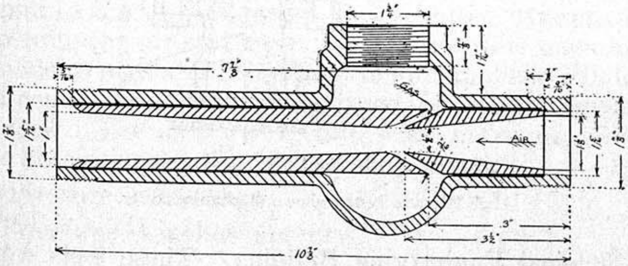


Fig. V.

attention to detail. This is to be used on large installations with gas under pressure of 10-25 lbs. per square inch. This mixer also differs in operation from the "Regular" and "McKee" in that the Surface Combustion Company put the gas under pressure and aspirate the air while in the "Regular" and "McKee" the air was under pressure and aspirated the gas.

The Eclipse Fuel and Engineering Company of Rockford loaned the Proportional mixer shown in Fig. VII. In this mixer the gas passes through the special regulator shown at the left and its pressure drops to practically zero. The suction of the fan then picks up the air and gas in proper proportion and mixes them and then delivers the mixture at the outlet at a pressure of about two ounces.

The carburetted water gas used in these tests was that regularly supplied in Madison at a pressure of about four to six inches of water, and having a heating averaging about 570 B. t. u. per cu. ft.

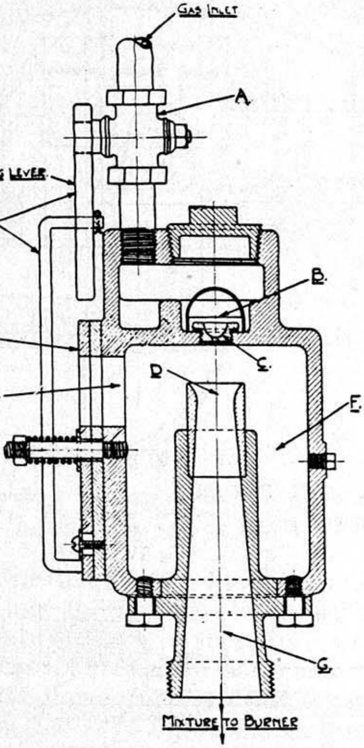


Fig. VI.

High Pressure System shown diagrammatically.

at the Chemical Engineering Building. These tests were made during cold weather and the drop in heating value between the plant and the Chemical Engineering Building was about 25 B. t. u.

The air was supplied under a maximum pressure of 5.2 inches of mercury or about 2.6 lbs. per square inch by a Reichelm rotary blower of ample capacity.

(Cut for Fig. VII not available at time of going to press.)

All temperature measurements were made with an optical pyrometer of the Holborn-Kurlbaum or Morse type which had been carefully calibrated against a standard platinum thermocouple. Since the tests extended over a long time interval the deterioration of a thermocouple would have been too rapid, hence the optical pyrometer was used. Below 800 degrees Centigrade the optical pyrometer is not so easily read as a thermocouple because the eye is less sensitive to changes in color at this point than at higher temperature. It is also difficult to make an accurate matching of color in the lamp filament and the field observed and for that reason the tests for constancy of temperature were made at about 900° C. A small sight hole about 1½ inch in diameter in the door of the furnace was provided for temperature measurement. A firebrick was set on end in the middle of the furnace, as shown in Fig. II, to serve as a "black body" upon which to sight the pyrometer. Since the furnace was completely closed, the brick received all the radiation and heating and thus approximated very closely a "black body."

COMBUSTION TESTS

It will be desirable to define the terms used in this report to designate the two types of combustion. That type of combustion where a high velocity air current draws in the gas supply and mixes the two and where the flame is allowed to burn freely as in a Bunsen burner or blow torch will hereafter be called *Bunsen Combustion.* That type of combustion where the flame under blast conditions impinges on broken quartz of carborundum and reflected to the roof of the furnace will hereafter be called *Surface Combustion.* In all tests with the "Regular" and "McKee" mixers for both Bunsen and Surface combustion the air and gas supplies were delivered to the furnace in the manner shown in Fig. II. The gas supply pipe was ¾ inch and the air pipe 1 inch, which proved to be ample.

UNREGULATED AIR, BUNSEN COMBUSTION, REGULAR MIXER. In these tests the air and gas supplies were wide open and no attempt made to regulate the amount of air supplied. While the products of combustion were not analyzed, later tests showed a large excess of air. The idea was to find what maximum temperature could be obtained with the furnace as it stood.

Gas Pressure—not taken.

Air Pressure—4 inches mercury.

	Test No. 1	Test No. 2
Gas used	950 cu. ft.	990 cu. ft.
Time	2 hr. 56 min.	3 hr. 8 min.
Max. Temp	1420° C.	1415° C.

UNREGULATED AIR, SURFACE COMBUSTION, REGULAR MIXER. For this test some firebrick were crushed to ½ inch diameter and laid in the furnace, as shown for quartz in Fig. II, for the flames to impinge upon. A piece of mild steel was put into the furnace instead of the firebrick for the blackbody in the temperature measurement. The maximum temperature obtained was 1420° C. but no records of gas consumed nor time were taken. It was found that firebrick do not stand up under this treatment for they sintered together and formed a smooth glassy surface in front of the burners. Then some carborundum firesand was spread on the slopes and the experiment repeated. No better results were obtained than before the maximum was about 1420° C. Owing to the great excess of air the steel block melted and ran into the brick; the crushed firebrick fused onto the refractory lining of the furnace. The furnace bottom was not new when the tests were started and the high temperatures and fluxes made it necessary to put in a new bottom.

First crushed firebrick mixed with water glass (20% solution) was rammed in for the bottom layer, then carborundum firesand mixed with 20% solution water glass was rammed in on top of that for the part in contact with flame. This proved to be a most refractory and permanent furnace bottom.

These tests show that with unregulated air and the "Regular" mixer there was no advantage in the Surface combustion over the Bunsen with the present adaptation. The material on which the flame impinges can not be fire clay because it will not stand under the gas flame.

REGULATED AIR, BUNSEN COMBUSTION, "REGULAR" MIXER. After the furnace had been repaired, tests were made to determine the temperature obtainable with a regulated air supply. Analyses of the products of combustion were made to determine when just the right amount of air for combustion had been admitted. No record of the individual gas analyses is here made because they were only a control of the air supply. The products of combustion were drawn through a silica tube inserted into the furnace and then kept over water saturated with carbon dioxide.

Test No. 3

Time	Temp.
1:50	Start
2:10	935° C.
:36	1195
:50	1260
3:15	1313
:29	1360
:50	1388
4:10	1416
:26	1418

Test No. 4

Time	Temp.
2:00	Start
:20	930° C.
:45	1180
:55	1230
3:10	1290
:25	1320
:45	1370
4:00	1400
4:11	1415

Typical analysis products of combustion:—CO = 0.0%; O_2 = 0.1%.

Gas Consumed, cu. ft.	745	710
Duration of test	2 hr. 36 min.	2 hr. 11 min.
Max. temperature	1418° C.	1415° C.

These two tests are good checks on each other and show that the maximum temperature obtainable under the conditions of test was 1417° C. The saving in time in tests 3 and 4 over No. 1 and No. 2 is 40 min.; the saving in gas consumed, 243 cu. ft.

Regulated Air, Bunsen Combustion, "McKee" Mixer. The "McKee" mixer shown in Fig. V was now inserted in place of the "Regular" and all pipes for gas and air supply kept the same size. The products of combustion were analyzed to determine when just the right amount of air had been admitted.

TEST NO. 5

Meter reading cu. ft.	Time	Temp.
314520	8:15	Start
804	:45	1339° C.
977	9:00	1481° C.
314195	:21	1591° C.

Gas analysis	CO = 0.0; O_2 = 0.1%
Gas consumed	675 cu. ft.
Duration test	1 hr. 6 min.
Max. Temp	1591° C.

The temperature was rising as rapidly at the end as 20 minutes before the end, but it was thought desirable not to extend the temperature any more on account of possible fusion of the furnace refractories.

Regulated Air, Surface Combustion, "Regular" Mixer. The furnace was now arranged for surface combustion and clean, pure quartz crushed and sized through ½ inch mesh sieve was piled 3 inches high throughout the length of the furnace in the manner shown in Fig. II. Three tests were run, but test No. 6 is not entirely valid on account of the lack of control over the air supply.

	Test No. 6	Test No. 7	Test No. 8
Gas consumed, cu. ft.	1120 cu. ft.	620	615
Duration test	3 hr. 18 min.	2 hr. 7 min.	2 hr. 5 min.
Max. temp	1530° C.	1416° C.	1416° C.

Reference to the tables will show that in Test No. 6 the temperature of 1416° C. was reached in 1 hr. 52 min. with a gas consumption of 650 cu. ft. Comparison of results in tests No. 7 and No. 8 with tests No. 3 and No. 4 as shown in the following tabulation seem to indicate that there is a saving of gas through the use of surface combustion.

COMPARISON, BUNSEN AND SURFACE COMBUSTION—"REGULAR" MIXER.

	Bunsen Comb.		Surface Comb.	
Test No.	3	4	7	8
Gas consumed cu. ft.	745	710	620	615
Duration test	2 hr. 36 min.	2 hr. 11 min.	2 hr. 7 min.	2 hr. 5 min.
Max. temperature	1418° C.	1415° C.	1416° C.	1416° C.

The time is shortened a trifle, but the saving in gas is 100 cu. ft. by using the surface combustion feature.

Regulated Air, Surface Combustion, McKee Mixer. The furnace was left exactly as for test No. 8 except that the McKee mixer was substituted for the "Regular" mixer.

TEST NO. 9

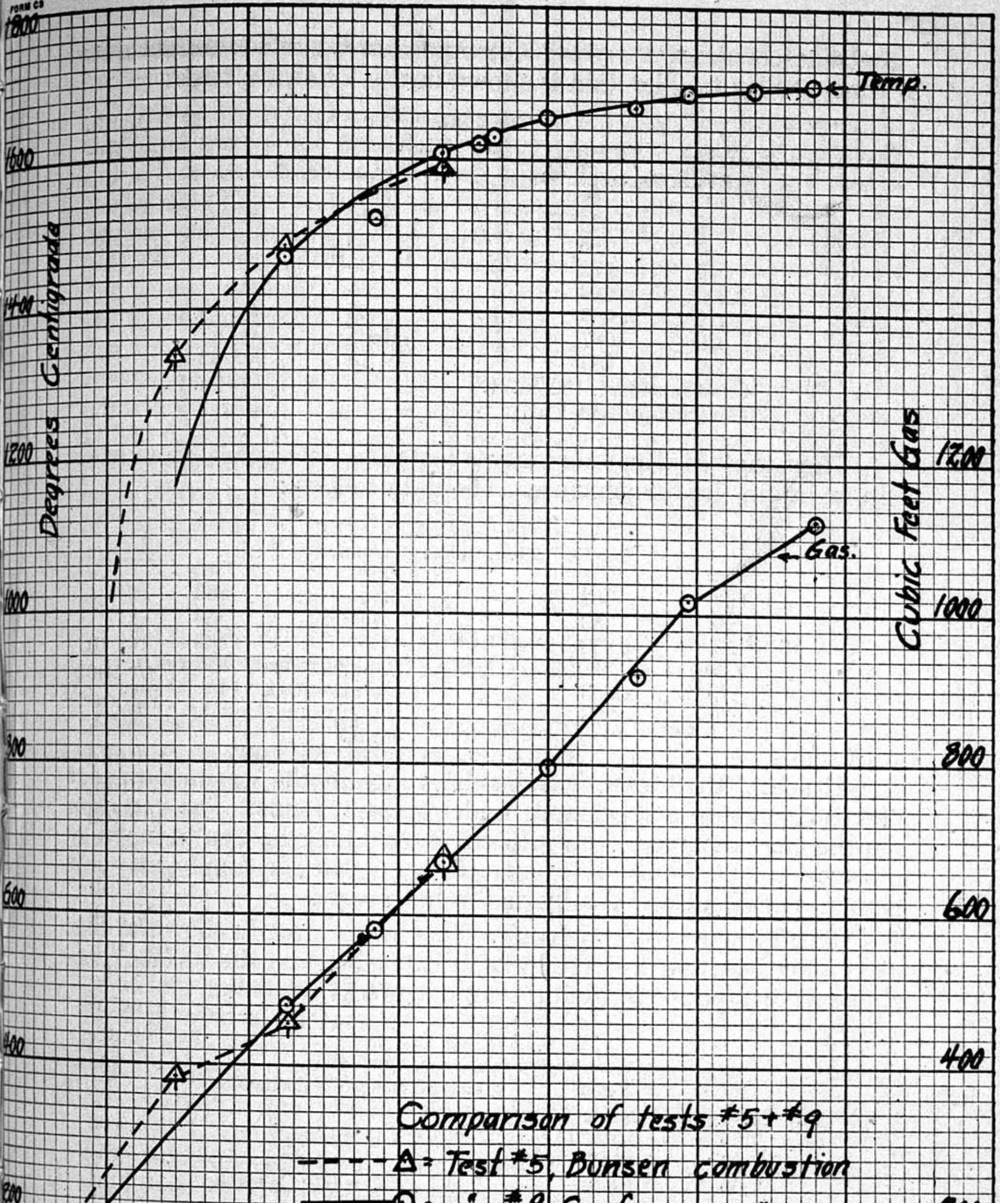
Meter reading cu. ft.	Time	Temp.
312920	1:55	Start
3400	2:40	1471° C.
3500	:52	1520
3590	3:01	1608
	:06	1620
3715	:15	1658
3835	:27	1670
3935	:34	1688
	:43	1694
314040	3:51	1700

Gas Consumed 1120 cu. ft.
Duration Test 1 hr. 56 min.
Max. Temp. 1700° C.

This is about as high a temperature as it is possible to get in this furnace with the appliances installed, as is apparent from the way the temperature time graph flattens out. That the temperature was correctly measured is borne out by the fused quartz which is herewith exhibited. The entire mass of quartz was sintered and caked; in front of each burner the quartz was concave and molten. The refractory of the furnace was also overheated for the melted materials was seen dropping from the roof.

The comparison between the Bunsen and Surface Combustion employing the "McKee" mixer, as shown in tests No. 5 and No. 9, is more favorable to the Bunsen than a similar comparison employing the "Regular" mixer. Since the temperature of 1416° C. was reached in such a short time with the "McKee" mixer, the comparison will be based on the temperature of 1591° C. From the accompanying graph it will be noted that the same amount of gas was used in both Bunsen and Surface combustion tests for the same period of operation, 66 minutes, but that the temperature was about 17 degrees Centigrade higher in the surface combustion test. Thus it would appear in this case that an efficient mixing of air and gas is of greater significance than the question whether the Bunsen or the Surface combustion principle be used.

Maintenance of Constant Temperature. It was deemed desirable to determine whether the furnace could be maintained at a constant temperature easier and cheaper by Bunsen or by Surface combustion. A temperature of 1000 degrees Centigrade was chosen as the point. The furnace was quickly brought to a temperature approximately this point and as soon as conditions


FORM C3
1800
1600
1400
1200
1000
800
600
400
200
Degrees Centigrade
Cubic Feet Gas
1200
1000
800
600
400
200
Temp.
Gas.
20
40
60
80
100
120
Time in minutes.
Comparison of tests #5 + #9
- - - - △ = Test #5, Bunsen combustion
——○ = " #9 Surface "

became constant, a record of temperature, gas consumption and time was kept. The data is shown in the following table:

TEST NO. 10
"Regular" Mixer.

Bunsen Combustion		Surface Combustion	
Time	Temp.	Time	Temp.
9:30	995° C.	9:15	988° C.
:40	980	:25	984
:50	972	:35	986
10:00	988	:45	992
:10	989	:55	992
:20	987	10:05	994
:30	985	:15	992
Gas Consumed, 109 cu. ft.			125 cu. ft.
Duration of Test 1 hr.			1 hr.

Next the "McKee" mixer was installed for surface combustion to maintain the temperature. The data follows:

TEST NO. 11
"McKee" Mixer, Surface Combustion

Time	Temp.	Time	Temp.
1:25	883° C.	2:35	883
:35	883	:45	883
:45	883	:55	883
2:00	880	Gas consumed = 158 cu. ft.	
:10	883	Duration test = 1 hr. 30 min.	
:20	883	Gas consumed per hr. = 105 cu. ft.	

It seems that there is little difference in the gas requirement for temperature maintenance under these systems. The variation in the gas consumed is only 16 cu. ft. and may be due to inability to read the 60 Light meter any closer, or the air supply may not have been equally well adjusted in both cases.

THE PROPORTIONAL MIXER. This mixer already shown in Fig. VII and elsewhere described was next tried out on the surface combustion to produce as high a temperature as possible.

TEST NO. 12
Proportional Mixer, Surface Combustion

Time	Temp.	Analysis, Products of Combustion
12:40	Start	
2:00	1070° C.	........CO = 1.2%
:26	1145	
3:00	1216	........CO = 0.0; O_2 = 0.0
:34	1239	
4:01	1260	
:31	1280	
:55	1300	

Gas consumed = 835 cu. ft.
Duration of test = 4 hr. 35 min.
Max. temp. = 1300° C.

This device proved to be too small for the furnace used and this result is really no indication what the mixer will do. It was found very useful in the experiments on the heat treatment of steels to be described later.

APPEARANCE OF FLAME. It was noticed that the appearance of the flame gave some indication of the character of the atmosphere in the furnace. With excess of air there was practically no flame at the exhaust holes on top of the furnace and around the door. Under neutral conditions there is a faint blue cone of flame at the exhaust hole, but none to speak of at the sight hole for the pyrometer. Under reducing conditions, with carbon monoxide content of 0.8 per cent, the flame on top the furnace is about four inches high and a blue flame about two inches long issues from the pyrometer sight hole. Increasing amounts of carbon monoxide cause larger flames. The adjustment of air supply is easier at 1100 degrees centigrade than at 850 degrees by noting the appearance of the flame. With high pressure combustion there is also difficulty in determining the character of the atmosphere from the appearance of the flame because of the rapidity of combustion and the great volume of gases resulting.

THE OXIDATION OF STEEL WHEN HEATED BY COMBUSTION OF CARBURETTED WATER GAS

In most operations for the annealing of steel the products of combustion come in direct contact with the steel. It seemed desirable to determine how much reducing or oxidizing conditions in the furnace affected the formation of an oxide coating. The composition of the products of combustion was varied from an extreme reducing condition to a slight oxidizing condition. The steel was in the form of round rods rolled from ingots from which specimens about two inches long were prepared which were heated for definite periods of time and then quickly withdrawn from the furnace and quenched in water. The specimens were measured before and after heating with a micrometer calipers. In order that the measurements were always made at the same place, a flat area was filed on the cylindrical surface of each specimen. The place where the measurement was made was carefully cleaned with fine emery cloth so as to present a bright surface at the time of measuring. It is believed that a negligible amount of iron was removed with the oxide. The carbon content was 0.95%.

TEST NO. 13

Steel = 0.95% Carbon

Products of Combustion Contained, 19.4% C O.

Diameter in Inches				
Before	After	Loss	Temp.	Time Exposed
.4685	.4682	.0003	925° C.	5 min.
.4698	.4695	.0003	890	10 min.
.4730	.4727	.0003	875	15 min.

TEST NO. 14

Products of Combustion = 1.1% C O.

Diameter in Inches				
Before	After	Loss	Time	Temp.
.4604	.4601	.0003	5 min.	980° C.
.4605	.4648	.0002	10 min.	973
.4704	.4702	.0002	15 min.	980

TEST NO. 15

Products of Combustion = 0.6% C O.

.4580	.4577	.0003	5 min.	980° C.
.4639	Cracked		10 min.	1002
.4592	.4586	.0006	15 min.	

TEST NO. 16

Products of Combustion = 0.4% O_2

.4732	.4728	.0004	5 min.	875° C.
.4777	.4771	.0006	15 min.	882

TEST NO. 17

Products of Combustion = 1.3% O_2

.4680	.4674	.0006	5 min.	870° C.
.4599	.4593	.0006	10 min.	870
.4634	.4624	.0010	20 min..	870

Thus it appears that the oxide coating which forms on this steel is not of excessive thickness, whether the steel is heated 5 minutes or 15 minutes; whether the atmosphere in the furnace is strongly reducing (containing 19.4% CO) or slightly oxidizing (containing 1.3% O_2); whether the temperature is 850° C. or 1000° C. Another agency is at work here. The combustion of hydrogen and the hydrocarbons produces water vapor. At a bright red heat such as obtained in these tests, the water vapor reacts with the iron to form magnetic oxide or iron and hydrogen, thus:

$$3\ FE + 4\ H_2O = FE_3\ O_4 + 4\ H_2.$$

For annealing operations in cold drawn work it is necessary to avoid the formation of this magnetic oxide because it spoils the dies. Thus it does not help much to have the atmosphere strongly reducing to avoid the scale, because the water vapor reacts vigorously with iron at a bright heat.

EFFECT OF REDUCING ATMOSPHERE ON THE CARBON CONTENT OF STEEL

Steel having 0.95 per cent carbon was exposed for periods of time varying from 15 minutes to one and one-half hours to products of combustion containing monoxide varying from 0.2 per cent to 4.7 per cent. Sections were cut from these specimens after treatment and examined with the microscope to determine the degree of decarbonization. The data is given below.

	Time Heated Minutes	Carbon Monoxide Per Cent	Temp.	Changes
No. 1	15	0.2	874° C.	No change
No. 2	15	2.5	870	No change
No. 3	15	7.2	874	Very little ferrite on surface
No. 4	30	4.7	874	Ferrite appreciable
No. 5	60	4.7	874	Decarbonization severe
No. 6	90	4.7	874	Became very soft.

Therefore in heat treatment where the metal is exposed to flames, the atmosphere should be very slightly reducing to prevent the reduction of tempered steel to soft iron.

CHEMICAL ENGINEERING LABORATORIES
UNIVERSITY OF WISCONSIN

SOME OBSERVATIONS ON GAS CALORIMETERS

By O. L. Kowalke

As read at the Eighteenth Annual Convention of the Wisconsin Gas Association at Milwaukee, March 25 and 26, 1919.

The accurate determination of the heating value of gas is of importance in Wisconsin to both producers and consumers. The investigations of the Calorimetry Committee of the American Gas Institute from 1908-1912 have provided the information necessary as to correct procedure and appliances for making such determinations. At the time those investigations were conducted, gas calorimeters were not in general use. The calorimeters available for tests were, in the main, new ones or such as had been in service for a short time under most favorable conditions. About eight years have passed since the Committee on Calorimetry made its tests and the calorimeters subsequently sent to this laboratory have provided data which seemed to be of sufficient interest to describe at this time. The general high efficiency found in Wisconsin, for practically all the calorimeters tested from outside the state, is due to the co-operation between the Gas Companies and the Inspection Division of the Railroad Commission.

The causes for the inaccuracies found in the cases under observation are: (1) incrustation on the inside and outside surface of the flues, (2) incomplete combustion.

An Improved Junkers Gas calorimeter made in Dessau, Germany, was reputed to give results too low by 100 B. t. u. Upon inspection it was found that water containing considerable solid matter in suspension had been used in the operation of the calorimeter. Comparative tests made with Improved Dessau Junkers and University of Wisconsin old style Junkers No. 872 gave the following results:

U. W. No. 872		IMPROVED DESSAU JUNKERS	
Test No. 1	562 B. t. u.	Test No. 1	448 B. t. u.
Test No. 2	564 B. t. u.	Test No. 2	425 B. t. u.
		Test No. 3	455 B. t. u.
Average	563 B. t. u.	Average	443 B. t. u.

The meters used in these tests were calibrated before use with a standard one-half cubic foot bottle; the thermometers were also calibrated against a standard: the gas supply was uniform. An odor of unburned gas was noticeable during the operation of the Dessau Junkers. A truncated cone with the base upward was mounted on the burner of each calorimeter. The Dessau Junkers burner had strips of copper about 1/8 inch wide crossing at right angles over the top of the burner. This device served to divide the flames into four parts and caused each of the parts to shoot slightly outward instead of straight up, as in the University No. 872. The flame, thus spread, impinged on the cold walls of the combustion chamber and portions of the gas escaped unburned, due to being cooled below the ignition temperature. The spreader was then removed from the burner and another set of tests made on the same sample of gas. The results are given below:

DESSAU JUNKERS—SPREADER REMOVED

Test No. 1	545 B. t. u.
Test No. 2	506 B. t. u.
Test No. 3	542 B. t. u.
Average	531 B. t. u.

Conditions were improved but there was still a difference of 32 B. t. u. between the University No. 872 and the Dessau Junkers, and the variation in results is too great.

Some strong hot caustic soda solution was poured into the space traversed by the products of combustion and left there for about an hour. Then this solution was poured out and fresh water used to remove all the caustic soda. Another set of comparative tests was made with the following results:

U. W. No. 872		DESSAU JUNKERS	
Test No. 1	537 B. t. u.	Test No. 1	529 B. t. u.
Test No. 2	539 B. t. u.	Test No. 2	527 B. t. u.
		Test No. 3	527 B. t. u.
		Test No. 4	532 B. t. u.
Average	538 B. t. u.	Average	529 B. t. u.

There is still a difference of 9 B. t. u. Since the incrustation in the water chamber could not be removed, and since the agreement was sufficiently close to satisfy the owner, no further tests were made.

The Junkers No. 872 calorimeter has been in use in this laboratory for purposes of instruction since 1905. It was noticed that the indications of the outlet thermometer were rather unsteady. So the space traversed by the products of combustion was filled with warm water and left to stand over night. In the morning the flues were brushed out with a bristle brush of the type used for cleaning rifles. It is quite impossible to remove all the incrustation due to sulphur in the gas. The brushing of the flues had a beneficial effect for the indications of the thermometer were steadier. A comparison of the readings on the outlet thermometer as observed in 1908 with those obtained at present showed that the variation is about 0.2 degrees Fahrenheit greater.

It also seemed worth while to determine whether, in the "Meker" form of burner, combustion is more complete than in the regular burner. The upper portion of the Meker burner was fitted on to the lower portion of the regular burner so that both burners projected the same distance into the combustion chamber. Six tests were made for each condition of burner. The Meker burner was adjusted (1) for the flame to show a faint luminous tip, (2) the blue inner cone of the flame close to the grid. The regular burner was adjusted to have a luminous tip just showing.

	REGULAR BURNER	MEKER BURNER	
	Faint luminous tip	Faint luminous tip	Blue inner cone close to grid.
	587 B. t. u.	579 B. t. u.	583 B. t. u.
	584	581	583
	583	580	578
	581	582	580
	582	581	585
	583	587	
Average	583	582	582

The Meker burner for gas calorimetry does not appear to have any advantage over the regular burner.

A new Sargent calorimeter was checked against the University Junkers No. 872 as soon as it arrived from the store. The same meter and the same thermometers were used on both calorimeters in the following manner: First the Sargent was tested, then the same meter and thermometer were shifted to the Junkers No. 872 and tests made from the same main. Finally the shift was made back to the Sargent. The Sargent was supplied with a rather wide spreader and the tests seem to show that better results can be obtained by leaving the spreader off the burner.

SARGENT CALORIMETER				U. W. JUNKERS No.872	
Spreader on		Spreader off		Regular	
Time	B. t. u.	Time	B. t. u.	Time	B. t. u.
9:30	545	11:15	559	10:00	557
9:40	547	11:30	559	10:10	555
				10:30	562
				10:40	566

Through the courtesy of Citizens Gas and Electric Company of Waterloo, Iowa, a curious sort of calorimeter was available for test. This device is called the "Lanphier Caloroptic," and its description and the rules for operating are here quoted from the instructions sheet.

OPERATION OF LANPHIER CALOROPTIC

"The instrument is a long barreled Bunsen burner with a micrometer sleeve revolving on the lower end of the barrel, each mark on the sleeve index is one B. T. U., and one complete revolution of the sleeve is 25 B. T. U. When the sleeve is down as far as it will go, the zero mark on the sleeve should rest on the vertical line on the barrel and record 300."

"The yellow or luminous tip on the inner flame cone is the indicator."

"To make the initial adjustment you must first know the exact heat value of the gas, and for illustration assume 560 B. T. U.; turn the sleeve until it reads 560 (as you would a micrometer caliper); assume no luminous tip shows; by means of the two pin screw-driver inserted in the barrel until it engages the gas nozzle, screw the latter up, withdraw the screw-driver, light the burner; do this until you get a very faint luminous tip, then screw down the gas nozzle (carefully) until color has just disappeared or very faintly shows; in all subsequent observations adjust to this condition."

"The Caloroptic is now ready for use, keep it burning as you would an old time jet photometer."

"Wishing to read your gas, observe the inner flame cone, assume a luminous tip showing, turn up the sleeve until you observe the color you had on the initial adjustment, then read the scale, as you would a micrometer caliper, except that you read B. T. U. instead of thousandths of inches."

"Assume a contrary condition, No yellow tip, screw sleeve **down** until initial color is obtained, then read."

"You will probably need no nozzle adjustment for months."

It was not possible to get the results according to the directions given above. Gas testing 595 B. t. u. in the Parr Gas calorimeter could not be made to burn with a luminous tip in the Caloroptic when the sleeve was set according to directions. Only when the sleeve was turned down to decrease the air supply was it possible to get the luminous tip to the flame. The gas orifice in the burner evidently was too small for the air openings.

The procedure in these tests was as follows: Gas from the mains was either diluted with carbon dioxide or enriched with benzole to get a range of heating values from 450 to 691 B. t. u. Gas poorer than 450 B. t. u. would not burn in the Parr Gas calorimeter. The Parr calorimeter was chosen because it used such small quantities of gas for tests and thus made the problem of producing small volumes of gas of various heating values very simple. The heating value of the gas was first determined by the Parr, then the gas was burned in the Caloroptic and the sleeve adjusted so that the flame showed a faint luminous tip on the inner cone. The reading of B. t. u. noted on the burner stem when the luminous tip showed was taken as the Caloroptic determination.

The following are the results obtained:

Parr Gas Calorimeter	Lanphier Caloroptic
450 B. t. u.	305
493 B. t. u.	340
545 B. t. u.	425
555 B. t. u.	470
594 B. t. u.	511
618 B. t. u.	542
630 B. t. u.	572
656 B. t. u.	632
691 B. t. u.	676

These data are shown in the accompanying graph. It is evident that the difference is large for the lower heating values where the heavy hydrocarbons are practically absent, but at the higher heating values the readings come together. It is necessary to have a steady pressure on the burner to get satisfactory checks on the setting of the sleeve. An agreement within 25 to 40 B. t. u. in the setting was as about close as the operator could get in these tests. For a rough approximation the Caloroptic would perhaps find some use, but as a means for making determinations to satisfy Regulatory Bodies it leaves much to be desired.

Grateful acknowledgement is hereby made to Mr. H. D. Valentine, Instructor in Chemical Engineering, for assistance in obtaining the experimental data of this report.

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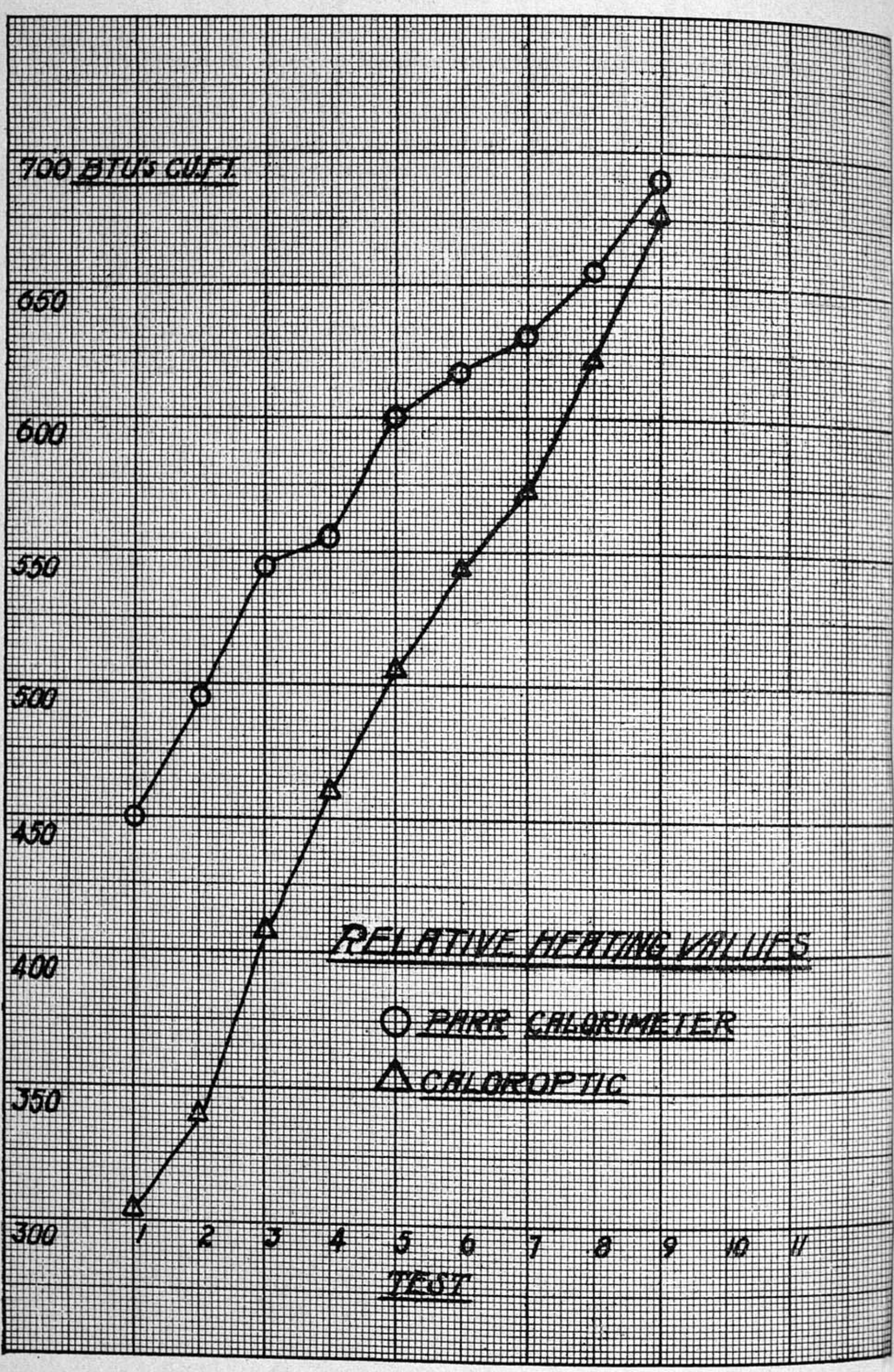
700 BTU's CU.FT.
650
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TEST
RELATIVE HEATING VALUES
○ PARR CALORIMETER
△ CALOROPTIC

[FROM THE TRANSACTIONS OF THE AMERICAN ELECTROCHEMICAL SOCIETY, Volume XXXV, 1919, being the Transactions of the Thirty-fifth General Meeting, at New York City, N. Y., April 3, 4 and 5, 1919.]

ELECTROPLATING ON IRON FROM COPPER SULPHATE SOLUTION

BY

O. P. WATTS

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-

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[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.

Chemical Engineering Laboratories,
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

[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.

[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.

[FROM THE TRANSACTIONS OF THE AMERICAN ELECTROCHEMICAL SOCIETY, Volume XXXV, 1919, being the Transactions of the Thirty-fifth General Meeting, at New York City, N. Y., April 3, 4 and 5, 1919.]

REMARKABLE PITTING OF ELECTROPLATING

BY

O. P. WATTS

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.

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

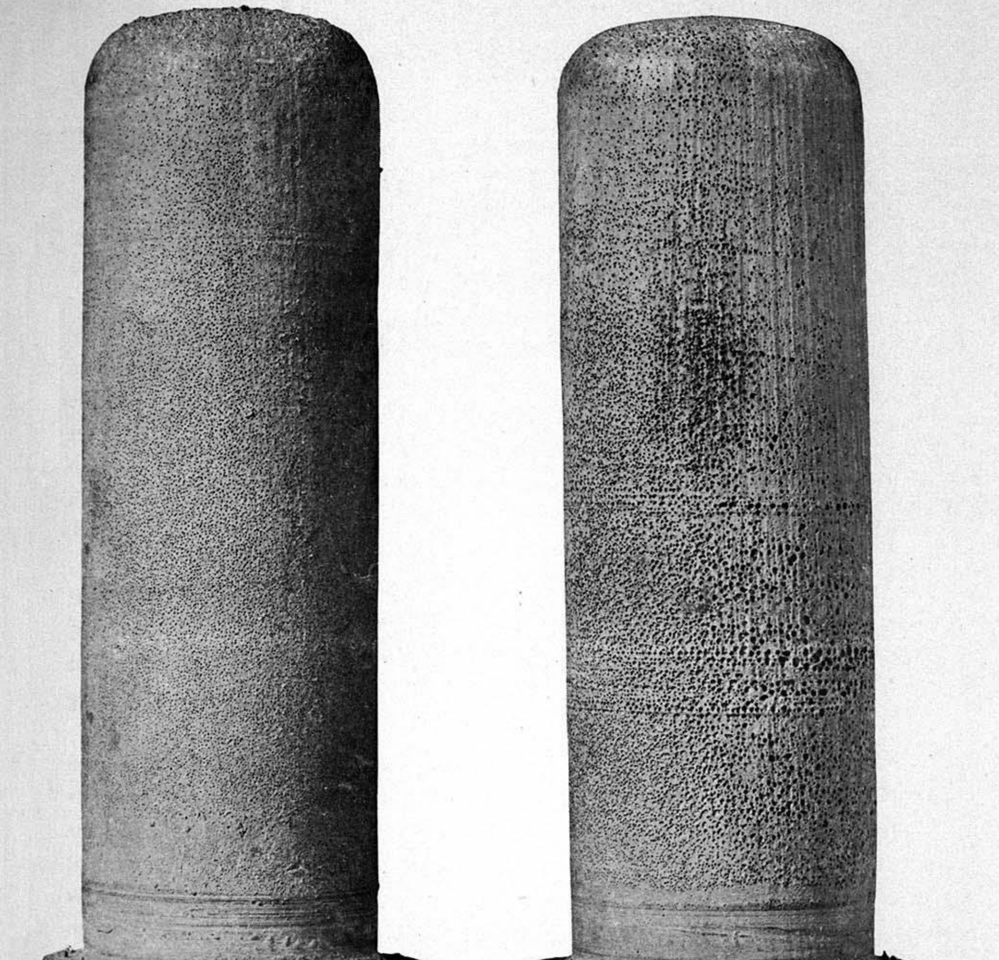

FIG. 1.

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.

Department of Chemical Engineering,
University of Wisconsin.

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.

TRANSACTIONS OF THE AMERICAN INSTITUTE OF MINING AND METALLURGICAL ENGINEERS [SUBJECT TO REVISION]

DISCUSSION OF THIS PAPER IS INVITED. It should preferably be presented in person at the Chicago Meeting, September, 1919, when an abstract of the paper will be read. If this is impossible, then discussion in writing may be sent to the Editor, American Institute of Mining and Metallurgical Engineers, 29 West 39th Street, New York, N. Y., for presentation by the Secretary or other representative of its author. Unless special arrangement is made the discussion of this paper will close Nov. 1 1919. Any discussion offered thereafter should preferably be in the form of a new paper.

Teaching Pyrometry

BY O. L. KOWALKE,* MADISON, WIS.

(Chicago Meeting, September, 1919)

THE measurement and control of temperatures have assumed positions of great importance in many industries. The manufacturers of by-product coke and carbureted water gas find that proper temperature control helps to produce a better product and economizes in the use of raw materials. In the manufacture of glass, enameled ware, brass, and high-temperature refractories, temperature control is now regarded as being coördinate in importance with the control of materials used. To control such processes as malleablizing cast iron, and hardening, tempering, and annealing of steel in a manner to meet exacting market requirements has, within recent years, involved the installation of large and expensive pyrometer equipments. In many of these installations, it was necessary not merely to measure but also to record the temperatures over a period of time and thus obtain a record of the entire heat treatment and an effective check on the workmen in charge.

In view of the importance of temperature measurement and control in such a wide variety of industries and the necessity for proper supervision of the installation and operation of the outfits, the following questions may be pertinent: What instruction is offered by the engineering colleges and what departments in the colleges are responsible therefor?

The latest available catalogs of ten prominent engineering colleges east of the Mississippi River showed courses in high-temperature measurements given by the departments of physics. These courses, in general, were described as comprising classroom and laboratory instruction in the theory of high-temperature measurements, together with exercises in the calibration of the various devices used. In some cases it was stated that consideration would be given, in the courses, to the practical applications in the industries. In only one college was the course required of all engineering students; in most colleges it was optional; in a few colleges, it was required only of certain groups. In colleges offering a course in metallurgical engineering, instruction in pyrometry was always given in connection with metallurgical laboratory work. The students in ceramic,

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chemical, and metallurgical engineering in three colleges were given somewhat formal instruction in pyrometry by their respective faculties. It did not appear that mechanical or electrical engineering students in any of the colleges, except one, were scheduled for instruction in pyrometry, although such students, after graduation, are frequently engaged in work requiring heat treatment of metal or temperature control.

Is a special course in pyrometry in the curricula for ceramic, chemical, mechanical, and metallurgical engineers justifiable? This may be a debatable question. Local conditions and plan of organization of the college usually govern the feasibility of such a requirement. Considerable time, however, is given to instruction of students in the above courses in the determination of the heating values of coal and gas, the quality of steam, the composition of gases, and the measurement of electrical energy. Is it probable that all these students, after graduation, will make use of the instruction in any of the above determinations more frequently than of a proportionate amount of instruction in pyrometry? The field of usefulness of pyrometers will be extended in keeping with the improvements in the instruments and a realization of the necessity for accurate temperature measurements and control. In view of the present wide application and importance of pyrometry, instruction in it should receive at least the same emphasis in the curricula for ceramic, chemical, and mechanical engineering that it apparently receives in the curriculum for metallurgical engineering in most colleges.

It would be difficult to prescribe the content of a course in pyrometry to meet the conditions in all colleges. Since most engineers will have to do with the measurement and control of temperature in industrial operation, it seems desirable to confine the scope of this discussion to industrial needs. The operation of the law of the survival of the fittest seems to have left the thermocouple, the radiation, and the optical pyrometers in possession of the field of high-temperature operations. Thus, a minimum content of course ought to include instruction in the principles of operation and the calibration and applications of each of these types. Historical matter and development of the fundamental temperature scales need be only briefly considered; but some time can profitably be devoted to the study of the construction of auxiliary equipment, such as furnaces, heat regulating and insulating devices.

The thermocouple is no doubt more widely used than any other device for measuring high temperatures, and it is also much abused. The instruction concerning it might well include: method of making, calibration by determining the electromotive force at the melting points of pure metals, calibration against a standard couple, effect of depth of immersion on resultant electromotive force due to heterogeneity, and protection against contamination. The measurement of the electromotive forces of couples by millivoltmeters and potentiometers may be studied with special reference to low against high resistance millivoltmeters, millivoltmeters against potentiometers with different depths of immersions, and varying temperatures in the lead wires.

Radiation pyrometers of the fixed and movable focus type and optical pyrometers of the Wanner and Morse types should be studied with reference to the principles involved in each, the construction, the methods of calibration, the limitations of each for various kinds of work, and the ease with which they may be manipulated. Special optical pyrometers, involving the matching of colored screens in the instrument against the field of vision, can be given some consideration.

Due to the limited use of resistance thermometers in the measurement of furnace temperatures, less emphasis may well be put on them than on thermocouples. It is worth while to point out the principles involved, the construction of the apparatus, and the methods of calibration. If the time can be spared, actual calibrations from fixed points are greatly worth while.

Since check calibrations on pyrometer installations are always necessary and since the engineer in charge will many times have to do such work with meager equipment, it will be worth the time spent to teach the student how to construct furnaces and heat-regulating devices. It may not be advisable to require the student to construct the furnaces used in the course, but it is desirable, wherever possible, for him to make the repairs.

The interest of the average student is not sustained in a course in pyrometry if it is devoted exclusively to problems in calibration, such problems being long and somewhat tedious. He takes a much greater interest, however, if he is given exercises that bring out the limitations and sources of error in the particular pyrometer employed. Among the problems that have been found stimulating to the student are: the determination of the temperature gradient in various kinds of firebricks; the temperature of decomposition of limestone; comparison of thermocouples with Seger cones, or with "Sentinel pyrometers" frequently used in the heat treatment of steel; and dehydration temperature of clay. The determination of the transformation temperatures in steels of various carbon contents by the differential couple and the simple cooling curve seldom fails to arouse interest; it also ties the principles of metallography and pyrometry together. The measurement of the temperature of molten copper in a ladle, with and without the oxide film, simultaneously with a thermocouple, a radiation pyrometer, and optical pyrometers of the Wanner and Morse types, is an excellent exercise to show the effect of emissivity. Many other problems can be devised; these are suggestions. Such correlation has been found to work well here and in other colleges because it gives an opportunity to link together a number of lines of study through the teaching of pyrometry.

TRANSACTIONS OF THE AMERICAN INSTITUTE OF MINING AND METALLURGICAL ENGINEERS [SUBJECT TO REVISION]

DISCUSSION OF THIS PAPER IS INVITED. It should preferably be presented in person at the Chicago Meeting, September, 1919, when an abstract of the paper will be read. If this is impossible, then discussion in writing may be sent to the Editor, American Institute of Mining and Metallurgical Engineers, 29 West 39th Street, New York, N. Y., for presentation by the Secretary or other representative of its author. Unless special arrangement is made, the discussion of this paper will close Nov. 1, 1919. Any discussion offered thereafter should preferably be in the form of a new paper.

Some Factors Affecting the Usefulness of Base-metal Thermocouples

BY O. L. KOWALKE,* MADISON, WIS.

(Chicago Meeting, September, 1919)

DURING the last few years the use of base-metal thermocouples has increased very considerably in various industries, due to the necessity for more precise control of temperatures. The base-metal couple has the advantages of being robust to a surprising degree, cheap as compared with platinum couples, sufficiently accurate for most operations, rapid in indicating changes in temperature, easily renewed or repaired, and of generating a much higher electromotive force than the noble-metal couples. There are, however, some factors, such as indicating and recording instruments, the insulation on the elements, the constancy and homogeneity of the wires, and the resistance to oxidation in the furnace, that limit the usefulness of the temperature-measuring device. It is the purpose of this paper to discuss in what manner these factors affect the usefulness of the couples.

MEASURING INSTRUMENTS

There are at present two sorts of measuring instruments in general use, millivoltmeters and potentiometers. The deflection of the millivoltmeter is proportional to the amount of current flowing through the movable coil, and the amount of current flowing in the entire circuit is dependent on the electromotive force generated and the total resistance of the circuit. It is obvious that the resistance of the couple will increase when heated and, for a given temperature, the increase is roughly proportional to the length of couple heated. In view of these changes in resistance, would a low- or high-resistance millivoltmeter give the more accurate readings?

Let E = electromotive generated by the couple, IR = volts drop through the millivoltmeter, Ir = volts drop through couple and the leads to the millivoltmeter; then

$$E = IR + Ir.$$

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Assume that the resistance of the millivoltmeter R is 2 ohms, and that the resistance of the couple and leads r is 0.01 ohm when 2 in. of the couple is heated to 1000° C., and further that when all of the effective length of the couple is heated to 1000° C. the resistance of couple and leads r is 0.10 ohm. The total resistance of the circuit may thus increase from 2.01 ohms to 2.10 ohms or 4.4 per cent.; therefore the current flowing is decreased proportionately and consequently the deflection of the millivoltmeter is also decreased. Now assume that the resistance of the millivoltmeter R is 30 ohms and that the same changes in resistance in the couple and leads r take place as above. Thus the increase in total resistance of the circuit is from 30.01 ohms to 30.10 ohms or 0.3 per cent.; the current decrease and deflection of the millivoltmeter will be a like amount. Thus, it is clear that a high-resistance millivoltmeter will give readings that are less affected by changes of resistance due to depth of immersion than a low-resistance instrument.

In the potentiometer system, the electromotive force from a standard cell is made to oppose the electromotive force generated by the couple. A galvanometer is placed in the circuit of the thermocouple in such a manner that no deflection is obtained when the electromotive force from the standard cell or its auxiliary just balances that from the thermocouple. Thus, no current flows in the thermocouple circuit when the measurement is made, hence the length of the couple and its resistance due to depth of immersion are immaterial with the potentiometer.

The reliability of the millivoltmeter depends on the permanence of the magnet, the correct adjustment for freedom of movement of the coil carrying the needle, and good electrical contacts in all the wires of the circuit. Unless a calibration is made, there is no way of knowing how much in error a given deflection may be. The reliability of the potentiometer depends on the permanence of the standard cell. When the potentiometer works, it is usually right; when it is not right, it won't work. The millivoltmeter is cheaper than the potentiometer; both are about equally robust. The indicating millivoltmeter can be read without manipulation; the indicating potentiometer must be manipulated for balance. Both types are made recording, but the potentiometer can be attached to more couples than the millivoltmeter.

INSULATION OF THE WIRES

Materials such as asbestos twine covered with water glass and also with water glass mixed with fine carborundum, woven-asbestos tubing, porcelain tubing, and fireclay bushings have been used for the electrical insulations of the wires of thermocouples. Obviously, a material used for this purpose should be capable of enduring high temperatures without breaking down, withstand a certain amount of rough handling, and not combine with the thermocouple when hot.

Asbestos twine when wound closely on the wires of the couple and covered with a paint containing sodium silicate makes a fair insulator. The asbestos breaks down, however, when heated to 1000° C. or more for extended periods of time and thus the wires are left bare, and liable to short circuit. In Fig. 1 are shown some pictures of couples wound with asbestos twine and painted with fine carborundum. After using these couples near 1000° C. for some time, it was noticed that the iron wire *B* had grown to nearly twice its original diameter and could be broken easily in one's fingers. The iron, asbestos, and carborundum had combined into a friable mass; there was no free iron left. The fracture has a greenish purple color. Iron at high temperatures combines readily with carborundum and thus the couple is destroyed. The woven-asbestos tubing breaks down readily and is not so permanent as the twine wrapped on the wire and painted with sodium silicate.

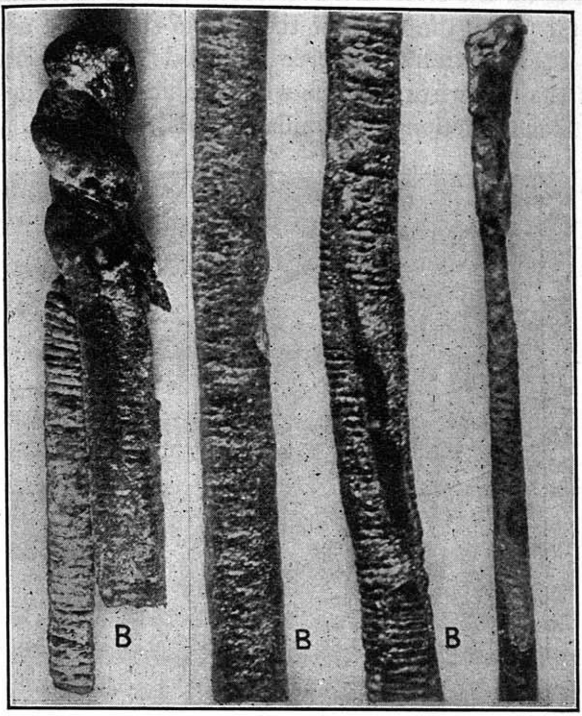

Fig. 1.—Couples wound with asbestos twine and painted with fine carborundum.

In Fig. 2 is shown a couple with wires insulated from one another by fireclay bushings 1 in. (25 mm.) long, about ⅜ in. (9.5 mm.) outside diameter and $\frac{3}{16}$ in. (4.7 mm.) bore. These bushings are used by several manufacturers of thermocouples and have been found very satisfactory in this laboratory. In the illustration, a slight fluxing of the oxides on the wire with the bushing is noticeable on the constantan wire which had been raised to 1100° C. On nickel-chromium wires, such fluxing action has not been observed. These bushings have shown good strength under hard use; they are easily replaced when broken and they are cheap.

Constancy and Homogeneity of Couples

Since the voltage generated by a couple for a given temperature is the summation of all the electromotive forces due to the contact of two dissimilar metal parts, the wires of the couple should be as homogeneous as possible if the electromotive force indicated is that generated at the hot junction of the two wires. If the wires are not homogeneous, there will be set up at each junction of dissimilar metals, a voltage that is a function of the temperature at that point. Should the depth of immersion of such a couple be varied, the resultant voltage will change, even though the temperature remains constant. It was found, after a series of tests[1] made in this laboratory, that there are several couples obtainable that are sufficiently homogeneous for those installations where an accuracy of about 25° to 50° C. will serve the purpose.

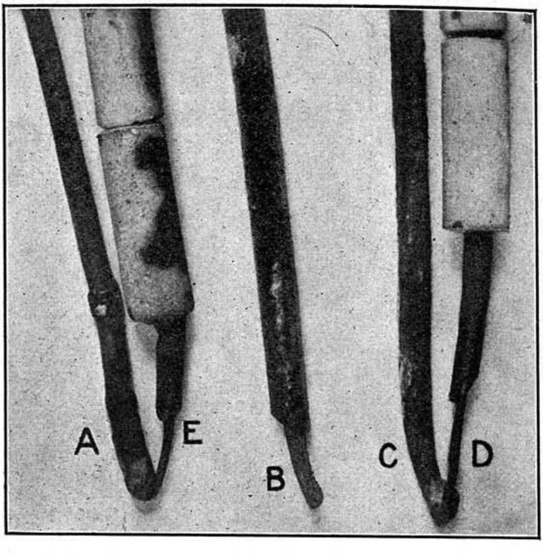

Fig. 2.—Couples in which wires are insulated from one another by fireclay bushings.

Couples purchased from a number of prominent makers were cut to lengths of about 18 in. (45 cm.). To each couple about 3 ft. (0.9 m.) of flexible lamp cord was soldered, and the wires, at soldered joints as well

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[1] Kowalke: *Trans.* Am. Electrochem. Soc. (1913) **24**, 377.

as all other required points, were insulated from each other. The couples were then calibrated, one at a time, over the range given by the manufacturer against a standardized platinum couple. First, all couples were calibrated with a length of 4 in. (10 cm.) heated. Second, all couples were calibrated with a length of 15 in. (38 cm.) heated to determine the effect and presence of heterogeneity in the wires. Third, all couples were subjected to a heat treatment for periods of 20 to 24 hr. each at temperatures of 400°, 600°, and 800° C. After the treatment at each of these temperatures each couple was calibrated singly.

Electrically heated tube furnaces were used for all the tests. One furnace was 10 in. (25 cm.) long and the other was 20 in. long, each having a tube about 1 in. bore. These were used for the calibrations at 4 in. and 15 in. depth of immersion, respectively. So that all the couples could be heated together for the treatments at 400°, 600°, and 800° C., a furnace 24 in. long and having a tube 2½ in. bore was used.

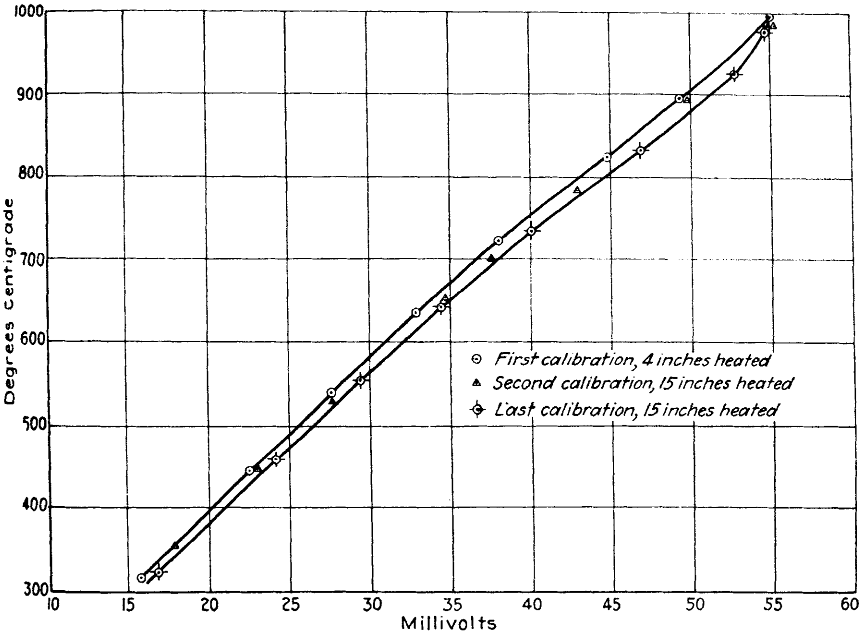

FIG. 3.—CALIBRATION OF COUPLE 20.

Asbestos disks were placed on the base-metal and the standard couples to keep them centered in the furnace. The hot junctions of the two couples were in contact. The temperature was raised to about 300° C. before readings were taken and then the temperature was increased by intervals of 100° C. At each point the temperature was maintained stationary for a period of 2 min. to insure equilibrium. The cold junctions of both couples during calibration were kept at 0° C. by means of an ice bath. All measurements were made on Leeds & Northrup

Type K potentiometers, a separate potentiometer being used for each couple.

The data on two of the couples only is presented here to illustrate how near to and how far from being homogeneous and constant the couples were found to be. The composition of the wires of the most satisfactory couple, Couple No. 20, is as follows: *Positive terminal*, Fe, 99.8 per cent.; *Negative terminal*, Cu, 52.3 per cent., Ni, 48.0 per cent. The composition of the wires of the couple found most unsatisfactory,

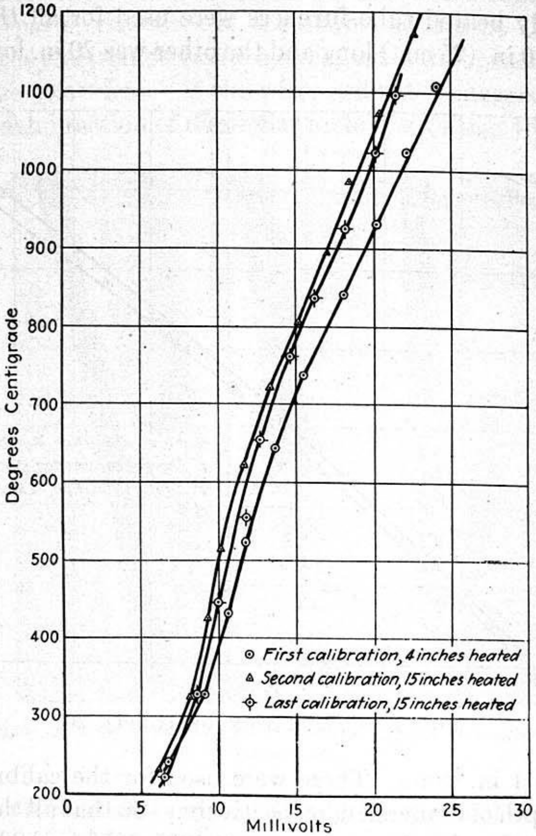

FIG. 4.—CALIBRATION OF COUPLE 18.

Couple No. 18, is: *Positive terminal*, Fe, 99.9 per cent.; *Negative terminal*, Al, 1.14 per cent., Ni, 98.3 per cent. These data are further shown graphically in Figs. 3 and 4, and Table 1.

It is apparent from the graphs that couple No. 18 shows a difference of 120° C. at 1000° C. between the immersions to 4 in. and 15 in., respectively, and that the variation of electromotive force with temperature is not uniform throughout the range. The lack of agreement of the calibrations with 4 in. and with 15 in. of the couple immersed is apparently

TABLE 1.—*Data on Couples*

	First Calibration, 4 In. Heated		Second Calibration, 15 In. Heated		Last Calibration after Third Heat Treatment at 800° C.	
	Degrees C.	Millivolts	Degrees C.	Millivolts	Degrees C.	Millivolts
Couple No. 20.	318	15.70	245	11.99	324	16.88
	445	22.51	352	17.97	459	24.12
	540	27.66	441	22.75	553	29.40
	634	32.99	530	27.62	645	34.59
	721	38.11	653	34.67	735	40.09
	825	44.85	700	37.66	835	46.93
	896	49.41	783	42.85	928	52.70
	997	55.02	893	49.84	980	54.77
			984	55.17		
Couple No. 18.	240	6.75	230	6.32	222	6.42
	330	9.09	325	8.34	330	8.61
	435	10.66	428	9.49	446	9.96
	525	11.75	516	10.38	554	11.18
	645	13.64	621	11.76	655	12.61
	738	15.49	723	13.43	763	14.65
	843	18.20	805	15.23	838	16.34
	933	20.28	895	17.05	927	18.25
	1026	22.19	981	18.51	1025	20.08
	1109	24.16	1072	20.46	1099	21.58
			1174	22.77		

due to a lack of proper annealing of the wires for the agreement of the second and the last calibrations is as good as that found on several other couples. It is further apparent from the graphs for couple No. 20 that the variation of electromotive force with temperature is regular throughout the range and that the constancy of the couple is satisfactory. There is a change of only 25° C. in the indications from first to last calibration.

RESISTANCE TO OXIDATION

The combination of iron with constantan for couples is one that gives practically a "straight line" for the relation of electromotive force to temperature; it also gives a higher electromotive force at a given temperature than most other combinations of wires; and it is further possible to get these two wires remarkably homogeneous. The great disadvantage of iron is its property of oxidizing rapidly at temperatures above 700° C. If iron were protected against oxidation by some means that would not affect the electromotive force the usefulness of the iron-constantan combination would be greatly extended. It has been shown by W. E. Ruder[2] that "calorizing" iron, "which consists in producing a

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[2] *Trans.* Am. Electrochem. Soc. (1915) **27**, 253.

rich aluminum alloy upon the surface of the metal" practically prevents oxidation below 1000° C.

One of the calorized wires used in these tests was donated by the Research Laboratory of the General Electric Co., the other calorized wire was purchased from the Brown Instrument Co. The uncalorized iron and the constantan wires were purchased from the Leeds & Northrup Co. The iron wires, both calorized and uncalorized, were approximately 0.14 in. (3.5 mm.) diameter. The wire from the General Electric Co. was straight and had a rather thin coating of calorizing; the wire from the Brown Instrument Co. came bent double on itself and the calorized coat was heavy so that some of the alloy chipped off when the wire was straightened.

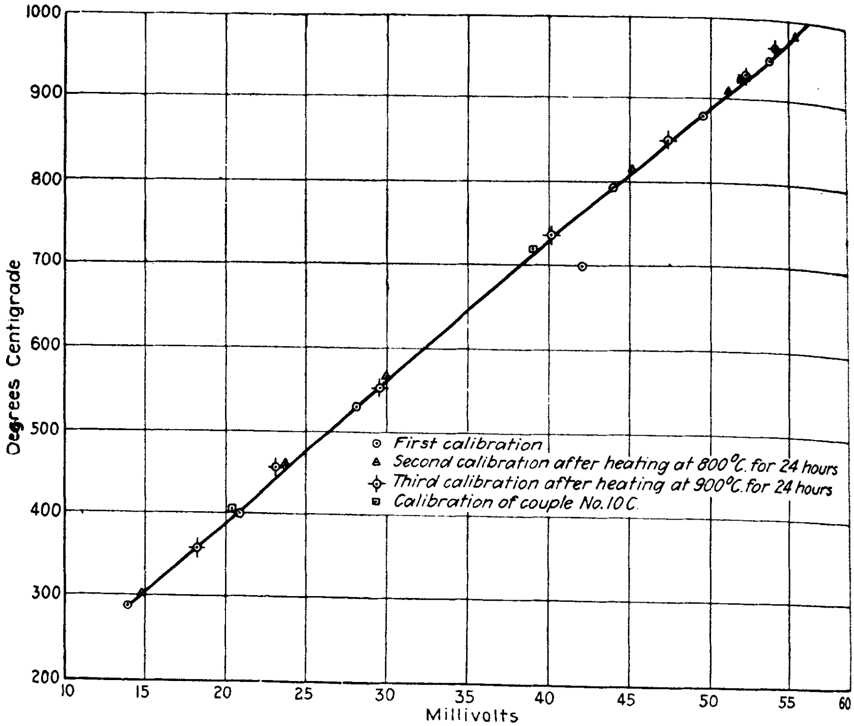

Fig. 5.—Calibration of couple 10B.

Three sets of couples were made: Couple No. 10B, constantan vs. calorized iron (General Electric Co.), Couple No. 32B, constantan vs. calorized iron (Brown Instrument Co.), Couple No. 81B, constantan vs. uncalorized iron (Leeds & Northrup Co.). Before making the couples the wires were heated with the electric current to a bright red heat for several minutes to remove any strains. The couples made were each 12 in. long. For the hot junction, the wires were fused in the electric arc, then fireclay bushings were strung on the constantan wires, and finally flexible copper lamp cord was soldered to each element.

For calibrating and for heat treatments the same types of furnaces and methods were used as have been previously described. The electromotive force measurements were made on Leeds & Northrup portable potentiometers. The couples were calibrated as annealed, then they were heated for 24 hr. at 200° C. and given a second calibration, then heated again for 24 hr. at 900° C. and calibrated a third time. After the third calibration, about 1½ in. (3.8 cm.) was cut from the hot-junction end of each couple and the remainder fused together again. Thus: Couple 10*C* was made from Couple 10*B*, Couple 32*C* was made from Couple 32*B*, Couple 81*C* was made from Couple 81*B*. The remaining couples were calibrated at only three points to see whether any changes in calibration had taken place due to changes in the wire or method of fusion. The results are shown in Table 2 and Figs. 5, 6, and 7.

TABLE 2.—*Comparisons of Calibrations of Calorized and Uncalorized Iron-Constantan Couples*

	First Calibration		Second Calibration after Heating at 800° C. for 24 Hr.		Third Calibration after Heating at 900° C. for 2 hr.	
	Degrees C.	Millivolts	Degrees C.	Millivolts	Degrees C.	Millivolts
Couple No. 10*B*	288	14.2	301	14.8	358	17.4
	400	20.9	458	23.7	453	23.2
	530	28.1	568	30.0	553	29.1
	700	42.1	815	45.2	738	40.3
	795	44.0	910	51.1	850	47.5
	880	49.5	980	55.5	929	52.4
	950	53.8			965	54.6
Couple No. 81*B*	375	17.9	374	19.8	371	19.0
	508	26.3	466	25.0	500	26.6
	605	32.3	572	31.1	609	32.8
	705	38.6	680	37.5	742	41.3
	811	45.5	769	43.0	823	46.0
	874	49.3	834	47.4	905	51.5
	973	55.5	912	52.4	977	55.5
			973	55.9		
Couple No. 32*B*	279	13.9	333	16.8	320	16.0
	529	29.3	439	22.8	435	22.5
	625	35.5	561	29.9	537	28.0
	711	41.2	650	35.0	627	33.2
	818	47.2	780	43.3	711	37.6
	887	51.7	847	47.4	812	44.9
	965	56.2	910	51.4	900	50.4
			990	56.2	1015	57.3

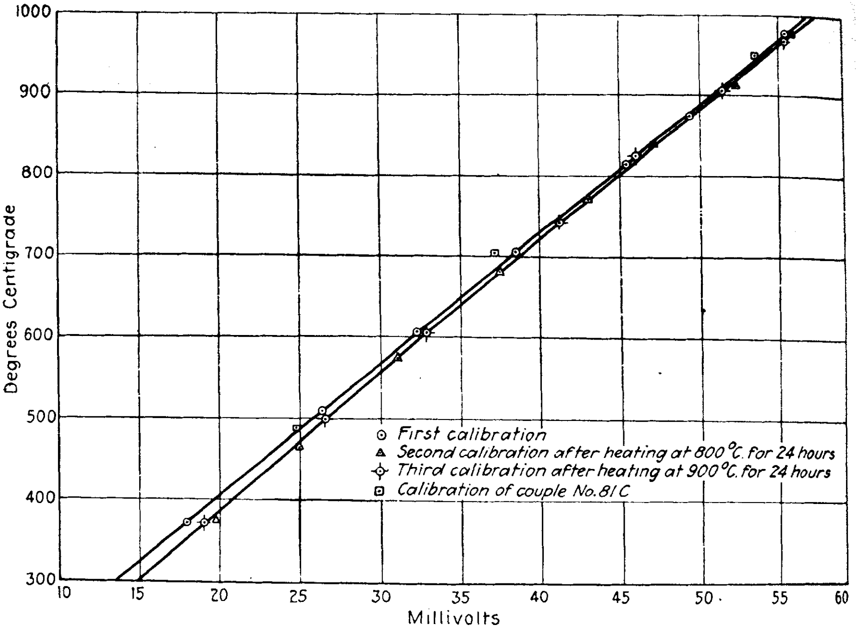

FIG. 6.—CALIBRATION OF COUPLE 81*B*.

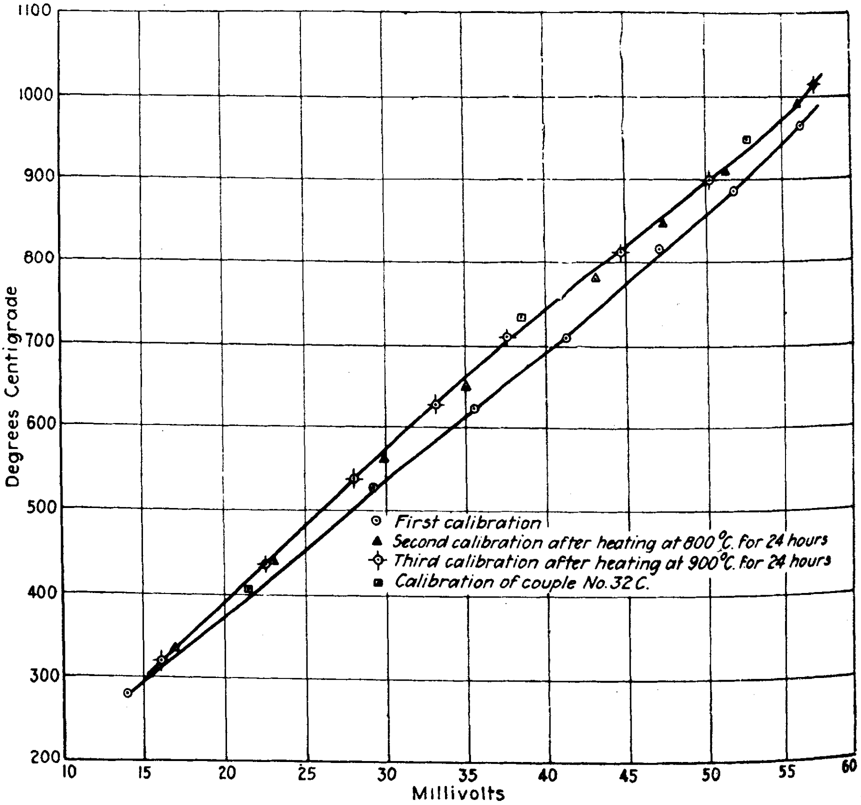

FIG. 7.—CALIBRATION OF COUPLE 32*B*.

TABLE 3.—*Calibrations of Couples* 10*C*, 32*C*, 81*C*.

No. 10*C*		No. 32*C*		No. 81*C*	
Degrees C.	Millivolts	Degrees C.	Millivolts	Degrees C.	Millivolts
406	20.4	408	21.8	485	24.9
720	39.1	735	38.5	702	37.2
927	52.0	949	52.9	948	53.6

As shown in Fig. 2, the constantan wires *E* and *D* and the uncalorized wire *B* have oxidized badly. The calorized wires *A* from the Brown Instrument Co. (couple 32*B*) and *C* from the General Electric Co. (couple 10*B*) have not oxidized to any extent upon being given three calibrations and two heat treatments. The wire *C* with the thin coating was in better shape than the wire *A* with the thick coating, which flaked off and developed oxidized spots. Comparison of Figs. 5 and 6 shows that calorized iron gives the same electromotive force against constantan as the uncalorized iron and that both couples are about equally constant.

Couple No. 32*B* did not give such good results as Nos. 10*B* and 81*B*. The first calibration of No. 32*B* shows a higher electromotive force for a given temperature than the other couples, but after the heat treatment at 800° C., couple No. 32*B* gave a calibration that checked very well with them. This discrepancy is probably due to insufficient annealing at the beginning.

Copper-Aluminum-Iron Bronze as an Acid-Resisting Alloy

By O. L. Kowalke

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BY O. L. KOWALKE

ALTHOUGH much has been written concerning copper-aluminum-iron bronze for bearings, gears, etc., in machinery, there does not appear to be much data available on its acid-resisting properties. In tensile strength and ductility it ranks with mild steel; it can be easily machined to a nice finish; it can be forged while hot and also rolled into sheets. Sound castings of a wide range in size can be made of it free from shrinkage-holes or blow-holes.

A number of other alloys have been studied in the University of Wisconsin laboratories for their acid-resisting properties, but most of them were rather weak mechanically. The satisfactory mechanical properties of copper-aluminum-iron bronze prompted a study of the resistance to corrosion in acids and alkalis. Commercial bronzes were preferred over those made in the laboratory. Through the courtesy of the American Metal Products Co., Milwaukee, Wisconsin, several commercial bronzes were obtained for these tests, but the results on two only, Bronzes A and B, whose average compositions and properties are given below, will be reported here.

	Bronze A	Bronze B
Composition:		
Copper	87.0 per cent	85.6 per cent
Aluminum	9.8 per cent	10.81 per cent
Iron alloy	3.14 per cent	3.57 per cent
Ultimate unit stress	74,800 lb. sq.in.	66,600 lb. sq.in.
Per cent reduction in area	19.0 per cent	13.0 per cent
Per cent elongation in 2 inches	21.0 per cent	11.5 per cent
Specific gravity	7.71	7.58

The specimens for the corrosion tests were practically uniform in size, having dimensions approximately 1 in. long by 0.07 in. wide by 0.07 in. thick, were finished smooth, and had square edges. Each specimen was stamped to identify it for composition and serial number, and its total surface was measured so as to determine the corrosion per square inch.

Most of the corrosion tests were made at room temperatures, 72 deg. F. and 85 deg. F.; a few tests were made at 194 deg. F. The regular "C.P." acids of the laboratory were used and made up to strengths desired by titration methods. For the tests at room temperatures the various acids were put into covered beakers in amounts of 200 cc. Two specimens of bronze were set on edge in each beaker in such manner that all the surface was exposed to acid and that they did not touch each other. The specimens were removed periodically, washed in water, dried thoroughly, and then weighed on an analytical balance. The combined loss in weight of both specimens was then computed as loss per square inch. For the corrosion tests at higher temperatures wide-mouthed flasks were provided with rubber stoppers through which were inserted glass tubes 3 ft. long, open at both ends, to serve as condensers. An electrically heated oven kept the flasks and contents at an average temperature of 194 deg. F. In other respects the procedure was identical with that at room temperature. The results of the tests are given in Tables I and II for Bronzes A and B respectively.

It will be noted in Table I that Bronze A is resistant to several acids and particularly to sulphuric, lactic,

TABLE I—BRONZE A

Cumulative Loss in Grams per Square Inch

Days	Temperature, 72 Deg. F.			Temperature, 194 Deg. F.
	50 per Cent	35 per Cent	10 per Cent	35 per Cent
		Sulphuric Acid		
7	0.0125	0.0033	0.0090	0.0094
14	0.0167	0.0075	0.0178	0.0624
21	0.0212	0.0131	0.0278	0.2016
28	0.0246	0.0177	0.0365	0.2520
		Hydrochloric Acid		
7	......	0.0484	0.117	......
14	......	0.2010	0.924	......
21	......	0.781	1.73	......
28	......	......	1.90	......
		Ammonia		
7	0.130	0.185	0.112	......
14	0.350	0.435	0.194	......
21	0.531	0.640	0.413	......
28	0.700	0.850	......	......
		Caustic Soda		
7	0.0005	0.0006	0.0010	*0.0014
14	0.0006	0.0006	0.0024	*0.0014
21	0.0008	0.0013	0.0036	*0.0021
28	0.0007	0.0016	0.0055	*0.0020
		Lactic Acid		
7	0.0025	0.0031	0.0031	0.0130
14	0.0051	0.0062	0.0077	0.0538
21	0.0082	0.0097	0.0126	0.0980
28	0.0111	0.0132	0.0168	0.1550
		Phosphoric Acid		
7	0.0025	0.0040	0.0056	0.0002
14	0.0046	0.0078	0.0113	0.0004
21	0.0081	0.0132	0.0197	0.0083
28	0.0114	0.0181	0.0281	0.0395
		Tartaric Acid		
7	0.0009	0.0015	0.0026	0.0013
14	0.0014	0.0025	0.0044	0.0029
21	0.0022	0.0037	0.0061	0.0099
28	0.0028	0.0046	0.0077	0.0155
		Acetic Acid		
7	0.0081	0.0076	0.0046	0.0026
14	0.0170	0.0139	0.0092	0.0083
21	0.0299	0.0243	0.0173	0.0398
28	0.0386	0.0312	0.0221	0.0713

* Gain.

phosphoric, tartaric, and acetic. Nitric acid attacks the metal readily, the concentrated acid acting violently. Hydrochloric acid and aqua ammonia both attack the metal too readily for commercial purposes. Caustic soda makes but little inroad on this metal either hot or cold; the slight gain during corrosion at 194 deg. F. is due to the formation of a film that was difficult to remove by rubbing with a cloth.

Table II gives the results for Bronze B, and the striking fact is the resistance to corrosion in sulphuric acid. By increasing the aluminum in this metal 1 per cent, the iron alloy about ½ per cent over the proportions in Bronze A, the resistance to corrosion is materially increased, even though the average temperature was 13 deg. F. higher. Nitric acid also attacks Bronze B too rapidly; hydrochloric acid attacks it more readily than Bronze A. Ammonia does not corrode this metal so readily as Bronze A.

TABLE II—BRONZE B

Cumulative Loss in Grams per Square Inch

Sulphuric Acid

	Temperature 85 Deg. F.		
Days	50 per Cent	35 per Cent	10 per Cent
7	0.0016	0.0020	0.0056
14	0.0016	0.0029	0.0072
21	0.0018	0.0035	0.0095
28	0.0024	0.0044	0.0120
35	0.0025	0.0049	0.0145
		Acetic Acid	
7	0.0156	0.0087	0.0076
14	0.0300	0.0183	0.0154
21	0.0492	0.0302	0.0256
28	0.0689	0.0442	0.0334
35	0.1001	0.0559	0.0447
		Ammonia	
7	0.0144	0.0302	0.0868
14	0.1376	0.1993	0.2087
21	0.2733	0.2806	0.2237
28	0.3810	0.3406	......
35	......	0.3791	......
		Caustic Soda	
7	......	0.0015	0.0026
14	......	0.0016	0.0045
21	......	0.0019	0.0059
28	......	0.0022	0.0072
35	......	0.0023	0.0078

It is interesting to note from the results below that the corrosion in 35 per cent sulphuric acid of a forged specimen of Bronze A is only about one-half that of the rolled sheet and cast varieties.

CORROSION OF FORGED, ROLLED SHEET, AND CAST BRONZE A IN SULPHURIC ACID 35 PER CENT.

Cumulative Loss in Grams per Square Inch at 72 Deg. F.

Days	Forged	Rolled Sheet	Cast
7	0.0014	0.0034	0.0033
14	0.0028	0.0066	0.0068
21	0.0041	0.0113	0.0111
28	0.0055	0.0136	0.0144

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LABORATORY TESTS ON THE REMOVAL OF SULPHUR COMPOUNDS FROM CARBURETTED WATER GAS

BY ERWIN C. BRENNER

As read at Twentieth Annual Convention of the Wisconsin Gas Association at Milwaukee, March 22 and 23, 1921.

This paper is presented as a final report on work done during the scholastic year, 1919-20, in connection with the Fellowship of the Wisconsin Gas Association in the Chemical Engineering Department of the University of Wisconsin.

The preliminary report presented at the meeting of the Association in March, 1920, gave a brief resume of the literature on methods sulphur removal; it also gave the limitations of the present iron oxide process and of the various other processes proposed and in operation. With the exception of the iron oxide process, but few of the other processes are applicable to present day gas plant practice without extensive changes in equipment and in operation. From a consideration of these limitations an ideal process would be one having the following qualifications:

(1) The process must be sufficiently elastic to cope with big fluctuations in gas production, or large increases in the sulphur content of the gas.

(2) The process must be applicable to both large and small plants without considerable change in present equipment or practice.

(3) The cost of such an installation and of its operation must be small.

The oxide process does not deal adequately with sulphur compounds other than hydrogen sulphide, nor does it remove hydrogen sulphide with the same speed as a wet process. It seemed worth while therefore to make a study of wet purification processes after consulting with some of the officers of the Association. This report deals with the investigation of hypochlorites as agents for the oxidation of sulphur compounds in carburetted water gas.

Theory. In the iron oxide process, the oxidation of the principal sulphur compound found in commercial gas, namely hydrogen sulphide, as generally accepted, takes place according to the following equations:

$$Fe_2O_3 \,.\, H_2O + 3\,H_2S = Fe_2S_3 + 4\,H_2O \qquad (1)$$

$$2\,Fe_2O_3 \,.\, H_2O + 6\,H_2S = 4\,Fe_2S + 8\,H_2O + 2\,S \quad (2)$$

$$Fe_2O_3 \,.\, 3\,H_2O + 3\,H_2S = 2\,Fe\,S + S + 6\,H_2O \quad (3)$$

Under ordinary conditions, but small amounts of carbon disulphide are removed from the gas by this process.

In this connection, Ritsema* calls attention to the fact that hypochlorite solutions oxidize carbon-disulphide as follows:

$$CS_2 + KOCl + KOH = K_2SO_4 + K_2CO_3 + 8\,KCl + 3\,H_2O \quad (4)$$

This then would be oxidizing carbon-disulphide to a sulphate. This property of potassium hypochlorite is due to its available oxygen content, and is common to other hypochlorites, as for example bleaching powder or so-called chloride of lime [Ca (OCL)$_2$].

Ritsema, however, does not mention what concentration of hypochlorite is necessary to carry out the above reaction, nor does he mention whether the reaction will take place when carbon-disulphide is present in gas in but small amounts. He also does not mention the effect of hypochlorites on hydrogen sulphide. Hence a laboratory investigation was made to determine whether hypochlorite solutions could be used to remove sulphur compounds from the carburetted water gas which was available.

Preliminary Determinations were made on pure hydrogen sulphide, using a calcium hypo-chlorite solution (bleaching powder), having about 3.5 grams of available chlorine per litre. Hydrogen sulphide, generated in a Kipp apparatus by the action of hydrochloric acid on ferrous sulphide, was bubbled through 200 cubic centimeters of this solution in a 500 cubic centimeter absorption bottle. It was found that when gas was passed through at a rate of about 0.5 cubic foot per hour, no hydrogen sulphide could be detected at the outlet of the bottle with moist lead acetate paper, though the distance the gas travelled through the solution was only two inches.

Carbon dioxide was then passed through a further quantity the same solution to determine whether carbon dioxide will displace chlorine from combination. Though pure carbon dioxide was passed through the solution for thirty minutes at the rate of 0.5 cubic foot per hour, no chlorine could be detected at the outlet of the absorption flask. Hence carbon dioxide will not displace chlorine from combination so long as the solution is alkaline. An analysis of the hypochlorite solution after passage of carbon dioxide showed no loss in available chlorine.

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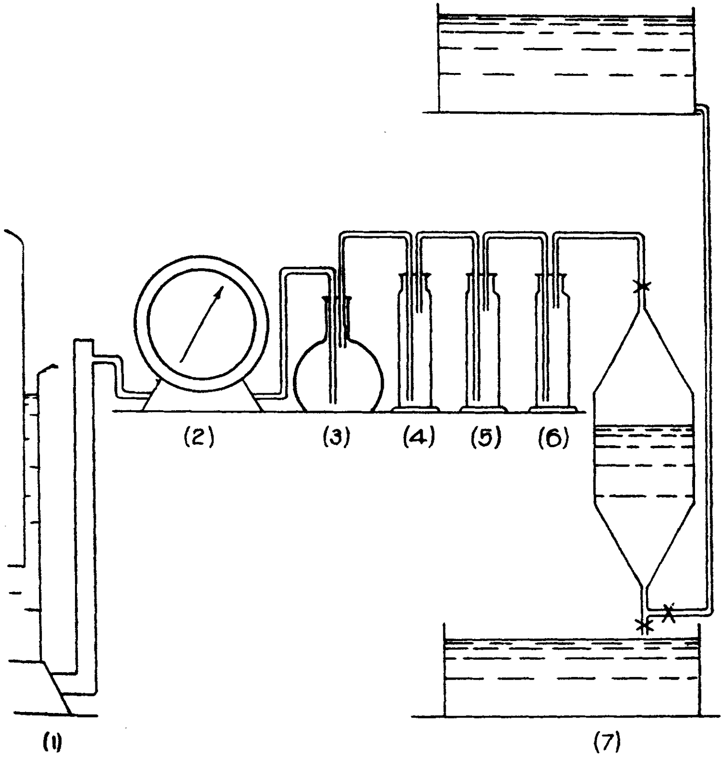
*Ritsema, Chemiker Centralbladt, 1904, ii 1495.

An investigation was then made to determine the value of hypochlorite as a means of removing hydrogen sulphide from a hydrogen sulphide and air mixture. In these experiments it was decided to use a sodium hypochlorite solution in place of the calcium hypochlorite solution of the preliminary determination. The sodium hypochlorite solution used was prepared by electrolysing a 10% common salt (sodium chloride) solution in a "Valhalla" cell. The hypochlorite thus obtained had as a maximum 5.4 grams of available chlorine per litre.

A diagram of the apparatus used for this set of determinations is shown below:



(1) 5 cu. ft. prover.
(2) Experimental gas meter.
(3) Hypochlorite absorption bottle (1 litre capacity)
(4) (5) (6) Catch bottles.
(7) Suction device.

In the first of these determinations the amount of hydrogen sulphide in the gas was varied from 60 grains per 100 cubic to 6 percent, and the quantity of sodium hypochlorite used was one litre having 2.035 grams of available chlorine per litre. It was found that for all dilutions of hydrogen sulphide, the efficiency of removal was about 95%, when using one-tenth cubic foot of gas; but that the amount of chlorine lost by the solution was considerably in excess of that necessary to completely oxidize the hydrogen sulphide present. The rate of passage of the gas was about 0.5 cubic foot per hour. The results thus obtained are shown by the following table:

Run	Grains Before	H_2S/100 cu. feet After	% H_2O Removed	Grains Before	Avail. Cl/L After	Chlorine Removed
I	4,100	1,230	70.1	2.035	.345	83.0 %
II	2,198	483	78.0	2.035	.795	61.
III	1,001	80	91.2	2.035	1.140	44.05
IV	380	8	98.1	2.035	1.759	13.6
V	60	2	97.0	2.035	1.761	13.5

In each of the above determinations the hypochlorite solution after passage of the gas showed a distinct cloudiness due to precipitated sulphur. Evidently oxidation in part takes place according to the following equation

$$2H_2S + O_2 = 2\,H_2O + 2\,S \quad (5)$$

which equation, using sodium hypochlorite as an oxidizing agent, would become

$$H_2S + Na\ OCL = H_2O + NaCl + S \quad (6)$$

An analysis of the gas after having passed through the hypochlorite solution showed the presence of free chlorine. To prevent this loss chlorine the hypochlorite solution was made strongly alkaline with caustic soda and the determinations above repeated. It was found that a hypochlorite of the same available chlorine content, but having an alkalinity of 2 per cent sodium hydroxide, completely removed all hydrogen sulphide and prevented any escape of free chlorine. The amount of gas passed through the train was 0.1 cubic foot at the rate 0.5 cubic foot per hour. Some sulphur was precipitated as before, but it was soon dissolved in the sodium hydroxide present.

Since hydrogen sulphide is readily absorbed by concentrated alkali, no determination of the per cent of hydrogen sulphide removed by the hypochlorite was possible. Alkali of the above concentration will also remove a great part of the carbon dioxide contained in the gas, and hence make an absorbent of this kind valueless as a gas-purifying material where the amount of carbon dioxide is high. Hence a number of determinations were made using a hypochlorite of varying alkali content. At the same time the amount of carbon dioxide removed by the alkali from a hydrogen sulphide, carbon dioxide and air mixture, was determined. The results obtained are shown by the following data:

Det.	Gm. NaOH Per L.	% CO_2 Before	% CO_2 After	% CO_2 Removed	Rate of Flow
1	10.2	6.32	2.66	58.	.5 cu. ft. hr.
2	8.85	6.32	3.73	41.	.5 cu. ft. hr.
3	7.25	6.32	4.86	23.	.5 cu. ft. hr.
4	6.32	6.32	5.51	13.	.5 cu. ft. hr.
5	5.85	6.32	5.74	9.1	.5 cu. ft. hr.
6	4.17	6.32	5.98	4.3	.5 cu. ft. hr.
7	2.07	6.32	6.24	1.2	.5 cu. ft. hr.

To determine the ratio of available chlorine consumed to hydrogen sulphide removed, a determination was made beginning with one litre of hypochlorite solution and passing a hydrogen sulphide, carbon dioxide and air mixture through it. At intervals, 25 cubic centimeter samples were removed from the absorbent and analyzed for available chlorine and alkali content. The percent carbon dioxide absorbed by the alkali was also noted. The results of the determinations are shown by the following table:

	% H_2 S.	Gm. per 100 cu. ft.	% CO_2	Gm. Cl. available per L.	Gm. Cl. present	Gm. Na O H per L.	Gm. Na O H present	Gas to Absorbent			Gm. Cl. remaining	Gm. Cl. consumed		Ratio H_2S absorbed	% of CO_2 absorbed	Rate of flow cu. ft. per hour	cc. of absorbent
								Cu. ft.	Gr. H_2S	Gm. CO_2		Consumed	Gm. $\rightleftharpoons H_2S$	$H_2S \rightleftharpoons$ to Cl. used			
A	.2953	181	5.68	2.845	2.845	10.25	10.25	.3	.0351	.866	2.626	.219	.105	33.4	35.5	.72	1000
B	.2953	181	5.68	2.626	2.580	9.84	9.59	.2	.0234	.578	2.494	.086	.0413	56.6		.82	975
C	.2953	181	5.68	2.558	2.43	9.76	9.28	.3	.03505	.867	2.32	.11	.0529	66.3	65.	.72	950
D	.2953	181	5.68	2.44	2.259	9.58	8.86	.3	.03505	.867	2.075	.184	.0884	39.7	46.	1.51	925
E	.2953	181	5.68	2.245	2.020	9.1	8.19	.3	.03505	.867	1.825	.195	.0937	37.4		1.02	900
F	390	245.6	5.4	1.935	1.645	8.84	7.51	.3	.0462	.824	1.507	.138	.0665	69.5	58.5	.945	850
G	.390	245.6	5.4	1.771	1.462	8.57	7.06	.3	.0462	.824	1.427	.035	.01683	275.0		1.30	825
H	.390	245.6	5.4	1.73	1.383	8.32	6.65	.3	.0462	.824	1.092	.291	.140	33	33.8	1.07	800
I	.390	245.6	5.4	1.365	1.059	7.66	5.94	.3	.0462	.824	.890	.149	.0717	64.5	25.6	1.63	775
J	.390	245.6	5.4	1.15	.862	7.65	5.74	.35	.0539	.961	.626	.236	.1136	47.5	24	1.51	750
K	.390	245.6	5.4	.835	.605	7.39	5.35	.3	.0462	.824	.412	.193	.0929	49.8	15.5	1.00	725
L	.390	245.6	5.4	.569	.398	6.44	4.5	.3	.0462	.824	.227	.171	.0823	56.1		2.0	700
M	.390	245.6	5.4	.3245	.219	6.48	4.37	.3	.0462	.824	.048	.171	.0823	56.1	11.9	1.63	675
N	.390	245.6	5.4	.0706	.0459	5.94	3.86	.193	.0297	.530		.0459	.0221			1.7	650

The column labeled "Hydrogen sulphide equivalent to grams of chlorine" was calculated on the basis of the reaction:

$$H_2S + NaO\,Cl = Na\,Cl + H_2O + S \quad (7)$$

and hence the values of this column also enter into the calculation of the column labeled "ratio of

$$\frac{H_2S \text{ absorbed}}{H_2S \text{ equivalent to chlorine consumed.}}"$$

The results of this determination hence show that more chlorine is consumed than is combined with the hydrogen sulphide of equation. (7)

Conclusion: The results in general of this series of determinations show:

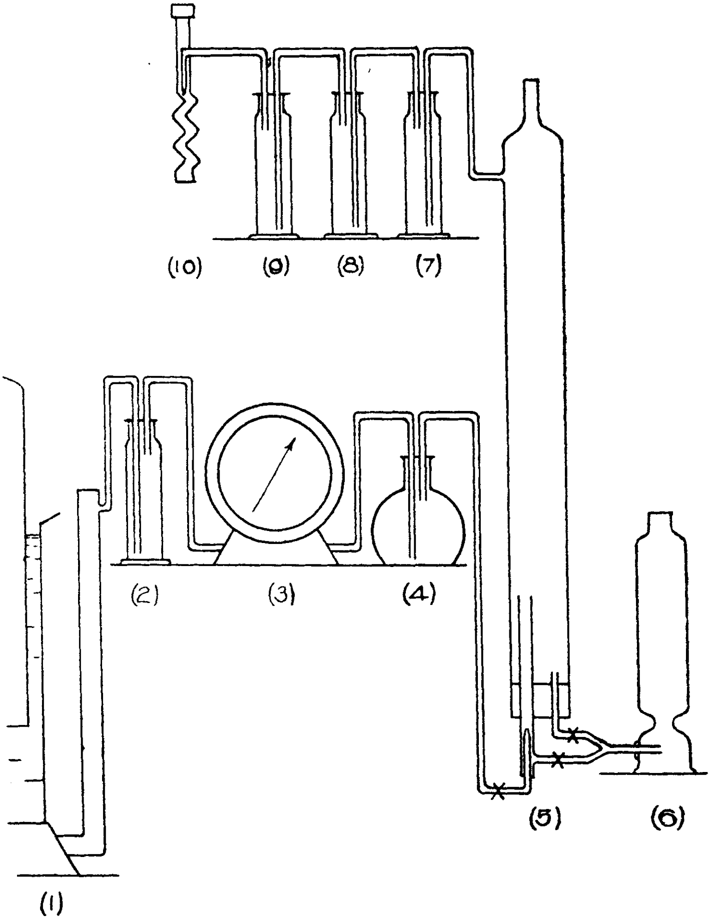
(1)That sodium hypochlorite in aqueous dilutions as low as .0706 grams of available chlorine per litre are capable of completely removing hydrogen sulphide in a gas by bubbling it through but three inches of the liquid.

(2)That a loss of chlorine by the hypochlorite solution can be prevented by making the solution slightly alkaline, without removing a large part of the carbon dioxide of the gas.

(3) That some of the sulphur as hydrogen sulphide is oxidized to sulphate.

FIXED SULPHUR REMOVAL EXPERIMENTS

The other investigation made was to determine the value of hypochlorite solutions as a means of removing carbon disulphide and other fixed sulphur compounds remaining in carburetted water gas after removing hydrogen sulphide. Sodium hypochlorite solutions like those used in the previous experiments was used. A diagram of the apparatus first used in these experiments is shown below:



(1) . 5 cu. ft. prover.
(2) Catch bottle for H_2S.
(3) Experimental gas meter.
(4) Hypochlorite absorption bottle.
(5) (9) Bureau of Standards* Design for total sulphur determination
(10) Suction device.

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*Standard Methods of Gas Testing. U. S. Bureau of Standards — Circular No. 48, Page 134.

The first determination of fixed sulphur compounds absorption by sodium hypochlorite were made by passing Carbureted Water Gas through a sodium hypochlorite solution having 27.9 grams of available chlorine per litre and 10.02 grams of sodium hydroxide per litre. The results of this experiment are summarized as follows:

Fixed sulphur compounds before absorption	12.0 Gr. 100 cu. ft.
Fixed sulphur compounds after absorption	11.0 Gr. 100 cu. ft.
Per cent sulphur removed	8.3%
Available chlorine before absorption	2.79 Gm. per L.
Available chlorine after absorption	2.66 Gm. per L.
Gas thru absorbent	2.30 cu. ft.
Rate of flow	0.5 cu. ft.
Gas analyzed	2 cu. ft. for each determination

Since not all sulphur remaining in municipal gas after hydrogen sulphide has been removed is present as carbon disulphide, this result cannot be accepted as representing the efficiency of carbon disulphide removal.

Hence the next determination made was on a gas high in carbon disulphide, to determine the value of sodium hypochlorite for removing carbon disulphide. To do this carbon disulphide gas was added to city gas as it comes from the mains. The results of this are summarized as follows:

Carbon disulphide and fixed sulphur compounds in gas before absorption	844 Gr. 100 cu. ft.
Carbon disulphide and fixed sulphur compounds in gas after absorption	762 Gr. 100 cu. ft.
Percent sulphur compounds removed	9.7%
Available chlorine before absorption	1.5 Gm. C1/L
Available chlorine after absorption	.93 Gm. C1/L
Gas thru absorbent	1.6 cu. ft.
Rate of flow	.5 cu. ft. hr.
Gas for analysis	1.2 cu. ft. for each determination

An attempt to improve this efficiency of absorption was made by using a hypochlorite solution of higher available clorine content, and by using this solution at a temperature of about 100° C. The following results were obtained under conditions indicated:

Carbon disulphide + fixed sulphur compounds of gas before absorption	.359 Gr. 100 cu. ft.
Carbon disulphide + fixed sulphur compounds of gas after absorption	.280 Gr. 100 cu. ft.
Per cent sulphur removed	22%
Available chlorine before absorption	45.7 Gm. 100 cu. ft.
Available chlorine after absorption	37.2 Gm. 100 cu. ft.
Gas thru absorbent	.980 cu. ft
Rate of flow of gas	.41 cu. ft. hr.
Volume of gas analyzed after absorption	.960 cu. ft.
Volume of gas analyzed before absorption	.980 cu. ft.

In a further attempt to improve this efficiency some catalytic materials were added under substantially the same conditions as above. The amount in each case as about 15 grams per litre of solution. The effect on the efficiency of sulphur removal of each of the substances is:

Sodium hypochlorite of 3 grams available chlorine and 10 grams sodium hydroxide per litre in the cold without catalyst	17.0%
The same at 100° C	9.64%
Cold + nickel oxide (Ni_2O_3)	18.0%
Cold + zinc oxide (ZNO)	16.7%
Cold + iron oxide (Fe_2O_3)	17.9%

The results thus obtained show a fairly constant percent of sulphur removal without appreciable increase due to the presence of catalytic materials. Hot hypochlorite solution, however, gave much poorer efficiencies than those obtained in the cold,–a fact confirmed by subsequent determinations. Evidently then the increased efficiency obtained when a hot and concentrated solution was used, was due to the higher available chlorine content of the solution and not to the increase in temperature of absorption.

To determine what effect a more intimate contact of gas and absorbent would have on the efficiency of removal, a volume of gas was passed repeatedly through a cold hypochlorite solution. The result is summarized as follows:

Carbon disulphide and fixed sulphur compounds in the gas before absorption	536 Gr. 100 cu. ft.
Carbon disulphide and fixed sulphur compounds in the gas after absorption	347 Gr. 100 cu. ft
Percent sulphur removed	35.25%
Gas passed thru solution	7 times
Rate of passage of gas	1.0 cu. ft. hr.
Available chlorine before absorption	3.61 Gm/L
Available chlorine after absorption	1.3 Gm/L
Volume of gas for sulphur analysis before absorption	.710 cu. ft.
Volume of gas for sulphur analysis after absorption	.587 cu. ft.

From the results of this determination it follows that the amount of sulphur compounds (principally carbon disulphide) absorbed, is directly dependent on the intimacy of contact between the gas and the absorbent.

To obtain a more intimate contact of gas and absorbent than was possible with the apparatus used up to this time, the gas was washed by passing it through a series of three absorption towers. The towers were packed with pebbles and arranged in cascade; the liquor flowing over the pebbles counter current to the flow of gas. The gas by this arrangement passed up a column of packing 27 inches high and 2 inches in diameter. The conditions existing and the results obtained using a concentrated and a weak absorbent are summarized as follows:

	Weak	Concentrated
Carbon disulphide + fixed sulphur in gas before absorption	78.2	78.2 Gr. 100
Carbon disulphide + fixed sulphur in gas after absorption	60.3	56.0
Percent sulphur removed	23%	28.5%
Volume of gas passed through	1.564	1.534 cu. ft.
Rate of passage of gas	.67	.6 cu ft. hr.

	Weak	Concentrated
Available chlorine per litre before absorption	.0470	3.082 Gm.
Available chlorine per litre after absorption	.0407	2.860 Gm.
Grams chlorine removed	.319	.557
Volume of absorbent used	3700 cc.	2500 cc.
Rate of flow of absorbent	7.5 L/hr.	8.2 L/hr.
Temperature of absorption	72° F.	72° F.
Volume of Gas for sulphur analysis	.80 cu. ft.	.80 cu. ft.
Grams NaOH per litre	.318	.685

A determination to check these results using a hypochlorite having 2.863 grams of available chlorine per litre and .320 grams of sodium hydroxide per litre under substantially the same conditions as the two above determinations, but using a rate of passage of gas of 0.5 cu. ft. per hour, gave an efficiency of removal of 30.44% of the sulphur compounds. The results of this and previous determinations show:

(1) That the removal of carbon disulphide and fixed sulphur compounds by sodium hypochlorite solution varies directly as the efficiency of the scrubbing device.

(2) That under these conditions, a reasonable variation in the amount of hypochlorite in the solution has but little effect on the amount of sulphur removed.

Using the tower gas-washing apparatus, a second determination was made on Madison city-gas to determine the amount of fixed sulphur compounds removable. The following is a summary of the conditions and the results:

Fixed sulphur compounds in the gas before scrubbing	10.01 Gr. 100 cu. ft.
Fixed sulphur compounds in the gas after scrubbing	5.4 Gr. 100 cu. ft.
Percent sulphur removed	46%
Volume of gas passed through	4.2 cu. ft.
Rate of passage of gas	.864 cu. ft. hr.
Available chlorine before absorption	.86 Gm/L
Available chlorine after absorption	.575 Gm./L

Volume of absorbent	4 litres
Rate of flow of absorbent	6 L/hr.
Amount of chlorine consumed	1.14 grams
Grams sodium hydroxide per litre	.234 grams
Volume of gas used for sulphur analysis before absorption	3.796 cu. ft.
Volume of gas used for sulphur analysis after absorption	3.413 cu. ft.

THE GAS INDUSTRY, A GOOD CUSTOMER OF THE UNIVERSITY

PROF. O. L. KOWALKE, CHEMICAL ENGINEERING DEPT.,
UNIVERSITY OF WISCONSIN

As read at the Twentieth Annual Convention of the Wisconsin Gas Association at Milwaukee, March 22 and 23, 1921.

It is unusual that you are asked to consider an educational problem. But the problem is one in which you are vitally interested; it concerns your employment of a product from the University. You are now a good customer and it is necessary that you continue to be so. To retain your patronage, satisfactory service must be rendered; you must know the capacity of the product; your confidence and good will must be retained.

To aid in the presentation of this topic certain analogies will be suggested between the gas industry and the University. Your business is sometimes called a public utility. Utility is synonymous with service; so you give a public service. What would justify a University if it were not public service?

The gas industry and the University each have a technical staff. In the University the function of the staff is to train young men for engineering and industrial service. Your raw materials now come to you from variable sources, and it is not always known how best to treat them, though they may obey certain well-known laws of chemistry, physics, and mathematics. The University also draws on many sources for young men of variable capacity and previous training and the technical staff is not always able to meet requirements in the matter of standards because the laws governing the workings of the human mind are not perfectly understood. Some companies are managed more successfully than others; some instructors are more successful than others in the training of young men.

Your sales and complaint departments are complementary. The first sells the product to your consumer; the second gives the customer an opportunity to express dissatisfaction with the commodity sold or service rendered, but at the same time strives to retain his good will. In a like manner the University after disposing its product among the industries, strives, through its representatives, to determine whether the service rendered by the young men is satisfactory. This is one of the opportunities which the University seeks for a discussion regarding inadequacies in its technical training. A frank expression of opinion is therefore invited.

You get new business through advertisments, demonstrations, and personal solicitation. You believe that the better the prospective customer understands what he can do with your product, the more likely he is to buy your commodity. The University publishes a general catalog and bulletins regarding special courses; it may also make personal explanations regarding specific advantages offered.

This opportunity is therefore taken to speak specifically about the training offered for chemical engineers, which, it is believed, is particularly suited for the gas industry today. The training is not that of a chemist; it is more along the lines of engineering than of chemistry. It is intended that the student shall be able to make a chemical analysis, but not that he be only an analyst in chemistry. Besides liberal instruction in theoretical chemistry the student is also required to take the basic courses in drawing, mathematics, physics, mechanics, and machine design that are required in the curricula for mechanical and electrical engineering.

The following tabulation of the curriculum in chemical engineering is self-explanatory.

First Year

First Semester		*Second Semester*	
General Chemistry	3 credits	General Chemistry	3 credits
Drawing	3 credits	Drawing	3 credits
English	3 credits	English	3 credits
Mathematics	5 credits	Mathematics	5 credits
Shop work	2 credits	Shop work	2 credits

Second Year

Mathematics	4 credits	Mathematics	4 credits
Physics	5 credits	Physics	5 credits
Machine Design	4 credits	Mechanics	5 credits
Quant. Chem. Analysis	5 credits	Gas & Fuel Analysis	2 credits
		Engineering Materials	2 credits

Third Year

Organic Chemistry	3 credits	Organic Chemistry	3 credits
Steam and Gas Engineering	3 credits	Steam and Gas Engineering	5 credits
Mechanics	5 credits	Descriptive Geometry	3 credits
Metallography	3 credits	Electrical Engineering	2 credits
Pyrometry	2 credits	Chemical Machinery	2 credits
Electives	3 credits	Strength of Materials	2 credits
		Electives	3 credits

Summer work in Chemical Engineering........5 weeks

Fourth Year

Electrical Engineering	4 credits
Physical Chemistry	3 credits
Electrochemistry	5 credits
Industrial Chemistry	3 credits
Thermochem. Calculations	2 credits
Steam and Gas Engineering	1 credit
Electives	2 credits

Machine Design	3 credits
Contracts	2 credits
Industrial Organ. Chem.	2 credits
Thermochem. Calculations	2 credits
Special problems	4 credits
Electives	5 credits

In the elective courses opportunity and encouragement are given for the sudent to broaden his vision and interests. He is encouraged to study economics, business methods, English, history, and the like. Among the electives, he may choose a course in gas manufacture and distribution. In this course the fundamental principles of chemistry, physics, and mechanics are emphasized as applied to the carbonization of coal and oil, heat conduction, refractory materials, and the distribution of gas. The technique of this industry can best be learned in the plant.

You have repeatedly employed the graduate in chemical engineering, hence you are a good customer. Customer is synonymous with patron. But a patron is defined as one who supports; one who helps a cause, a work. You have done more than support; you have given liberally from your funds to establish a Fellowship in Gas Engineering in the Department of Chemical Engineering. Thus you have a vital interest in this matter of training young men.

The question may well be asked, "Why did this Association establish the Fellowship?" Two reasons may be suggested; first, to obtain information of value to the Association, second, to train men for subsequent employment in the industry. Up to this time the chairman of the Chemical Engineering Department chose and nominated to the Board of Regents the most promising candidate for the Fellowship. The chairman also took the initiative in the choice of problem, but consulted with the President of this Association and other members. Informal discussions have been held as the work progressed, and the final reports have been presented at the annual meetings of this Association.

The following suggestions are offered for your consideration in order to obtain better results and greater interest on the part of students in the gas industry. Because the men hitherto appointed to the Fellowship have had neither knowledge of the problem to be studied nor practical experience in the gas business, considerable time had to be spent by each Fellow to become familiar with his problem. There should be some way in which the student could become more familiar with the practices in the gas industry before beginning work on his problem.

During the summer following the junior year, the student in chemical engineering is required to work at the University eight hours each day for a period of five weeks in a laboratory course in chemical manufacture. This is a most favorable opportunity to observe the ability and initiative shown by the student.

It is proposed to select from this group three or more men of proper personality and good records as students to take temporary summer employment in your plants, that is, from about the middle of July to the middle of September. During this time the men are under your supervision. Reports on such summer work will be required of the student, reports from your executives to the chairman of the chemical engineering department regarding the record made by the student would be highly desirable. By the end of the senior year it would be possible to make a choice for the Fellowship from those who have shown aptitude for the work. During the summer following the fourth year the student should have the opportunity again of working in a gas plant so that he may become more familiar with the problem he is to study during the coming scholastic year.

It is hoped that this proposal will provoke some discussion and that suggestions will result from it. This is a matter in which you are vitaly interested and your views are earnestly sought. The Chemical Engineering staff desires to give an account of its stewardship of the patronage which you have so generously extended.

A paper presented at the Thirty-seventh General Meeting of the American Electrochemical Society, in Boston, April 8, 1920, President Bancroft in the Chair.

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PHYSICAL CHARACTERISTICS OF SPECIALIZED REFRACTORIES.[1]

By M. L. Hartmann[2] and O. A. Hougen.[3]

Abstract.

Comparative tests of the resistances of twelve different kinds of refractory bricks to rapid cooling by an air blast after heating to 1350° C. This was repeated up to ten treatments with nine bricks, while three were completely disintegrated at the seventh, fourth and third treatment. The percentage loss of weight is stated, which varied from 0.3 percent with bonded carborundum (carbofrax C) to 100 percent with the last three samples.

[J. W. R.]

Part I.—Spalling Losses.

Most refractory bricks when subjected to sudden changes of temperature or to excessive strain at high temperatures break and shell off in various ways and in different amounts. This effect is noted particularly when only one face of a brick is heated. In the arches of furnaces, a pinching effect often takes place due to sudden changes in temperature which results in disrupting the brick. Such action may cause complete destruction of a furnace. This disrupting action is commonly known as spalling. Almost all refractories exhibit spalling, the different materials showing wide variation in the magnitude of this effect.

Spalling is due chiefly to three causes:

(a) Expansion or contraction of individual grains due to temperature changes.

(b) Change of crystalline structure.

(c) Chemical reactions within the structure.

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[1] Manuscript received March 3, 1920. This and the following paper record the results of portions of a general investigation aiming to contribute some definite and accurate information concerning the physical properties of special refractory bricks as compared with the more common fireclay refractories.

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Magnesia and silica refractories show excessive spalling losses in practice. Spalling of magnesia brick is due chiefly to the conversion of "A" Magnesia to the "B" form,[4]. In silica brick, spalling is due chiefly to the conversion of quartz to tridymite and cristobalite.[5] Fire bricks usually contract upon heating, due mainly to the closing of pores by the fusion or sintering of portions of the bond rather than to any crystallographic conversion.

Spalling has usually been reported in general terms as the result of actual furnace operation. No figures showing actual comparison of the spalling of different bricks under the same conditions are available in the literature. To obtain comparable results in commercial installations would be exceedingly expensive and time consuming, and hence a more rapid test is needed for procuring comparable data.

Some previous work has been done on this by Nesbitt and Bell.[6] The bricks to be tested were heated at 1350° C. for one hour in the doorway of a furnace, with one end flush with the interior wall. They were then removed and cooled rapidly by immersion of the heated end to a depth of 4 inches in a fixed amount of water for three minutes. This operation was repeated ten times for each brick, and the final results reported in percentage loss (by weight) of material which had broken off.

Nesbitt and Bell also tried the method of rapidly cooling in a blast of air, but adopted the water quenching method because it seemed to give more rapid cooling and consequently the spalling effect was augmented.

However, there are many objections to the quenching method as a general method: (1) It is applicable only to fireclay bricks. (2) In practice, bricks are never subjected to similar treatment. (3) The water has a disruptive action on porous bricks by seeping into the pores and forming steam. (4) Water at 1300° C. reacts chemically with some materials; this is especially noticeable with magnesia and carborundum bricks.

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[4] J. W. Mellor, Trans. Eng. Ceramic Soc. (1917), 16, 85-100.

[5] D. W. Ross, "Silica Refractories," U. S. Bureau of Standards, Technologic Paper (1919).

[6] Chem. & Met. Eng. (1916), 15, 210; Proc. Am. Soc. Test. Mat. (1916), 16, 350.

Revised Air-Blast Method.

Preliminary tests showed that almost as severe results were obtained by the air-blast as by the quenching method. For example, the average spalling loss on Grade B fireclay by water quenching was 79 percent and by the air-blast method it was 65 percent. The quenching method used was identical with that of Nesbitt and Bell.

The air-blast method finally adopted for our work was as follows: The bricks to be tested were thoroughly dried at 110° C., weighed and heated in the openings of the front wall of a specially designed oil-fired furnace, with ends flush with the inside walls. The furnace construction is shown in Fig. 1. The front wall was constructed of recrystallized carborundum bricks, with twelve openings 2¾ in. x 4¾ in. (7 cm. x 12 cm.) in which the bricks under test were inserted with the end flush with inner wall of the furnace. This allowed only one end of the brick to be heated. The use of a neutral highly refractory brick as a support prevents sticking of the brick under test. Freedom from sticking is very important, because when the bricks under test adhere to the furnace bricks large pieces of the somewhat weakened test brick may be broken loose by the force required to pull the brick from the furnace. The front wall was insulated with firebrick to prevent excessive heat losses. When the temperature of the furnace reached 1350° C. the bricks were inserted in the openings of the wall, and each brick left in the furnace for one hour. Each brick was then taken out and set on the cold end with the hot end exposed to an air blast for 15 minutes. This operation was repeated ten times for each brick. The blast was supplied by a ¾-in. (2 cm.) hose delivering air at the rate of about 27 cubic feet (0.76 cu. m.) per minute. This amount of air apparently produced nearly as rapid cooling as quenching in water. Examinations of the bricks were made at the end of each cooling, to detect the developments of checks, cracks or spalling. At the end of the final cooling all particles which could be easily broken off by the fingers were removed. The bricks were weighed and the percentage loss calculated from the original weight.

The behavior of the various bricks during test considered in order of their resistance to spalling are given below. In making comparisons it must be borne in mind that while the percentage weight of material broken off by spalling is important, the manner of spalling and the final condition of the brick after the test must be considered.

(1) Bonded carborundum brick (Carbofrax C). The spalling was negligible, the slight loss of 0.3 percent being due to abrasion in handling. These bricks contain about 95 percent carborundum. Very faint check lines were visible while the bricks were hot, but there were no visible cracks after the final cooling. (See Fig. 2.)

(2) Bonded carborundum brick (Carbofrax A). The losses by spalling usually occur by the breaking off of large pieces. This was more or less irregular, a few bricks showing high spalling and others showing practically no spalling. Small check lines were visible on the bricks after the test. The average percentage spalling of nine bricks was six percent. (Fig. 3.)

(3) Bonded carborundum bricks (Carbofrax B), containing about 90 percent silicon carbide gave an average spalling loss of 8 percent. The losses occurred usually in large pieces, although there was also some spalling in small fragments. The bricks were badly checked after the test. (Fig. 4.)

(4) Grade A fireclay bricks (apparent density 1.78) very coarse in texture, gave a spalling loss of 9 percent. Spalling was uniform. It did not occur by large pieces shelling off but rather in the separate crumbling off of the coarse grains. Some fine check lines were visible in the bricks after testing. (Fig. 5.)

(5) Recrystallized carborundum bricks (Refrax). These bricks are composed entirely of carborundum, held together by the intergrowth of crystals. No bonding material is used. The average spalling loss amounted to 12 percent. The spalling occurred in the form of medium-sized pieces. Most of the spalling occurred during the first few coolings. Only a few short cracks were visible after the test. (Fig. 6.)

(6) Bauxite bricks, of a well-known make, coarse in texture (apparent density 1.91) gave an average of 43 percent spalling loss. These bricks showed a very peculiar and unaccountable behavior, practically the whole loss occurring at the fifth heating, little spalling occurring either before or after. Fine check lines were visible after the test.

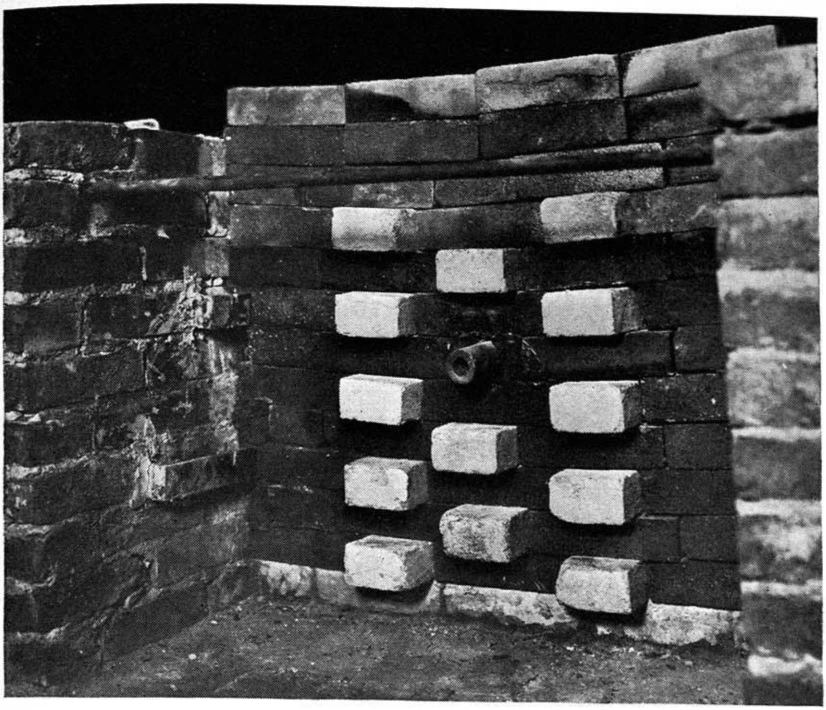

FIG. 1. Furnace Front used in Spalling Tests.

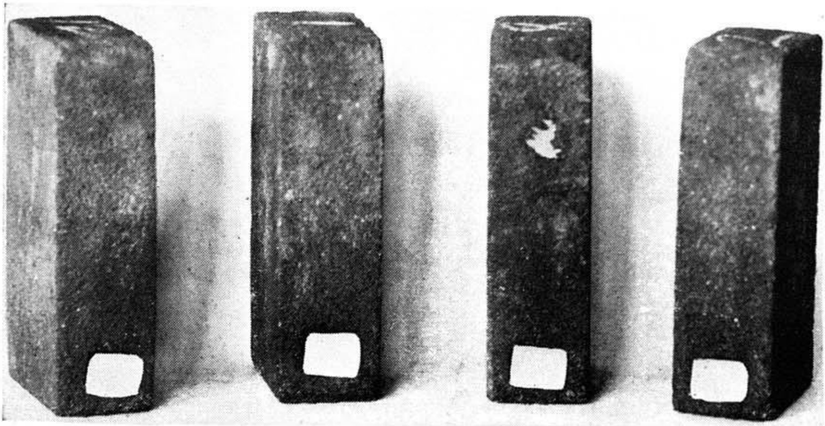

FIG. 2. Carbofrax "C" Bricks After Test.

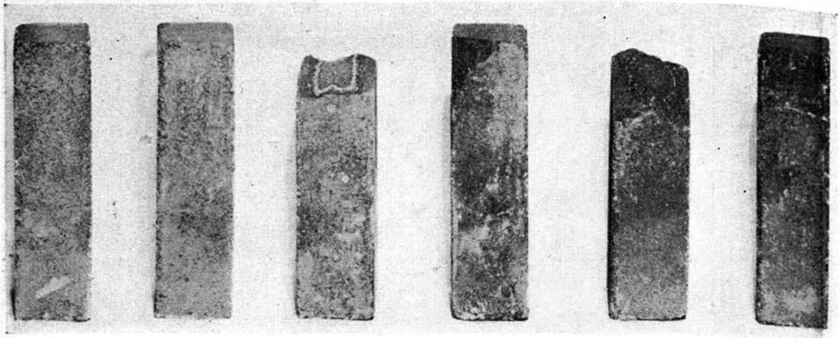

FIG. 3. Carbofrax "A" Bricks After Test.

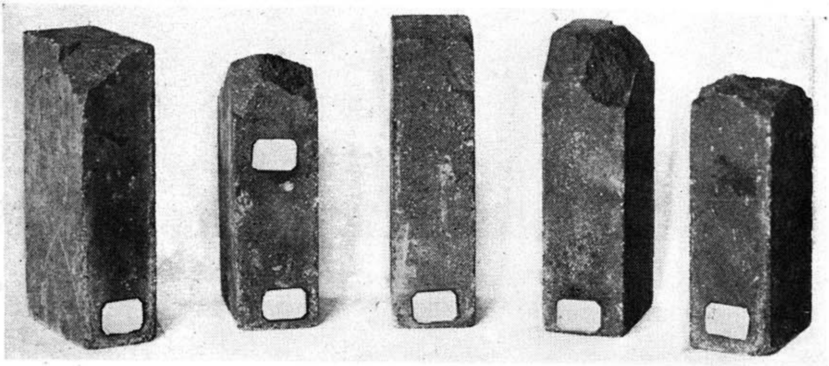

FIG. 4. Carbofrax "B" Bricks After Test.

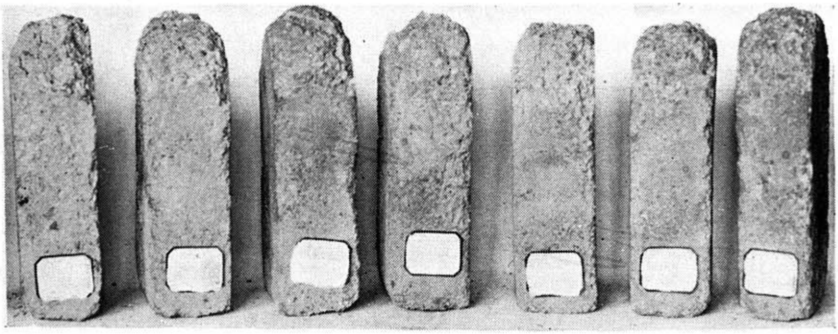

FIG. 5. Grade "A" Fireclay Bricks After Test.

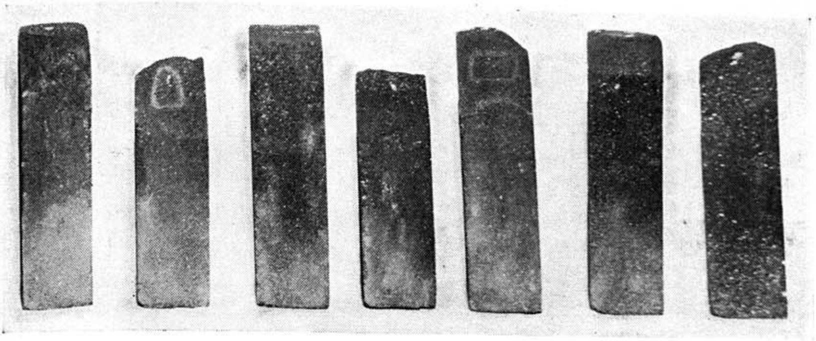

Fig. 6. Recrystallized Carborundum Bricks After Test.

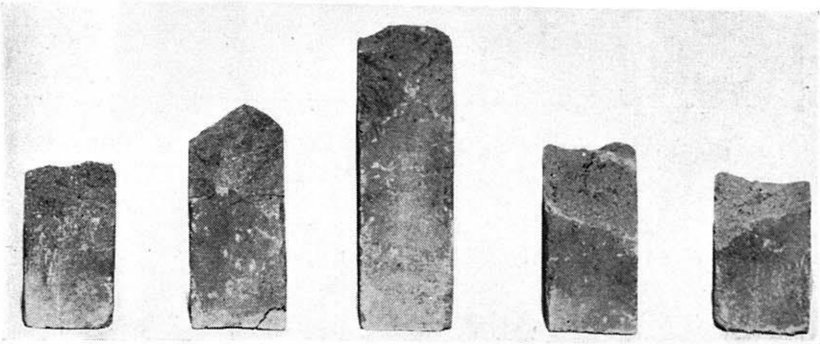

Fig. 7. Natural Zirconia Bricks After Test.

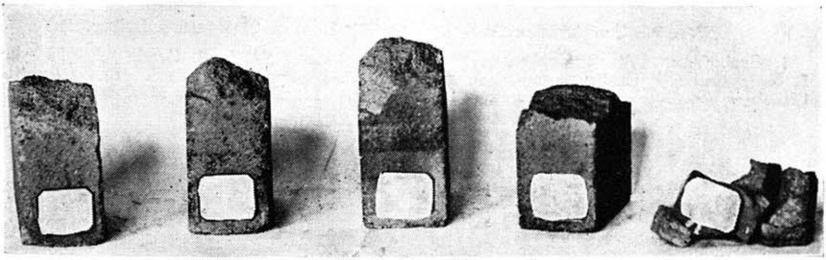

Fig. 8. Grade "B" Fireclay Bricks After Test.

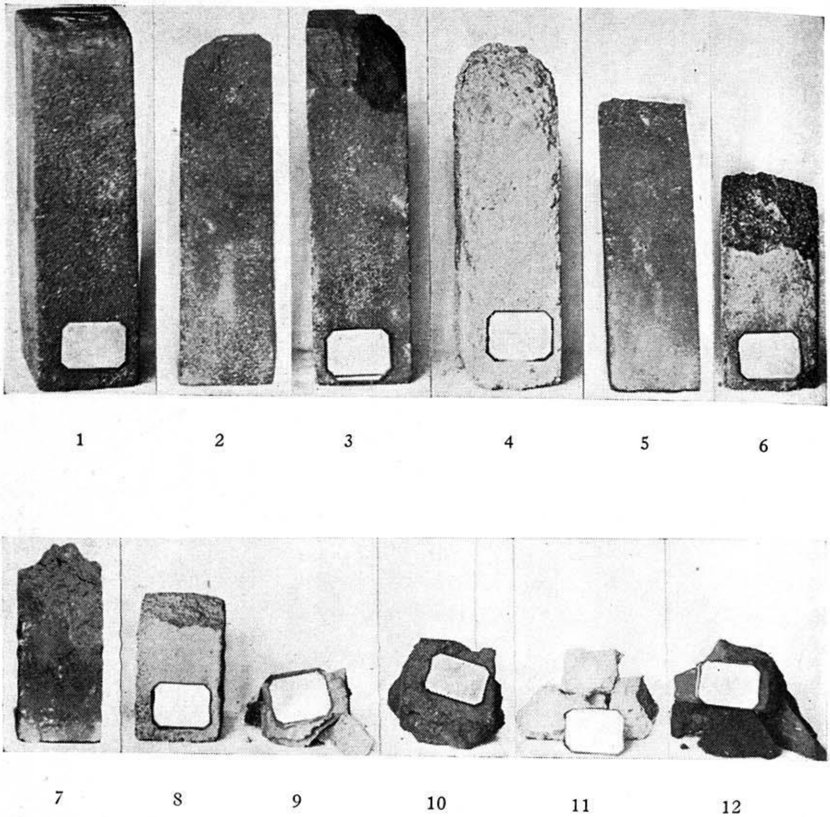

Fig. 9. Comparative Average Spalling Loss of Refractory Bricks.

1. Carbofrax "C." 2. Carbofrax "A." 3. Carbofrax "B." 4. Grade "A" Fireclay. 5. Recrystallized Carborundum. 6. Bauxite. 7. Zirconia (natural). 8. Grade "B" Fireclay. 9. Grade "C" Fireclay. 10. Chrome. 11. Silica. 12. Magnesia.

(7) Zirconia bricks, made of commercial natural zirconia, and containing approximately 80 percent zirconium oxide. Average spalling loss amounted to 53 percent. Many large cracks developed and large pieces broke off during the test. The spalling and cracking was about equal in all of the bricks tested. (Fig. 7.)

(8) Grade "B" fireclay bricks (apparent density 2.04). This variety has a close-grained texture. The bricks had an average spalling loss of 65 percent. There were large variations in the results, as shown by Fig. 8.

(9) Grade "C" fireclay bricks (apparent density 2.09), of very dense, close-grained texture, showed a spalling loss of 90 percent.

(10) Chrome bricks (apparent density 2.83), of standard make, coarse grained, were completely shattered at the end of the 7th cooling. Compared with other kinds of bricks which stood up through the ten heats, this is equivalent to a spalling of 155 percent. The pieces of bricks became very soft, and could be easily broken.

(11) Silica bricks (apparent density 1.66) of lime-bonded standard make, gave very excessive spalling, being complete at the end of the 3d and 4th cooling, equivalent to 225 percent on the basis of ten coolings.

(12) Magnesia bricks (apparent density 2.27), a dense fine-grained brick of standard make. These bricks exhibited complete spalling at the end of the 3d cooling, equivalent to 375 percent on the basis of ten coolings. They became very soft and fragile at 1350° C., making them very difficult to handle without breaking.

CONCLUSIONS.

The results of all tests are summarized in the following table and comparative results shown graphically in Fig. 9.

	Percent	
1. Bonded Carborundum (Carbofrax C)	0.3	at end of 10th cooling
2. Bonded Carborundum (Carbofrax A)	6	at end of 10th cooling
3. Bonded Carborundum (Carbofrax B)	8	at end of 10th cooling
4. Grade A Fireclay	9	at end of 10th cooling
5. Recrystallized Carborundum (Refrax)	12	at end of 10th cooling
6. Bauxite	43	at end of 10th cooling
7. Zirconia (natural)	53	at end of 10th cooling
8. Grade B Fireclay	65	at end of 10th cooling
9. Grade C Fireclay	90	at end of 10th cooling
10. Chrome	100	at end of 7th cooling
11. Silica	100	at end of 4th cooling
12. Magnesia	100	at end of 3rd cooling

In general, coarse-grained bricks and bricks of high porosity show least spalling losses.

Without exception, all bricks show some checking when subjected to sudden cooling. These check lines are always visible during the first cooling, subsequent coolings render these checkings more visible and usually they develop into cracks and spallings. In the case of carborundum bricks checking is usually visible only when hot.

All bricks lose their sound, metallic ring after quenching or air-cooling.

From five to ten bricks were used in each test. These were purchased in the open market and undoubtedly do not give absolute results for the various types of refractories. The general order of magnitude of spalling is probably correct, however, and inasmuch as no results of similar tests have been previously published, these preliminary results may be of value.

Research Laboratory, The Carborundum Company,
Niagara Falls, N. Y., February 15, 1920.

[FROM THE TRANSACTIONS OF THE AMERICAN ELECTROCHEMICAL SOCIETY, Volume XXXIX, 1921, being the Transactions of the Thirty-Ninth General Meeting, at Atlantic City, N. J., April 21, 22, and 23, 1921.]

The Effect of Copper and Silver Salts on the Corrosion of Iron by Acids

BY

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and

HAROLD C. KNAPP

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.

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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.

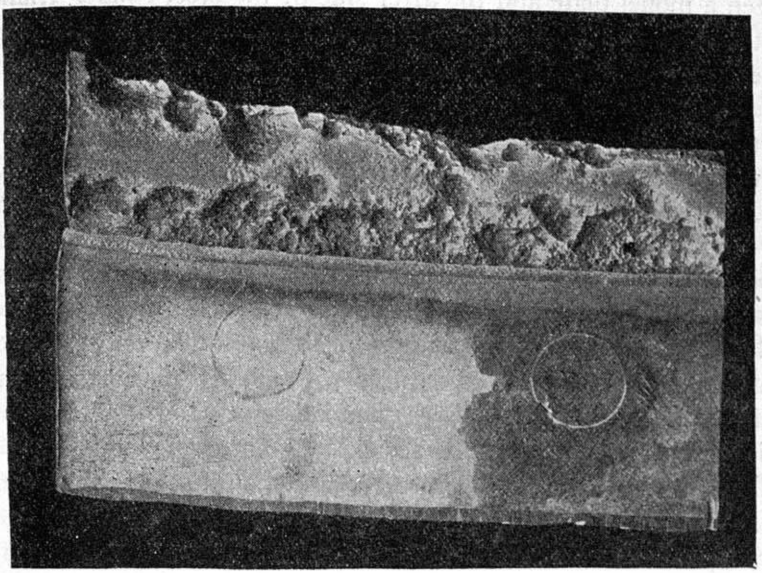

FIG. 1.

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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University of Wisconsin.

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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[1] Chief Chemist and Chem. Engr., Swift & Co., Chicago, Ill.

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

[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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[3] Chief Chemist, American Rolling Mill Co., Middletown, O.

[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.

[FROM THE TRANSACTIONS OF THE AMERICAN ELECTROCHEMICAL SOCIETY, Volume XXXIX, 1921, being the Transactions of the Thirty-Ninth General Meeting, at Atlantic City, N. J., April 21, 22, and 23, 1921.]

PRINCIPLES OF ALLOYING TO RESIST CORROSION

BY

OLIVER P. WATTS

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.

PRINCIPLES OF ALLOYING TO RESIST CORROSION.[1]

By OLIVER P. WATTS.[2]

ABSTRACT.

A plea for intelligent use of metallography and metallurgical principles in attempts to find non-corrodible alloys. The general principle is laid down that the less corrodible alloys are either metallic compounds of simple chemical formula (which are apt, however, to lack malleability) or solid solutions of the more resistant metals in each other. The protective action of small amounts of one metal in another is described; an interesting test proving the protective action of copper in steel is given.—

[J. W. R.]

In recent years much attention has been given to the production of alloys designed to resist atmospheric and chemical corrosion. Some of the better-known products of this nature are tantiron, duriron, copper steel, stainless steel, monel metal and nichrome. In view of our knowledge of the chemical properties of the elements and the light which metallography has given us regarding the nature and constitution of alloys, it is surprising that the principles of alloying for protection have not already been clearly and fully set forth in the extensive literature devoted to the corrosion and protection of metals. This, however, does not appear to be the case. The new corrosion-resisting alloys seem to have been discovered entirely by trial, without any general principle to guide in the selection of the element or elements to be added to the metal which it is desired to render more resistant to corrosion.

It is not sufficient to add to the metal to be protected some other metal which is very resistant to corrosion, for instead of pro-

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[1] Manuscript received February 15, 1921.

[2] Associate Professor, Chem. Eng., University of Wisconsin.

tecting, the addition frequently accelerates corrosion. This was shown a century ago by the experiments of Stodart and Faraday[3] in alloying several metals of the platinum group with steel. They say, "If two pieces, one of steel, and one of steel alloyed with platinum, be immersed in weak sulphuric acid, the alloy will be immediately acted upon with great rapidity and the evolution of much gas, and will shortly be dissolved, whilst the steel will be scarcely at all affected. In this case, it is hardly possible to compare the strength of the two actions. If the gas be collected from the alloy and from the steel for equal intervals of time, the first portion will surpass the second some hundreds of times."

It is easy to make a corrosion-resisting alloy from two metals which themselves are highly resistant, such as the noble metals, but the real problem is to take a cheap metal and add to it a small or a moderate amount of some other element that will render the resulting alloy resistant. Theoretical considerations would lead to the conclusion that of all the possible forms in which two elements alloy, the chemical compound will prove most resistant to attack. The truth of this is seen in the work of Moissan and his students in the making of new silicides and borides. He formed the desired compound in an excess of metal, which by boiling with acids was dissolved, leaving behind the chemical compound. But these same experiments show that it will not do to have both free metal and compound present in the alloy if it is to resist corrosion; the alloy must be all compound. For many uses of corrosion-resisting materials, malleability, or at least freedom from marked brittleness, is a necessity; but the brittleness of all ordinary chemical compounds is one of their most general characteristics, and the compounds formed between two metals are no exception to the universality of this rule. The use of alloys which are wholly compounds must be confined to places where brittleness is not fatal to their employment.

The protective effect of additions of copper and of nickel to iron has been known for several years. In seeking a reason for the protective effect of copper and nickel, in contrast to the accelerative effect of alloying platinum with iron, the writer found from published articles that both copper[4] and nickel form with iron,

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[3] Trans. Royal Soc., 1822, 262.

[4] Trans. Am. Electrochem. Soc. (1912), 21, 358.

within the limits in which their addition is beneficial, solid solutions, *i. e.*, homogeneous substances in which neither metal can be detected by the microscope. Duriron, tantiron, etc., are iron-silicon alloys which contain about 15 percent of silicon. These are solid solutions, and exhibit remarkable resistance to corrosion. Monel metal, the natural alloy of nickel and copper, has found extensive application on account of its unusual resistance to corrosion by various chemicals; this also is a solid solution. One of the most important of the recent non-corrosive iron alloys is stainless steel, which is an alloy of iron with about 13 percent. of chromium and 0.3 percent of carbon. Tammann and Trietsche[5] state that iron and chromium form a series of solid solutions, and the photograph of stainless steel shown in Fig. 1, for which the writer is indebted to E. D. Fahlberg, shows that the presence of a small percent of carbon does not alter this.

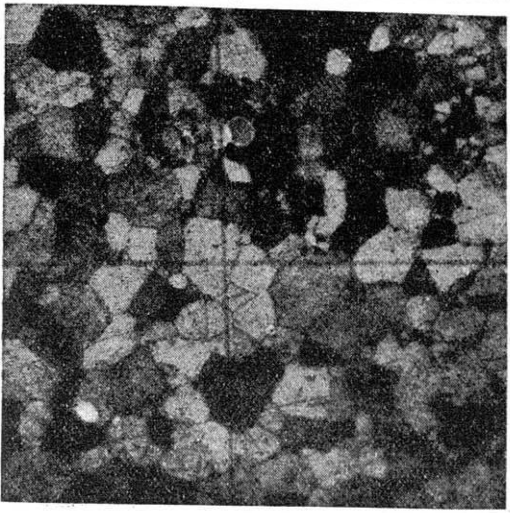

FIG. 1. Stainless Steel, Annealed—Magnified 100 Times.

A consideration of the five corrosion-resisting alloys mentioned above leads to the conclusion that to increase the resistance to corrosion of any metal there should be alloyed with it another metal which is more resistant to corro-

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[5] Zeit. anorg. Chem.. **55**, 402.

sion, and which forms a solid solution with the metal whose resistance to corrosion it is desired to enhance.

That only a trace of the alloying element can produce remarkable effects is shown by "copper-steel." Two pieces, each 5 cm. square and of the same thickness, one of ordinary steel and the other containing about 0.25 percent of copper, were placed in 200 cc. of normal sulphuric acid for 20 hours at 30° C. The former lost 5.507 grams and was nearly all dissolved, but the latter lost only 0.063 gram in weight.

A test which the writer has found very useful for quickly distinguishing highly resistant alloys of iron is immersion for a couple of minutes in a strong and slightly acidified solution of copper sulphate. Only the most resistant alloys, such as duriron and stainless steel, fail to acquire a deposit of copper.

If the alloy specialist must have ductility in his alloy he is advised to experiment with metals more resistant to corrosion than the basic metal which he proposes to use, *i. e.*, metals below it in the electrochemical series in those electrolytes against whose attacks he desires it to be immune, and which form a solid solution with the basic metal. If brittleness is no detriment, he can hardly do better for resistance to acid solutions than to test various silicides of the metals.

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DISCUSSION.

H. S. RAWDON[1]: I had a question I wanted to ask Mr. Watts if he had been here concerning the micrograph shown on page 255. He states that it is stainless steel. Ordinarily we understand by that term steel of 13 percent chromium. He says "Tammann and Trietsche state that iron and chromium form a series of solid solutions." Recently we had occasion to examine practically all the commercial types of stainless steel, and all the chromium steels showed large amounts of carbide,

[1] Physicist, Bureau of Standards, Washington, D. C.

in fact, a prominent feature of the structure is the carbide of chromium and iron. The steels that are high in nickel are of the type of solid solution shown here in this Figure 1, and I was wondering if he had had this sample analyzed so that he knew exactly whether he was dealing with chromium steel or a high nickel steel. I am rather of the opinion he had a high nickel steel and did not know that he was working that type of material.

D. M. STRICKLAND[2]: I believe the author has presented thoughts which are of some value and should be considered when preparing rust resisting alloys. I have obtained certain of the alloys mentioned and have used them in work under my own observation, and the results of these tests show that I am not able to substantiate all the claims that Mr. Watts makes for his alloys. On page 255 his general conclusion is, that to increase the corrosion resistance of any metal, there should be alloyed with it in the form of a solid solution another metal which is more resistant to corrosion. He bases this conclusion on one experiment and one alloy. I took this same alloy and immersed samples in solutions other than the sulphuric acid mentioned, and obtained results which do not corroborate his statements. I believe Mr. Watts has not presented sufficient investigational data to warrant his comprehensive conclusions.

Time does not permit the presentation of a discussion which I have prepared, but when it is published in the Transactions you will find that the data submitted show that the alloy, the same as used by Mr. Watts, does not always conform to his own conclusion. (See below).

HENRY HESS[3]: Now, one matter indirectly raised is very far-reaching, it touches on the making of steel in a very important phase. With relatively few exceptions, new alloys are the result of cut-and-try methods rather than of logical developments; it is, therefore, entirely pertinent to ask for any guide or literature on the substances that will form solid solutions. If there is such a thing in existence I do not know it. If there is no such guide, the statement of the author regarding the formation of

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[2] American Rolling Mill Co., Middletown, Ohio.

[3] Philadelphia, Pa.

solid alloys leaves each man to make his cut-and-try experiments as heretofore; there is, therefore, no value in that general statement to the steel maker. At the same time, if Mr. Watts or any other member present can contribute something along that line, he will contribute something that is really valuable to the industry, whether the contributing member is a university man or a man out of the industry, is a matter of indifference; undoubtedly, if the university man can contribute that thing, he will be doing a great deal for the standing that will be accorded to the university by the industry generally.

J. W. RICHARDS[4]: To answer one of the points brought up by Mr. Hess, in Landoldt and Börnstein's Table (last edition), for instance, are given the fusing points, curves and the composition of a large number of binary alloys, not many tertiary alloys, and in these you would find some indication of which metals form solid solutions. In the books on metallography, such as Hoyt's or Gina's, there is more or less information in the diagrams as to which metals form solid solutions with others. In Bullen's book on steel there is considerable information about the relations of the other elements to steel, which form solid solutions and which do not.

WM. M. CORSE[6]: Before leaving this question of corrosion I should like to make a practical suggestion. It would be a very good idea if this Society expressed its interest in the subject of corrosion by asking the Division of Research Extension to work on this very interesting and valuable subject; and I would, therefore, move, if it meets with the approval of the chairman, that the Electrochemical Society at this meeting suggest to the National Research Council, through its Division of Research Extension, that the topic of corrosion be considered as an active and practical subject.

COLIN G. FINK: It is needless to say that the Society will gladly support a movement of this kind. The matter will be handled through the regular channels at the next Directors' meeting. I should like to summarize the various points that have

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

[6] Gen. Mgr., Monel Metal Products Corp., Bayonne, N. J.

been brought out in this symposium in order that some of you, who have a hazy idea of what has been said, might get a clearer perspective. First of all, this symposium has emphasized that iron or steel containing about a quarter of one percent copper will withstand atmospheric corrosion better than iron or steel without copper. Secondly, iron and steel containing about a quarter of one percent copper, when completely immersed in ordinary tap water or slightly acidulated water, does not resist corrosion as well as pure iron does. Thirdly, in boiler practice and in hot-water systems, the presence of oxygen greatly accelerates corrosion, and the removal of oxygen from the boiler water practically eliminates corrosion. I think that point is pretty well established. Fourthly, similar to oxygen, carbon dioxide in boiler water derived from soluble iron bicarbonate, increases corrosion, and its removal practically eliminates corrosion.

Now as to the corrosion resistant alloys: All elements, such as chromium, silicon, nickel, etc., added to iron, tend to reduce corrosion, but detailed investigations are lacking. We are really just at the very beginning of that line of research. The corrosion of alloys is becoming of increasing importance, and although great progress has been made in recent years, the satisfactory co-ordination of results is lacking. So much for the points brought out in the symposium. As to suggestions for the future: First, we need more careful, more thorough investigation of the surface film, *e. g.*, determination of physical and chemical properties of this film; also, its composition. The paper by Shepard is a highly interesting one. He talks about the corrosion of lead and yet he never mentions that surface film that is so highly important. It reminds me very much of a chemist who was supposed to make an analysis of a road-bed. You know how many of our automobile roads are constructed nowadays. There is the thin asphalt surface, and underneath that a layer of concrete, and then your broken stone under that. The chemist takes a drilled sample and he reports so much lime, and so much silica. What do we care about the lime and silica? You would not be able to estimate the life of your automobile tires on that road from that chemist's analysis. You would want to know more about the asphalt "film," its physical properties, thickness, hardness, etc. First of all, then, there is the question of the composition of the surface film; secondly, the porosity of that film. Practically nothing has been said during the symposium about the porosity. Time and again we have hinted at it, but there are no investigations published, no careful investigations, which deal with the porosity of the film. Thirdly, there is the tenacity of the film, the power of the film to adhere to the underlying metal and of the film to hold together without cracking or peeling. The film may be plastic like rubber, or it may be discontinuous as though it were composed of so many grains of sand; the elastic and the discontinuous film may be of identical composition, and yet entirely different in their protective action. Then, fourthly, there is the micro-structure of the metal, and of the surface of that metal directly underneath the surface film. We need more papers along this line. We need also papers on the mechanical and chemical treatment of metal alloys and the effect of such treatment on the surface film and underlying metal, *i. e.*, the metal directly underneath the film. A clear illustration of this point: a link of the Newburyport bridge was rolled out into sheets and then we were told that these sheets would not stand up as well as the links have stood up for so many years. And why? Because you have produced an entirely different film! Simply because the metal is the same as that of the links, does not prove that the resistance to corrosion will be the same. We also need a better classification of the corrosion phenomena. We ought to define the limits, we ought to be more specific when we talk about atmospheric corrosion, whether we are talking about an atmosphere free from acid fumes or an atmosphere which is practically dry all the year around. Then, when we talk about immersion tests, we want to be pretty careful in defining what acids and what strengths and what temperatures we used. Now, finally, we ought to decide upon a standard measure of corrosion. We have one gentleman who reports in ounces per square foot and forgets all about the time element. Another, reports loss in grams per square foot, which is a bad combination of French and English systems. We must decide upon one uniform measure of corrosion, and the one I would like to propose and have mentioned before, is the milligram per square centimeter per year unit. If that isn't considered satisfactory let us determine upon some other so that when we record our results let us do so in the same conventional standard in order that we may readily compile and compare results.

W. D. RICHARDSON[7]: May I ask, in order to add a bit of clarity to this compilation, if, in the term "surface film," he intends to include the film or absence of the film concerned in passivity?

COLIN G. FINK: Yes, indeed. Take the case of aluminum metal; we know so little about its film. Dr. Bancroft refers to a case of amalgamation and how the metal all goes to pieces; he knows that the thing does occur, but he does not know why it occurs.

E. A. RICHARDSON[8] (*Communicated*): While Dr. Watts' conclusion that "to increase the resistance to corrosion of any metal there should be alloyed with it another metal which is more resistant to corrosion and which forms a solid solution with the metal whose resistance to corrosion it is desired to enhance," may be true in many cases, yet in general the problem of corrosion resistance is not so easily solved as the above statement might infer.

For instance, the following examples are contrary to Dr. Watts' conclusion: Silicon forms a solid solution with iron and is also more resistant to atmospheric corrosion, yet when alloyed with commercially pure iron, at least up to 4.5 percent, materially decreases its resistance to atmospheric corrosion. The same is true of arsenic and tin when alloyed with commercially pure iron and exposed to atmospheric corrosion.

It is interesting to note that the three elements named above all increase the grain size of iron, yet Dr. Watts' conclusion makes no mention of grain size. While his conclusion applies in a general way to corrosion problems, it does not apply rigidly to all cases.

D. M. STRICKLAND (*Communicated*): Mr. Watts has presented in this paper many thoughts which should be considered

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[7] Chief Chemist, Swift & Co., Chicago, Ill.

[8] Chemist, National Lamp Works of General Electric Co., Cleveland, Ohio.

when preparing corrosion-resisting alloys. Certain of his conclusions, however, are open to question. I take exception to his theory that increased corrosion resistance properties are added to a metal when alloyed in solid solution with a more resistant metal. He uses as proof for this assertion, results obtained when copper steel is immersed in normal sulphuric acid. This conclusion does not hold true for all types of metals and for all conditions of corrosion. Experiments in which we also used copper steel fail to verify this conclusion. For example, use another acid reaction. Metallic copper is almost insoluble in concentrated hydrochloric acid. One would assume from Mr. Watts' statement that iron, which we find to dissolve seven times as rapidly as metallic copper, would be more resistant if alloyed with copper. Dr. Cushman[9] has shown that this is not the case. We have conducted experiments using concentrated (38 percent) hydrochloric acid, in which copper iron containing 0.20 percent copper lost five times as much weight as pure iron, while copper steel lost ten times more than pure iron.

We have conducted experiments which show that the weight loss of copper iron is eight times the weight loss of pure iron when test pieces are subjected to the action of concentrated nitric acid. Metallic copper dissolves in this acid very rapidly, a 26-gauge sheet 2 x 3 inches dissolves in 2 minutes.

Metallic copper is but slightly attacked when immersed in a solution of aluminum sulphate. According to the author, copper steel should be more resistant under such test conditions than pure iron. Such is not the case. We have repeatedly obtained results which conclusively establish the marked resistivity of pure iron over copper iron, and copper steel when immersed in aluminum sulphate solutions.

Metallic copper loses 50 to 100 times as much weight as iron when both are subjected to the action of concentrated ammonia. Perhaps Mr. Watts believes that in this instance, since copper is the less resistant, the more pure iron you add to the copper the more resistant it becomes, and as the iron content increases and the copper decreases you approach a more and more resistant

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[9] Anomalies Encountered in a Study of Immersion Tests of Iron and Steel. A. S. Cushman and G. W. Coggeshall, Am. Electrochem. Soc., 1921, 39, 81.

alloy. We are able to substantiate such a belief, as our experiments have shown that copper steel and irons lost 3 to 4 times as much weight as pure iron when test pieces were subjected to such alkaline condition.

Mr. Watts bases his claim on a single experiment, and only supports his assertion by the results obtained on the action of copper steel when immersed in sulphuric acid. I have shown that his chosen alloy, copper steel, does not in all instances yield corrosion results which verify his own conclusion. The author presents no constructive experimental data concerning the corrosion resistance of aluminum steel alloys, nickel steel alloys, or chromium steel alloys. Since conflicting and contradictory results are obtained using copper steel, no doubt it will be found that other alloys do not conform to the author's theory.

Obviously, Mr. Watts' conclusion is too broad and is not adequately supported by investigational data.

O. P. WATTS (*Communicated*): As indicated by its title, the paper under discussion is an attempt to state general principles to serve as a guide in the selection of elements to be alloyed with a given metal for the purpose of producing a corrosion-resisting alloy. The principles stated are based, not on the author's own experiments, but on a consideration of the constitution of the more important corrosion-resisting alloys now in use. The author's view of the importance of the solid solution in alloying to resist corrosion originated several years ago in the attempt to find for his own satisfaction an explanation of the resistance to corrosion imparted to iron by the addition of copper or nickel, electro-negative metals which might, therefore, be expected to accelerate rather than retard corrosion. At that time the number of resistant alloys which were known to be solid solutions were too few to justify the presentation of this view to the public. Even now its acceptance is perhaps a matter of faith rather than evidence, but the writer believes that there are just as exact and definite principles underlying the composition and constitution of alloys resistant to corrosion as hold in any other field of chemical action, and for want of anything better the above views are presented as a working hypothesis.

The photograph concerning which Mr. Rawdon inquires is of a sample of stainless steel received from the American Stainless Steel Co., and was said to contain about 13 percent of chromium and 0.3 percent of carbon. No mention was made of nickel, and the writer has made no analysis of it. If it were a nickel instead of a chromium steel it would have to contain 50 percent or more of nickel to have withstood a certain corrosion test to which this sample was subjected.

Tests On A Brady B. T. U. Indicator

by

O. L. KOWALKE

of

University of Wisconsin, Madison, Wis.

Presented at

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of the Wisconsin Gas Association

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TESTS ON A BRADY B. T. U. INDICATOR

By O. L. Kowalke

About a year ago when the Brady B.T. U. Indicator was offered for sale in Wisconsin, requests for information concerning this device came to the Chemical Engineering Department from various sources. Tests were therefore made to determine, (1) how accurately the heating value of manufactured gas could be measured, (2) how to operate the instrument most effectively. The results of these tests are now submitted to this association. During the progress of the work the manufacturers of the Indicator were kept informed as to the results obtained and were also invited to make suggestions as to the best methods for operation.

The data presented were obtained by Messrs. G. H. Head and A. C. Vobach, seniors in Chemical Engineering.

Theory of Brady B. T. U. Indicator.

"The Brady B. T. U. Indicator is based on the discovery that there is a simple linear relation between the heating value of gases and the amount of primary air necessary to just cause the yellow tip to disappear from the center of a Bunsen burner flame. The heating value of hydrocarbons in general is very closely proportional to the amount of oxygen necessary for complete combustion. Hence if the air necessary for complete combustion were measured it would be a means of determining the heating value of these compounds."*

Within a glass cylindrical tube a truncated cone shaped brass chamber is mounted with the largest end at the bottom. The gas under test is conducted into the brass cone shaped chamber; the air for combustion is in the annular space between the glass tube and the brass gas chamber. Water from a movable reservoir may enter the gas and air chambers simultaneously and force the gas and air out through a mixing chamber into a burner.

Thus as the water rises in the glass tube the ratio of air to gas is increased since the gas chamber tapers towards the top. When the gas-air mixture is first lighted the flame is yellow, but as the supply of air becomes greater, as the water level rises, the yellow decreases and a blue inner cone

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*U. G. I. Contracting Co. Circular.

develops. When the yellow tip has disappeared and the top of the inner blue cone has formed a definite arch the water flowing into the gas and air chambers from the reservoir is shut off. Now the heating value can be read off on the scale attached to the side of the glass cylinder, by noting the level of the water inside.

Methods of Testing.

Standard Testing, Equipment, and Methods. A Sargent continous flow gas calorimeter (Junkers type) equipped with calibrated thermometers was used. The water supply was maintained at room temperature. The gas under test was drawn from a 60 cu. ft. holder and passed through a three liter bottle filled with wet excelsior to insure saturation. Thence the gas passed through an American Meter Company wet test meter passing 0.1 cu. ft. per revolution, then to a bell type of pressure regulator and finally to the burner. The meter was calibrated frequently against a standard one-half cubic foot proving bottle.

In the operation of the Sargent calorimeter, the gas flow was maintained at the rate of seven cu. ft. per hour; the water supply entering the calorimeter was at room temperature and the flow regulated so that a rise of about 8 degrees C. (14.4 degrees F.) was obtained; the damper was set to give the highest outlet temperature for the water; the flame was adjusted so that just a tinge of yellow appeared at the tip. For each test 0.2 cu. ft. gas was burned. This water was weighed on a scale sensitive to 0.01 of a pound.

In computing the results, corrections were made for barometer in the regular way and also for humidity of the air as described in Bureau of Standard Circulars No. 36. All tests were made in duplicate by the operators independently and an agreement within 3 B. T. U. was required.

(b). Brady B. T. U. Indicator Instalation and operation. The Brady Indicator was assembled as described in the directions furnished with the instrument. It was placed in a wooden box, of suitable size, painted a dull black on the inside and provided with an opening in the top for the escape of products of combustion. The front of the box was partially closed with a black cloth hung loosely from the top. To observe the flame an opening about 3 inches by 4 inches was provided; to permit the shutting off of water and the lighting of the burner a larger opening was left in the lower right-hand corner. This enclosure prevented the interference of air currents with the steady burning of the flame and enable the observer to note the change from a yellow tip to a definite arch on the blue cone with greater precision;

it also prevented the observer from watching the water level as it rose in the glass tube and to shut off the water at the same point. A shelf on the outside of the box was so placed that the bottom of the water reservoir was on a level with the top of the burner.

The Brady Indicator was operated according to the instructions furnished. It was not clear at first just what flame characteristic should determine the point of shut-off and some experience had to be gained. Mr. Brady* in calibrating disregards the yellow tip entirely and goes by the appearance of the tip of the blue cone. "When this becomes sufficiently distinct to see a blue line arching over the tip of this inner cone the water should be stopped flowing."

In making observations on the Brady two operators worked independently each making five test and these were then averaged. The observers were able to check each other within about four B. T. U. In all comparison tests of the Brady with the Sargent, gas was taken from a 60 cubic foot holder and the lines thoroughly purged.

Results of Tests.

The calibration curve furnished with the Indicator directed that the displacement of gas and air from the instrument between the marks 430 B. T. U. and 545 B. T. U. on the scale should take place in 14 seconds. When operated according to these directions the following results were obtained.

	Brady	**Sargent**	
	578 B. T. U.	521 B. T. U.	
	581 "	518 "	
	558 "	551 "	
	550 "	527 "	
average	567 "	530 "	average difference 37 B. T. U.

Next a series of tests were made in which the displacement of air and gas was made at slower rates. The purpose of this being to determine what was the proper rate for this particular instrument.

The data were plotted on coordinate paper showing observed B. T. U. on the Brady as ordinates and time of displacement of air and gas as abscissae. The graphs had the same general shape, but did not arrange themselves in the order of correct heating value. At the high rates of displacement of gas and air the B. T. U. reading on the Brady

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*Private communication.

were all higher than on the Sargent flow calorimeter, and at the slow rates of displacement the Brady indications were lower than the Sargent.

The data in the table below were taken from the graphs mentioned above and show the difference between the Brady B. T. U. and the flow calorimeter B. T. U. Thus when operated at a rate of 14 seconds the Brady in one case reads "+ 59" or 59 B. T. U. too high. It will be seen that the algebraic summation of the differences above and below the correct value is zero in the column for the rate of 35 seconds. displacement in the Brady. For all test thereafter the Brady was operated at a rate of 35 seconds.

Date	B. T. U. on Sargent Flow Calorimeter	Difference between Brady and Sargent		
		at 14 sec.	at 30 sec.	at 35 sec.
3-21-21	521	+59	+27	+19
4- 5-21	527	+23	−12	−19
4- 6-21	551	+7	−23	—30
4- 8-21	518	+62	+21	+11
4-12-21	548	+52	+17	+10
5-12-21	519	....	+21	+11
5-24-21	562	....	+12	−2
			+64	0

algebraic sum

It now remained to determine whether the rate of 35 seconds for displacement of gas and air would give correct indications over a wide range of heating values. The 60 cu. feet holder was filled from the city mains and the sample thoroughly mixed. Simultaneous tests were made on this sample with the Brady and the Sargent flow calorimeters. Call this test (a). Then to the gas remaining in the holder from test (a) there was added city gas saturated with benzol until the holder was again filled. This second sample was again tested on the Brady and the Sargent as before, and the result labeled test (b). To the gas remaining in the holder from test (b), gas from the mains saturated with benzol was again added until the holder was filled. This sample was tested as before and the results called test (c). For test (d) a fresh sample of gas was taken from the mains into the holder. For tests (e) the gas remaining in the holder from test (d) was diluted with carbon dioxide. For test (f) the residue from test (e) was further diluted with carban dioxide.

Test	Sargent B. T. U.	Brady B. T. U.	Variation	Remarks
(a)	527	525	− 2.0	City gas
(b)	559	543	−16.0	Enriched by benzol.
(c)	570	552	−18.0	Enriched by benzol
(d)	552	541	−11.0	City gas
(e)	483	504	+21.0	Diluted by carbon dioxide
(f)	446	484	+38.0	Diluted by carbon dioxide

Thus it appears that the Brady has the tendency to read too low when the gas becomes richer and reads too high when the heating value drops from the point when the instrument was standardized. The Brady B. T. U. Indicator was never meant as an instrument of precision,* but the results obtained in these test show that after being properly calibrated on a certain quality of gas the indications are within reasonable limits of accuracy.

There is a linear relation between the heating values of hydrocarbons and the oxygen required for complete combustion.

$$\text{Thus:}\ -\frac{\text{Oxygen for } CH_4}{\text{Oxygen for } C_2H_6} = \text{(approximately)}\ \frac{\text{Heating value } CH_4}{\text{Heating value } C_2H_6}$$

If methane is taken as the basis and calculations made for other hydrocarbons in the above manner the following are obtained:—

Gas	Oxygen required	Correct Heating Value	Calculated Heating Value	Difference
CH_4	2.0 mol.	1009 B. T. U.	1009 B. T. U.	....
C_2H_4	3.0 mol.	1588 B. T. U.	1513 B. T. U.	−75
C_2H_6	3.5 mol.	1764 B. T. U.	1765 B. T. U.	+ 1
C_6H_6	7.5 mol.	3807 B. T. U.	3780 B. T. U.	−27

The agreement between the calculated and the observed values is seen to be good indeed. But when carbon monoxide and hydrogen are considered in a similar manner using methane as a basis, the relation between oxygen required and heating value is not a simple proportion.

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*Proc. Tech. Section Am. Gas Assoc. 1919.

Gas	Oxygen required	Correct B. T. U.	Calculated B. T. U.	Difference
CO	0.5 mol.	344	252	−92
H_2	0.5	348	252	−96

The presence of incombustibles like carbon dioxide and nitrogen will also affect the linear relation.

From the tests here presented, it appears that diluents such as carbon dioxide and nitrogen and combustibles like hydrogen and carbon monoxide have a marked effect on the indications of the instrument. The instrument will give reasonable approximations when calibrated on a gas similar in heating value and composition to that which is required to be tested.

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On the Removal of Naphthalene from Manufactured Gas

by

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ON THE REMOVAL OF NAPHTHALENE FROM *MANUFACTURED* GAS

By O. L. Kowalke and A. W. Pesch

In compliance with the suggestion from the Educational Committee of the Wisconsin Gas Association, a report is hereby submitted of a study and compilation of published information on the removal of naphthalene from manufactured gas. The report covers the work done during the current year under the grant of the Fellowship established by the Association at the University of Wisconsin.

The recent rather general revisions of gas standards from the high calorific value of about 600 B. t. u. per cu. ft. to about 520 B. t. u. per cubic foot and the abolition of the candle-power requirements have given rise to new conditions. The service to the consumer is improved. Higher temperature of distillation are possible and thereby increasing the yield of gas per unit of coal or oil carbonized, but the contest of condensible hydrocarbon vapors may be decreased. Reductions of the content of condensible hydrocarbons will, in general, leave dangerous amounts of naphthalene in the gas sent into the distribution system.

Naphthalene is a white solid having a melting temperature of 176.9 deg. F. and a boiling temperature of 424.4 deg. F. It crystalizes in large thin plates and for that reason a relatively small amount can easily stop the flow of gas in a main or service pipe. The vapor tension is such that one cubic foot of air at 95 deg. F. can carry 61.16 grains of naphthalene, at 50 deg. F. it carries 6.66 grains, and at 32 deg. F. 1.97 grains. Thus when the temperature of air falls below that temperature at which it is saturated with naphthalene, crystals will be desposited. When the temperature of the air is again raised some of the naphthalene may be evaporated and carried forward. Manufactured gas will carry more naphthalene than air owing to the solvent action of the condensible hyprocarbons present. Cooling such gas below the saturation temperature results in the condensation of both hydrocarbons and napthalene in a liquid form.

To prevent naphthalene *from being deposited in the* mains and services several means may be employed:—

(a) By *preventing its formation during the* process of *carbonization.*

(b) By separating it from the gas in the condensing and cooling apparatus.
(c) By washing the gas with a solvent, and
(d) By adding a solvent to the purified gas.

(a) Preventing the Formation of Naphthalene During Carbonization

Much has been published regarding the proper temperatures for carbonization to avoid naphthalene, but all such data apply to low temperature conditions and are not readily applicable to present practice. An extended discussion of this point is therefore not advisable. It has been claimed that heavy charges of coal in horizontal retorts prevent the formation of excessive amounts of naphthalene; that in vertical retorts, because the gas passes through the center and cooler portion of the charge, a smaller amount of naphthalene is made; that in carburetted water gas plants owing to the higher content of heavy hydrocarbon vapors naphthalene troubles are not so serious.

(b) Removal of Naphthalene by Cooling and Condensation

Whether the gas laden with condensible and tar vapors shall be cooled rapidly or slowly is a question on which gas engineers are not agreed.

Rapid cooling of gas results in the formation of a large number of minute droplets or "fog" of liquid hydrocarbons held in suspension in the gas. Such a fine suspension or "fog" may be effective in dissolving naphthalene but it means that the gags must have a low velocity and be kept in contact with the "fog" for a long time. It has also been argued that rapid cooling causes too great a loss of the "illuminants" from the gas.

Slow cooling provides more opportunity for the gas, tar, and naphthalene to come to the equilibrim condition. During the slow rise of gas in a suitable condenser, the tar droplets have a chance to increase in size and fall downward. Thus, it is claimed, there is a slowly descending rain of tar droplets which effectively washes out both tar and naphthalene. The fine mist of tar must be completely removed from the gas or else the naphthalene is carried forward into the distribution system.

Much data has been published to show that condensation alone cannot remove naphthalene sufficiently complete so that no deposits will be found in cooler portions of the system. The tar "fog" and hydrocarbon vapors may carry naphthalene forward beyond the scrubbers. Tar, however, in the condensers, takes out much of the naphthalene from the raw gas with comparatively little cost. In many instances the naphthalene content is so reduced that no trouble is experienced through further cooling.

(c) Removal of Naphthalene by Washing with Solvents

To insure the removal of naphthalene to such an extent that cooling the gas to any temperature, however low, will not result in any condensation, a system of washing with a solvent is usually necessary. Among the solvents which have been used for this purpose are:—anthracene oil, creosote oil, lighter tar oils, petroleum fractions such as "gas oil", and tars.

1. **Anthracene Oil.** Anthracene oil is obtained from coal tar and is that fraction distilled above temperature of 270 deg. C. or 518 deg. F. Because the boiling point is 94 degrees higher than that of naphthalene anthracene oil contains practically no naphthalene. Pannertz[1] claims that a good anthracene oil should yield, on a distillation test, 0—120°C. yield 3—4%; from 120°—200°C. not over 3%; from 200° — 270° not over 4 to 8%. The oil should not show any deposit after standing for one half hour at 23 deg. F. The absorbing power of anthracene is determined by passing gas saturated with naphthalene at the rate of about one cubic foot per hour through about 20 c. c. of oil. A good oil should reduce the naphthalene content to about 1.2 grains per 100 cubic feet.

A rotary scrubber of the "Standard" type with four bays is recommended with oil in each of the bays. It is well to remove the tar before scrubbing. Pannertz reports that he reduced the naphthalene in gas to about 1.6 grains per 100 cu. ft. by using a "Standard" washer, and about 0.12 pounds of oil per 1000 cu. ft. gas washed.

Washing with anthracene oil also removes some of the benzol and toluol. An oil of initial specific gravity of 1.111 will have a density of about 1.06 when no longer useful, due to the absorption benzol and toluol.

Bueb[2] advises the addition of 4 percent of benzol to anthracene oil to prevent the absorption of "illuminants". Oil so treated will absorb 25 per cent of its weight in naphthalene when used in a rotary washer consisting of three bags placed behind the P. & A. tar extractor.

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[1] Jnl. Gasbel. **48** : 921 (1905) : **50** : 568 (1907); **54** : 912, 1004 (1911); **56**: 509 (1913).

[2] Jnl. Gaslight **76** : 699 (1900); Jnl. Gasbel. **44** : 15 (1901).

Barth[1] points out that for naphthalene washing only 0.25 to 0.50 pounds of oil are used per 1000 cu. ft. of gas while for stripping benzol 25 to 44 pounds of oil per 1000 cu. ft. gas are needed.

Bunte[2] claims that naphthalene may exist in the gas in the form of fine crystals, especially, when the gas has been cooled rapidly. In such case washing at 77 to 86 deg. F. should be carried on in a rotary washer of several chambers.

Anthracene oil is not available at reasonable prices in this country. Hard pitch is the by-product in distilling tar for anthracene and since the market for hard pitch is limited, the tar distiller runs the end product to a soft pitch. In Europe hard pitch finds a ready market in the fuel briquetting industry.

2. **Creosote Oil.** Creosote oil has been used extensively for stripping benzol and toluol from gas and it is more easily obtained in this country than the anthracene oil. Naphthalene troubles have been experienced in plants where creosote oil was used for stripping benzol because in time the oil became saturated with naphthalene. In the process of removing the benzol and toluol from the wash oil, the temperature of distillation did not get high enough to drive out the naphthalene and through repeated use the wash oil became saturated.

Leather[3] used a tower scrubber wherein 10,000,000 cu. ft. of gas was treated with 200 gallons of creosote oil, the oil being recirculated. As soon as the oil was saturated, naphthalene troubles began again. Distillation with steam removed the naphthalene and made the oil fresh for further use.

Branson[4] reports on a plant where rotary washers were used with creosote oil. The light oils and naphthalene were distilled from the saturated oil, thus making the creosote oil available again.

Copp[5] reports a similar method and claims that naphthalene was completely removed and that a better quality of benzol was obtained.

3. **Lighter Tar Oils.** These oils do not dissolve the "illuminants" from the gas so readily as anthracene and creosote oils. Should the lighter tar oils be fairly rich in benzol, they may even enrich the gas while at the same time removing naphthalene. Gas so enriched will not deposit naphthalene in the solid state.

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[1] Jnl. Gasbel. **49** : 495.

[2] Jnl. Gasbel. **63** : 181 (1920).

[3] Trans. Inst. Gas Eng. (1899), P. 113.

[4] Gas Wld. **73** : 272 (1920).

[5] Gas Age **69** : 265 (1918).

At Derby, England, an oil called "Derby Solvene"[1] was used in two bags of a "Standard" washer. The oil had the following characteristics:— sp. gr., 0.908; distillation test — up to 130 deg. C. — 4.0%, from 130 — 150 deg. C. — 15%, from 150 — 170 deg. C — 48.5%, from 170 — 190 deg. C. — 23%, from 190 — 200 deg. C. — 5.0% above 200° C. — 4.0%. The oil contained a fair amount of xylenes and oils between toluol and creosote oil but it was not so volatile as benzol. The quantity of oil used was 0.1 gallon per ton of coal carbonized and the naphthalene was reduced to 2 grains per 100 cu. ft.

Bayer[2] used an oil having benzol 0.4%, light oil (100 — 180° C.) — 67. 6%, middle oil (180 — 230° C.) — 25. 0%, naphthalene 3.9%, and heavy oil 3.1%. The naphthalene was reduced by using this oil, but the mantles in some street lamps became blackened.

4. **Petroleum Oils.** The fraction from crude petroleum called "gas oil" has been used successfully as a solvent for naphthalene. In an oil gas plant in California[3] naphthalene trouble was overcome by washing the gas with fuel oil; the heating value and candle power were not affected. Calkins and Moorehouse[4] report the use of Indian Territory gas oil for scrubbing carburetted water gas at Galveston. They use the oil in a washer and found that it absorbed twice as much naphthalene as their water gas tar. Bernauer[5] used gas oil successfully and found that the use of the naphthlaene laden oil subsequently in the carbureter of a water gas machine only increased the naphthalene in the gas by a very small amount.

5. **Tars.** Water gas tar has been used most frequently as a solvent for naphthalene, but tars from oil gas, vertical retorts and specially collected coal gas tar have also been employed. Tars have been used both hot and cold with satisfactory results, provided the contents of water and naphthalene were low to begin with. The Committee on Naphthalene of the British Institution of Gas Engineers[6] points out that there must be an intimate contact between tar and gas for a sufficiently long time. When using hot tar there is less chance for absorption of light oils, a tendency for the tar to give up some "illuminants", and a higher degree of solubility of naphthalene. The use of cold

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[1] Jnl. Gaslight. **105** : 783 (1909).

[2] Jnl. Gasbel. **54** : 496 (1911).

[3] Am. Gas Lt. Jnl. **95** : 275.

[4] Am. Gas. Inst. Proc. **4** : 727.

[5] Gas Wld. **73** : 273 (1920).

[6] Trans. Inst. Gas. Eng. (1917) p. 228.

tar has the advantage that the vapor tension of naphthalene is kept down and thus it is claimed that less naphthalene gets back into the gas.

Fletcher[1] reports that naphthalene has been removed by circulating water gas tar in the hydraulic main in a steady stream. At the Caryl Plant in Liverpool, England, he used the three chambers on the inlet side of a "Standard" washer. The tar was run from a tank through a special regulating cock at the rate of 50 gallons per day for a make of gas of 800,000 cu. ft. With this ratio of tar to gas he was able to reduce the naphthalene from 9.5 grains per 100 cu. ft. in the raw gas to 3.4 grains per 100 cu. ft. By doubling the amount of tar and circulating it two or three times instead of once in the washer the naphthalene was reduced to between 3.5 grains and a trace per 100 cu. ft. gas. A good water gas tar will not eliminate naphthalene altogether, but makes the gas much easier to handle.

Wyant[2] made a naphthalene scrubber from an old tubular condenser by removing the tubes and filling the shell with wooden grids. The shell was 6 ft. 6 in. diameter by 20 ft. high. A collecting tank was provided to catch the tar from seal in the water gas plant and also from the hot tar scrubbers. The tar at a temperature of 110 deg. F. was circulated by a pump at the rate of 8 gallons per 1000 cu. ft. of gas. The gas from the retorts was passed in succession through primary condensers, the exhauster, immersion washers, the hot tar scrubber, and the secondary condensers.

The Committee on Naphthalene, American Gas Institute[3] described three water gas tar washing plants for naphthalene. At plant (E) there was used a steel shell 8 ft. diameter by 22 ft. high, containing three layers of grids 4 ft. deep spaced one inch apart. The gas passed upward and the tar downward. The tar was circulated by means of a pump at the rate of 0.14 gallons per 1000 cu. ft. gas, and was removed from the circulating well and renewed before becoming saturated with naphthalene. The temperature employed in the washer was 105 deg. F. Plant (F) used a steel shell 8.5 ft. diameter by 24 ft. high filled with grids made of ½ inch boards spaced ½ inch apart. The temperature of the scrubber was maintained at 118 deg. F. The tar used contained about 7 per cent naphthalene before use and about 25 per cent when it was discarded. It was suggested here that air at 180 deg. F. be blown through the discarded tar to remove the naphthalene and then to

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[1] Gas Jnl. **141** : 248 (1918).

[2] Am. Gas Lt. Jnl. **100** : 261 (1914). Jnl. Gas Light. **126** : 506 (1914).

[3] Proc. Am. Gas Inst. **8** Pt. I : 657 (1913).

conduct the warm air with its charge of naphthalene to the boilers or to the benches. Thus the tar could be used over again. At Plant (I) tar was used at the rate of 0.05 gallons per 1000 cu. ft. gas from inclined retorts and at the rate of 0.072 gallons per 1000 cu. ft. gas from horizontal retorts. The tar, initially, was practically free from naphthalene and when discarded contained 7.75 per cent and 11.29 per cent respectively when used for gas from inclined and horizontal retorts respectively. A rotary washer of the "Standard" type was used and the temperature was kept at about 70 deg. F.

J. A. Brown[1] describes an installation where a scrubber was placed at the outlet of the carbonizing chambers, so arranged that condensed tars and liquors or a mixture thereof could be circulated with a pump. Scrubbing with hot tar resulted in complete absorption of naphthalene and no decrease in heating value. A hot tar scrubber of this type, 4 ft. diameter by 36 ft. high was erected at Peoria, Illinois. Tests now show more naphthalene at outlets from mains than at the works.

Zwarg[2] maintains that using water gas tar alone in a rotary washer will not reduce the naphthalene below 17.5 grains per 100 cu. ft. gas. He recommends the use of water gas tar in the first chamber of the washer only and anthracene oil for the second chamber. The tar is to be discarded when the fraction between 392 — 518 deg. F. after cooling for one hour at room temperature deposits 21 per cent of solid naphthalene.

Mann[3] at Cleveland used 400 gallons of anthracene oil in each of four sections of a Kloenne washer. A new charge of 400 gallons was added every second day to the top section and the others moved down; thus each batch remained in the washer 8 days. The oil absorbed 35 per cent by weight of naphthalene. Owing to the cost of anthracene oil, water gas tar was substituted, and 400 gallons of tar added to the washer each day. About 25,000 cu. ft. of gas were treated per gallon of tar. The washer was used continuously.

d. Removal of Naphthalene By Introducing Solvent Into Purified Gas.

The deposition of naphthalene can be prevented by introducing a hydrocarbon vapor which condenses at the same temperature as naphthalene, and produces a liquid solution of the naphthalene that can be collected in the drips. In small plants where the expense of a washing equipment is

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[1] Am. Gas Jnl. **114** : 271 (1921); Gas Jnl. **154** : 205 (1921).
[2] Jnl. Gasbel. **54** : 837 (1911).
[3] Prog. Age. **23** : 111 (1905).

not feasible; in plants where benzol and toluol are stripped from the gas, but where some naphthalene may still be left; in plants where the gas may have a heating value of 500 B. t. u. or lower and be deficient in condensible hydrocarbons, the introduction of a condensible hydrocarbon at the outlet of the holder or the outlet of the purifier has been found to be a satisfactory means of preventing deposist of naphthalene. The hydrocarbons that have been employed for this purpose are:—slovent and heavy coal tar naphthas, condensates from the compression of oil gas, light petroleum (paraffin) oil such as white spirit, and burning oil or kerosene. The oils have been introduced into the mains as a liquid and allowed to run to the drips, as a finely atomized mist, and as a vapor produced by heating the oils.

A Committee of the British Institution of Gas Engineers[1] reports that at most plants petroleum oils were used which had a fairly high boiling point. Since only a comparatively small portion of these oils can be picked up by the gas through evaporation, it was necessary either to vaporize the oils with heat or to atomize them when putting them into the mains. In case of the more volatile oils, both the Livesey and rotary washers were used.

Because of its cheapness, availability and effectiveness, kerosene was used a great deal.

W. Fletcher[2] describes some installations for introducing the solvent as used in Liverpool, England. One of these consisted of a rectangular cast iron box divided by a horizontal partition. A 4-inch gas inlet and outlet pipe was fitted onto the upper compartment; oil from an overhead tank was fed through a sight feed into the upper chamber; steam at 15 pounds per sq. in. was fed in at the bottom. The oil was thus vaporized and passed with the gas and steam into the distribution system. About 8.5 per cent of the oil was vaporized and the remainder was allowed to run to a seal pot. The second installation consisted of a steel shell 2 ft. 2 in. diameter by 3 ft. 11 in. high fitted with 6 inch gas connections at the bottom and top for inlet and outlet respectively. A closed copper heating coil 90 feet long was mounted inside and fed with steam at 40 pounds per sq. in. The oil was fed in at the top of the vaporizer and allowed to drop on the hot copper coil; the unvaporized portion of the oil drained out through a siphon. Here 25 gallons of oil were used to treat 2¼ million cubic feet of gas per day with a residue of 1.5 gallons per day.

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[1] Trans. Inst. Gas Eng. (1917) p. 228; Gas Jnl. **137** : 551—4 (1917).

[2] Gas Jnl. **141** : 249 (1918).

Glover[1] recommends that a burning oil of 0.78 — 0.82 specific gravity be used and that it should vaporize readily at 300 — 320 deg. F. The oil should be introduced at the outlet of the purifiers or at the inlet of the holder and it was claimed that 25 gallons would treat one million cublic feet daily under ordinary conditions.

Vince[2] at Minehead, England, used a gas heated vaporizer capable of vaporizing 0.75 gallons of oil per hour with 60 cu. ft. of gas. The oil vaporized was 3 gallons per wee for an output of 500,000 cu. ft.

Parkinson[3] claims that 15 gallons paraffin burning oi (kerosene) are sufficient to deal with one million cu. ft gas containing 12 grains naphthalene per 100 cu. ft.

Davidson[4] believes that introducing a solvent into the mains is the cheapest way to control naphthalene deposits The amount of solvent necessary will depend on the nature of the gas, but that 10 gallons of solvent per million cubic feet of gas is sufficient. The solvent should be one, the great bulk of which, distills over between 266 and 392 deg. F.

The Committee[5] from the British Institution of Gas Engineers reports that about 10 per cent of the gas is by-passed through the vaporizer and then mixed again with the main stream. Mixing of the two streams should be made promptly in order to produce as fine a mist as possible

Sharp bends should be avoided at the point where the mixing occurs.

Spraying or "atomizing" the oil into the main is another method of introducing the solvent. According to the report to the British Institution of Gas Engineers[5] in some cases the oil is atomized with compressed gas and in other cases the oil is pumped under high pressure through a jet. It is essential that the spray be very fine in order to carry far, and that sharp bend in the pipe immediately ahead of the spray be avoided.

Botley[6] atomizes the oil with compressed gas at 25 pounds per sq. in. He prefers a refined petroleum oil not exceeding 0.80 specific gravity and claims that the mist is carried to the end of the system.

Kennedy[7] at Colorado Springs dropped gasoline into the mains by means of a device consisting of a sheet iron tank

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[1] Jnl. Gaslight **132** : 582 (1915).

[2] Jnl. Gaslight **136** : 540 (1916).

[3] Gas Jnl. **151** : 616 (1920).

[4] Trans. Inst. Gas Eng. (1913) p. 177.

[5] Trans. Inst. Gas Eng. (1917) p. 228; Gas Jnl. **137** : 551 (1917).

[6] Jnl. Gaslight **72** : 1093 (1898) Gas Wld. **72** : 283, 301 (1920).

[7] Gas Age **32** : 310 (1913).

fitted with a regulating valve and a pipe that entered the main ahead of the governor. Gasoline was fed at the rate of 90 drops per minute and during the winter of 1913 he used 188 gallons at a cost of $33.84.

APPENDIX

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Note:—For a bibliography of articles prior to 1904, see A. H. White and S. Ball, Am. Gas Light. Jnl. 81 : 605, (1904) Jnl. Gaslight **88** : 326.

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On the Removal of Sulphur Compounds from Manufactured Gas by Means of Sodium Hypochlorite

by

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ON THE REMOVAL OF SULPHUR COMPOUNDS FROM MANUFACTURED GAS BY MEANS OF SODIUM HYPOCHLORITE

By H. R. Broker and O. L. Kowalke

The Executive Committee of the Wisconsin Gas Association two years ago suggested the problem of the removal of sulphur compounds from manufactured gas for study under the grant of the Fellowship established at the University. A report on the preliminary work was made by E. C. Brenner at the meeting in March 1921. This report covers the work done by H. R. Broker in continuation under the grant.

It seemed worth while to repeat some of the earlier experiments on a larger scale to determine whether the results could be duplicated and whether the organic sulphur compounds could be removed more completely. The preliminary tests by Brenner showed that hydrogen sulphide was completely removed but that carbon disulphide was only partially taken out. It was believed that carbon disulphide comprised the greater part of the organic sulphur compounds, although traces of thiophenes, thioethers, and isothicyanates have been found.*

Experimental.

The general procedure in making a determination was as follows: The total sulphur in the gas as taken from the storage holder was determined by means of the modified Dreschmidt apparatus as recommended in Circular No. 48 of the U. S. Bureau of Standards. Simultaneously, in a duplicate apparatus, the total sulphur was determined on gas from the same holder but after it had been passed through the tower containing the hypochlorite solution.

The difference in the results of the tests for total sulphur on the gas directly from the holder and on that after it had passed the hypochlorite tower showed the amount of total sulphur removed.

The hydrogen sulphide was determined on a separate sample from the storage holder by bubbling the gas through a 12-bulb absorption train containing ammoniacal cadmium chloride wherein the sulphur in the hydrogen sulphide was precipitated as cadmium sulphide.

The difference between the total sulphur on the original sample and the sulphur as hydrogen sulphide is the sulphur

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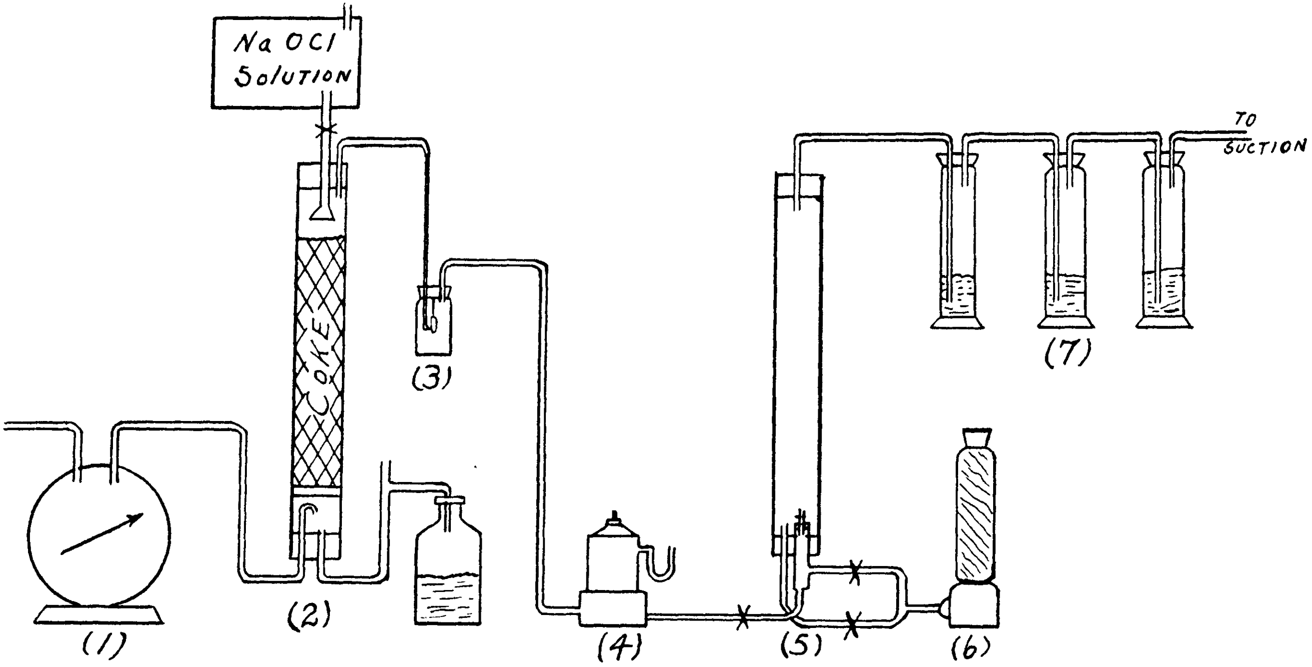
*Powell, A. R. Bur. Mines Rept. No. 196-H24.



1 WET GAS METER
2. PURIFYING TOWER
3 LEAD ACETATE TEST PAPER
4. PRESSURE REGULATOR

5
6 } BUR. STAND. TOTAL
7 SULPHUR APPARATUS

present in the form of organic sulphur; the difference between the total sulphur in the treated gas and sulphur as organic sulphur in the original gas is the amount of organic sulphur removed. No evidence of hydrogen sulphide was obtained by means of lead acetate paper in a test bottle at the outlet of the hypochlorite tower.

The procedure in removing sulphur compounds was substantially as follows. As shown in the accompanying diagram the gas from the holder passed a wet test meter then into the hypochlorite tower and finally into the sulphur determination apparatus.

The hypochlorite tower was a glass tube 2 inches in diameter and 44 inches long packed for a length of 36 inches with evenly sized metallurgical coke about one half inch in diameter. The hypochlorite solution was allowed to flow from an overhead reservoir steadily down over the coke filling in the tower. The gas under test flowed upwards through wetted coke filling.

Results.

1. **The Removal of Organic Sulphur.** The results of tests on the removal of organic sulphur compounds are given in the following table:

Run number	I	II	III
Total sulphur in raw gas Grains / 100 cu. ft.	7.0	6.1	5.2
Total sulphur as hydrogen sulphide Grains / 100 cu. ft.	2.4	1.3	1.5
Total sulphur as organic sulphur Grains / 100 cu. ft.	4.6	4.8	3.7
Total sulphur in purified gas Grains / 100 cu. ft.	1.9	1.6	1.4
Percent of organic sulphur removed by tower	59.0	67.0	62.0
Available chlorine before absorption Grams / Liter	2.2	5.5	4.34
Available chlorine after absorption Grams / Liter	1.0	4.6	3.8
Volume of absorbent Liters	12.0	19.0	18.0
Gas Purified Cubic feet	6.125	10.0	9.20
Rate of passage of gas through tower Cu. feet / Hour	0.756	0.650	0.715

With a smaller tower Brenner secured about 40 percent removal or organic compounds. It is also apparent that a greater amount of sulphur could be removed if the rate of flow of gas were cut down or the tower enlarged. The per cent removal obtained here, 67 percent, is quite satisfactory.

2. **Removal of Illuminants.** From the analysis of the hypochlorite before and after a test, it was found that a greater amount of chlorine was being used than was required for the removal of the sulphur compounds by simple oxidation. A part of the chlorine loss might be due to the action of the hypochlorite on the unsaturated hydrocarbons. It is well known that hypochloraus acid reacts with ethylene to form ethylene chlorhydrin.

$$C_2H_4 + HOClCH_2ClCH_2OH$$

Analyses were therefore made of the gas before and after it had passed through the tower. The following results are typical of what was observed, and it appears that the longer the gas is held in contact with hypochlorite the more of the unsaturated compounds are removed.

Rate of passage	Illuminants Orig. gas (CO$_2$ free	Purified Gas	% Removal of Illuminants
.44 cu. ft. / hr.	12.6%	10.9%	13.5%
.70 ”	12.6%	11.3%	10.3
1.50 ”	10.8	10.4	3.7
3.00 ”	10.8	10.7	0.9

3. **Chlorine and Chlorine Compounds in Purified gas.** In all the tests made thus far it appeared that more chlorine was taken out of the hypochlorite than could be accounted for in the removal of hydrogen sulphide and some carbon disulphide. Gas from the mains was highly charged with carbon disulphide vapors and then passed through the hypochlorite tower. After which the total sulphur was determined. Provision was made to determine the chlorine in the products of combustion in the sulphur testing apparatus in order to learn how much chlorine left the tower.

The results of two representative runs are as follows:

Run Number	I	II
Total sulphur in raw gas Grains / 100 cu. ft.	42.5	152.7
Total sulphur as hydrogen sulphide Grains / 100 cu. ft.	2.5	2.5
Total sulphur as organic sulphur Grain / 100 cu. ft.	40.0	150.2
Total sulphur in purified gas Grains / 100 cu. ft.	30.4	142.8
Volume of gas purified Cubic feet	9.30	8.90
Total hydrogen sulphide removed Grains	2.33	2.23
Total organic sulphur removed Grains	8.93	6.59
Chlorine in purified gas Grains / 100 cu. ft.	250.0	263.0
Available Chlorine before absorption Grams / Liter	3.75	1.5
Available chlorine after absorption Grams / Liter	2.63	0.23
Volume of absorbent Liters	18.0	18.0
Total chlorine used Grains	302.0	343.0
Total chlorine in products of combustion Grains	23.2	21.0
Chlorine required for the removal of H_2S Grains	2.40	2.30
Chlorine required for the removal of CS_2 Grains	(1) 32.92 ** (2) 16.46	24.28 ** 12.14

Note:—(**) The chlorine required for the removal of CS_2 was computed in two ways. (1) assumes a direct oxidation in which 8 molecules of NaOCl are required to oxidize one molecule of CS_2. (2) assumes the chlorination of CS_2 to give CCl_4 and SO_2.

An exact accounting of all the chlorine used cannot be rendered because of the unstable nature of hypochlorite solutions. It is striking, however, that the chlorine carried over with the purified gas approximates that required to convert the carbon disulphide removed into carbontetrachloride according to assumption (2). The percentage of sulphur removed in this gas having a high sulphur content is decidely less than that obtained in the previous runs.

The next problem was to determine the nature of the combination in which the chlorine escaped from the tower with the gas. Carburetted water gas was passed through the tower at the normal rate of 0.75 cubic feet per hour. From the tower this gas was passed through two bottles containing starch iodide solution. The first was alkaline with sodium hyproxide and the second acid with acetic acid. After the passage of two cubic feet of gas no color change had occurred in either bottle, showing the absence of free chlorine. If any hypochoraus acid had been present, the solution of starch iodide acid with acetic acid would have shown its presence. From this test it was concluded that the chlorine was in the form of a fairly stable compound.

In order to eliminate all other possible reactions, it was decided to pass the carbon disulphide through the tower with pure hydrogen, on which the hypochlorite would have no action. Pure hydrogen was allowed to take up CS_2 by passing it over a small amount of the liquid in a bottle, after which the mixture passed through the tower and was burned in the total sulphur apparatus. The products of combustion were passed through a 5% solution of potassimum carbonate. When this solution was acidified and treated with silver nitrate, a heavy precipitate of silver chloride was formed, showing the presence of a considerable quantity of chlorine in the products of combustion.

This same mixture of hydrogen and carbon disulphide after leaving the tower was passed through an aqueous caustic potash solution before being burned in the sulphur testing apparatus. When this solution was acidified no chlorine could be detected with silver nitrate. Thus no free chlorine nor any hydrochloric acid were formed as the hydrogen-carbon disulphide gas mixture passed through the hypochlorite tower. These results therefore point strongly to the fact that carbon disulphide is changed to carbon tetrachloride by the hypochlorite.

Conclusions.

From the foregoing experiments it appears that the major reactions taking place when sulphur compounds are removed from manufactured gas by means of alkaline hypochlorite solutions are as follows:—

(1) The small amount of hydrogen sulphide contained in the gas used was oxidized to water and elemental sulphur, the chlorine of the hypochlorite going to sodium chloride. The elemental sulphur is slowly dissolved in the sodium hydroxide of the alkaline hypochlorite solution.

(2) Alkaline hypochlorite may react with carbon disulphide to some extent to form a carbonate and a sulphate as stated by Ritsema,* but in addition to this reaction, carbon disulphide also reacts with hypochlorite **to form carbon tetrachloride** and possibly a small amount of chloroform.

(3) The carbon dioxide is quite completely removed by the caustic in the hypochlorite solution. Unless the hypochlorite solution is maintained in an alkaline condition, carbon dioxide will liberate hypochloraus acid from the hypochlorite solution.

(4) The unsaturated hydrocarbons of the formula C_nH_{2n} may react with NaOCl by breaking the double bond and forming mono-or dichlor additions compounds.

(5) Hypochlorite will have no action on carbon monoxide, hydrogen, oxygen, or nitrogen in the gas.

(6) The objection to the use of hypochlorites for the removal of organic sulphur compounds from manufactured gas by this method is the introduction of chlorine compounds into the gas. Upon combustion, the chlorine compounds are disseminated into the atmosphere.

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*Ritsema, Chemiker Centralbladt, 1904. i i 1495.

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THE DEZINCIFICATION OF BRASS

BY

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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 non-ferrous 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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[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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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.

Volumes of Gases of Various Heating Values Required to Boil Water in Kettles of Various Sizes

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VOLUMES OF GASES OF VARIOUS HEATING VALUES REQUIRED TO BOIL WATER IN KETTLES OF VARIOUS SIZES

By O. L. Kowalke and L. E. Biemiller

This is a report on some tests made in 1922 by Mr. Biemiller under the Fellowship in Gas Engineering established by the Gas Section of the Wisconsin Utilities Association.

The purpose of the investigation was to determine what would be the amount of gas used to bring a given weight of water to a boil and then maintain the boiling temperature for a period of 20 minutes in kettles of the same material but of different sizes, and using gases of different heating values. The period of twenty minutes was chosen because it approximated the time required to boil potatoes.

Equipment.

The Detroit Jewell gas stove used was donated by the Madison Gas and Electric Company to whom grateful acknowledgment is hereby made. The stove had four burners of which only one was used. That burner was a front top "radial" burner with eight wings having an overall diameter of practically six inches. There were 64 holes in the burner each being the size of a No. 40 drill. The orifice at the outlet of the gas cock on the burner was the size of a No. 34 drill. The top of the grid supporting the kettle was 1½ inches above the top of the burner and all tests were made under these conditions, so that the bottom of the kettle was practically 1½ inches above the burner.

The gas consumed was measured by an American Meter Co. wet test meter of 1/10 cu. ft. per revolution. The meter was calibrated frequently.

The kettles used were of spun aluminum and to each a cover was snugly fitted. A thermometer set in a rubber stopper was inserted through a hole in the cover to indicate the temperature of the water. The dimensions of the kettles are given in the table below and the shapes are shown in Fig. 1.

SIZES OF KETTLES.

	KETTLE NUMBER 1	2	3
Depth, inches	4.5	3.75	2.75
Diameter, inches at top	8.5	6.25	5.75
Diameter, inches at bottom	6.5	4.75	3.75
Pounds water used	2	2	1
Depth of water in kettle in inches	$1\frac{17}{64}''$	$1\frac{59}{64}''$	$1\frac{29}{64}''$

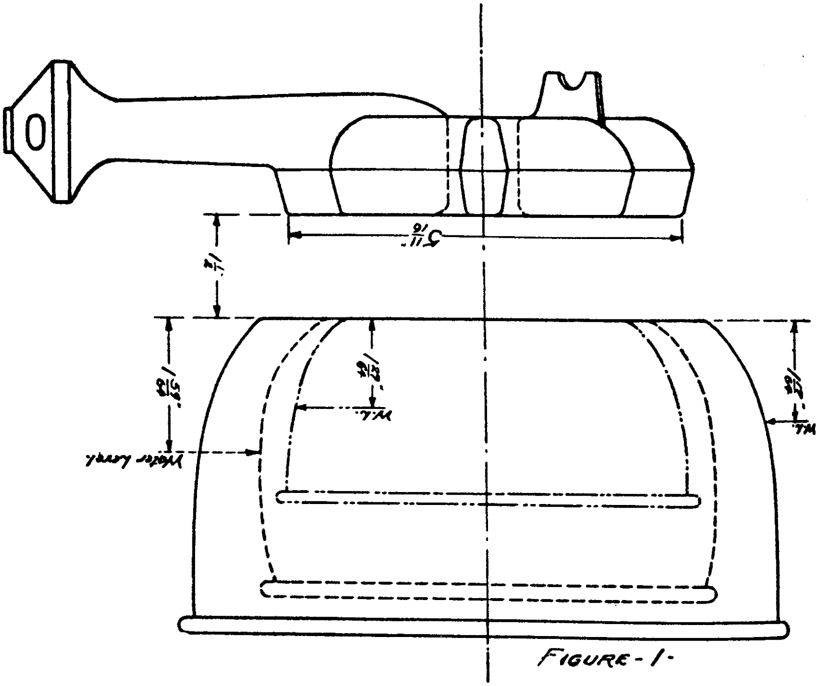


FIGURE-1-

Procedure.

Gases having heating values of 480, 503, 518, 562, and 610 B.t.u. per cu. ft. respectively were made by mixing carburetted water gas with either Blau-gas or hydrogen in a holder of 60 cu. ft. capacity. In each case the heating value was determined with a calorimeter of the Junkers type.

The air supply was adjusted for each of the qualities of gases made so that there was just a faint luminous tip to the flame. The size of the orifice on the cock was not changed and the pressure on the line was kept constant by weighting the holder.

To make a test the following procedure was observed. A known weight of distilled water at 25 deg. Cent. was placed in the kettle under test, the cover put on; the thermometer was then inserted so that the bulb was completely immersed in the water. With the burner cock wide open and the gas lighted, the kettle was placed over the flame and the time noted on a stop watch. When the temperature of the water reached 99 deg. Cent. the time was again noted on the stop watch. At this point the gas was turned down until the flame was of a size sufficient to maintain the water just at boiling. The water was maintained at "at a boil" for 20 minutes, by the watch, during which time the burner would probably have to be turned on or down. Three tests of this character were made for each sample of gas and with each kettle. The volume of gas used was noted when the water had reached 99 deg. Cent. and also when the 20-minute boiling period had elapsed.

From these data it is possible to compute the B. t. u. used to bring the water to boiling, to maintain boiling for 20 minutes, and the sum of both portions. These results are shown in Table I.

TABLE I.

The results are given in the following table, and each value shown here is the average of three determinations.

B. t. u. USED.

B. t. u. of gas used	KETTLE NO. 1			KETTLE NO. 2			KETTLE NO. 3		
	Heat	Boil	Total	Heat	Boil	Total	Heat	Boil	Total
480	1035	698	1733	1063	445	1508	582	393	975
503	1027	731	1758	1033	459	1492	566	394	960
518	1021	728	1749	1017	442	1459	578	431	1009
562	1015	727	1742	1002	491	1493	567	416	983
610	979	703	1682	986	445	1431	570	401	971

CUBIC FEET OF GAS USED.

B. t. u. of gas used	KETTLE NO. 1			KETTLE NO. 2			KETTLE NO. 3		
	Heat	Boil	Total	Heat	Boil	Total	Heat	Boil	Total
480	2.16	1.45	3.61	2.22	.93	3.15	1.21	.82	2.03
503	2.04	1.45	3.49	2.05	.91	2.96	1.13	.78	1.91
518	1.97	1.41	3.38	1.97	.85	2.82	1.12	.83	1.95
562	1.81	1.29	3.10	1.78	.87	2.65	1.01	.74	1.75
610	1.61	1.15	2.76	1.62	.73	2.35	.93	.66	1.59

Heat = period of heating during which water is brought up to boil.
Boil = 20 minute period during which water is kept "just at a boil."
Water used: Kettle No. 1 — 2 pounds.
Kettle No. 2 — 2 pounds.
Kettle No. 3 — 1 pound.

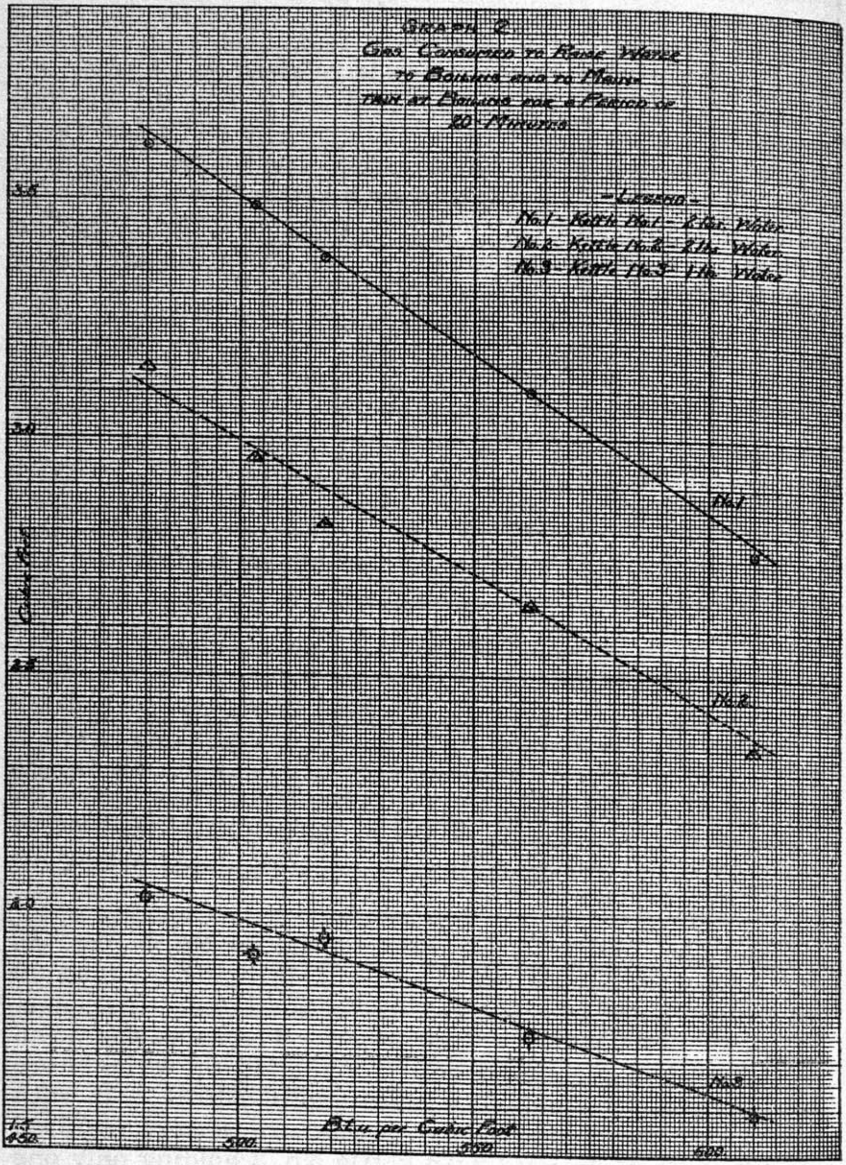
Discussion of Results.

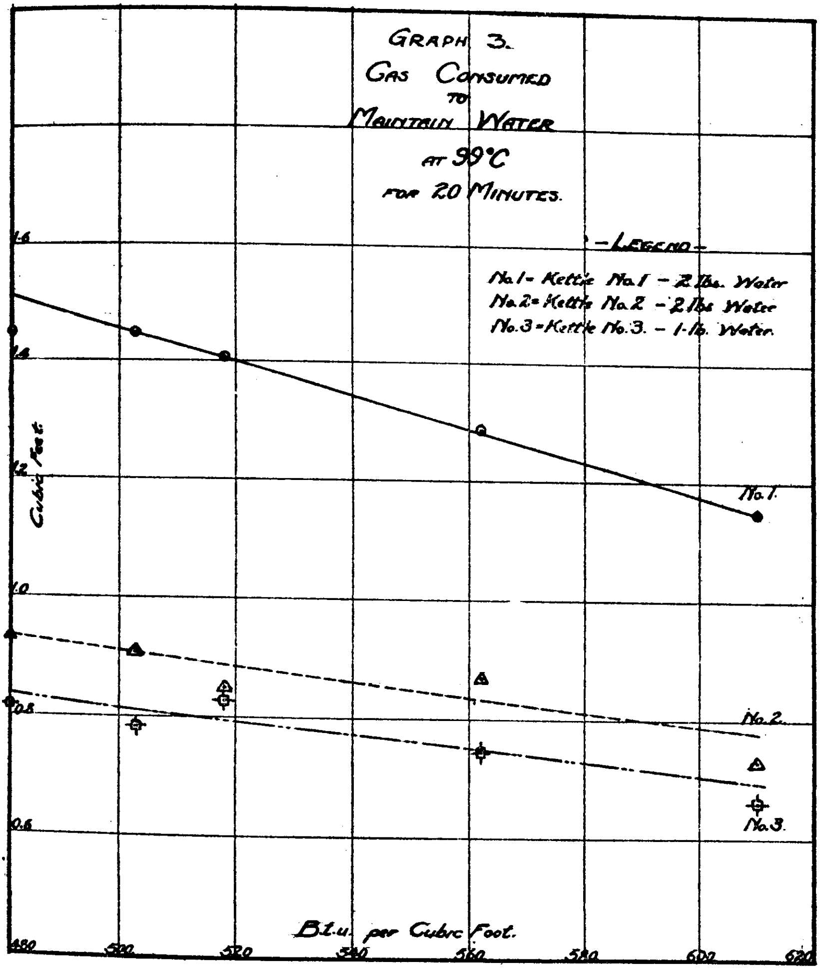
It was possible to make fairly accurate measurements of the volumes of gases required to bring the temperature of the water to 99 deg. Cent. To measure accurately the volumes of gases used to maintain the water "just at a boil" is difficult and introduces a large personal equation, because the burner cock did not permit fine adjustments. For much of the work two observers took data and it is believed that the personal equation is reduced to a low figure.

From Table I. it may be seen that the B. t. u. to raise the temperature of the water from 25 deg. Cent. to 99 deg. Cent. is practically the same for all gases used with any given kettle; to maintain the water in each kettle "just at the boiling temperature" for 20 minutes required practically the same B. t. u. for all gases with any given kettle. This means that a greater volume of gas of 480 B. t. u. will be required to do the same work as a gas of 610 B. t. u. per cu. ft. The volumes of gases are roughly inversely proportional to the B. t. u. per cu. ft. as is shown in Graph 2. This ratio holds for the gas consumed to bring the water from 25 deg. Cent. to 99 deg. Cent. because here the operation of a calorimeter is roughly approximated. This ratio does not hold for the gas consumed to maintain the water just at boiling for 20 minutes as is shown in Graph 3. The striking features of these results as shown in Graph 2 are as follows:—

1. That the large kettle, No. 1, required much more gas than the small kettle, No. 2, in which an equal weight of water was heated. To heat two pounds of water from 25 deg. Cent. to 99 deg. Cent. and to maintain it at 99 deg. for 20 minutes required about 0.4 cu. ft. more of any given gas for kettle No. 1 than for kettle No. 2. Kettle No. 2 had a diameter at the bottom almost identical with that of the outside ring of burner holes.

2. To heat one pound of water in kettle No. 3 from 25 deg. Cent. to 99 deg. Cent. and to maintain it at 99 deg. Cent. for 20 minutes required more than one-half the volume of gas used for the same operation in kettle No. 2, where two pounds of water were heated. For instance, with gas of 540 B. t. u. with kettle No. 2 holding two pounds there were required 2.78 cu. ft. of gas; with kettle No. 3 holding only one pound of water 1.84 cu. ft. of gas were used, or 1.3 times more than one-half the amount.


Graph 2.
Gas Consumed to Raise Water to Boiling and to Maintain at Boiling for a Period of 20 Minutes.
- Legend -
No.1 - Kettle No.1 - 2 Lbs. Water
No.2 - Kettle No.2 - 2 Lbs. Water
No.3 - Kettle No.3 - 1 Lb. Water
No.1
No.2
No.3
Cubic Feet
3.5
3.0
2.5
2.0
1.5
450
500
550
600
B.t.u. per Cubic Foot



In Graph 3, is shown the volumes of the various gases used to maintain the temperature at 99 deg. Cent. for periods of 20 minutes. The prominent features are:—

1. That the amount of gas used to perform this operation in kettle No. 1 with two pounds of water varies from 0.36 cu. ft. to 0.56 cu. ft. more for gas of 610 to 480 B. t. u. than the amount required for kettle No. 2 with two pounds of water.
2. In spite of the fact that kettle No. 3 had only one pound of water, yet to maintain the temperature of this amount of water at 99 deg. Cent. required almost as much gas as the same operation carried on in kettle No. 2 with two pounds of water.

The surface exposed in kettle No. 1 was the largest of the three kettles employed; the diameter of the base was slightly larger than the diameter of the circle inclosing the openings in the burner top. Doubtless the heat radiated from the surface of kettle No. 1 was greater than that radiated from kettle No. 2 and hence more gas was required to maintain the temperature of 99 deg. Cent.

The diameter of kettle No. 3 at the bottom was much smaller than the burner top. In this case the flames played outside the bottom of the dish and did no effective work, but much heat was wasted.

It would seem to follow from these tests that the most effective use is made of the heat in gas when the base of the kettle has a diameter about equal to the diameter of the circle inclosing the holes in the burner.

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[FROM THE TRANSACTIONS OF THE AMERICAN ELECTROCHEMICAL SOCIETY,
Volume XLII, 1922, being the Transactions of the Forty-second General Meeting,
at Montreal, Que., Canada, September 21, 22 and 23, 1922.]

Electroplated Zinc and the Diffusion of Electrodeposits Into Zinc

BY

WALTER G. TRAUB

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.

ELECTROPLATED ZINC AND THE DIFFUSION OF ELECTRO-DEPOSITS 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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[4] Research Dept., Oneida Community Ltd., Kenwood, N. Y.

[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.

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EDITORIAL

SOMETHING NEW

By Walter Fraine

During the late war the U. S. Bureau of Standards spoke of the electro-plating industry as a "key industry," i. e., "an industry which, while it is not of itself a great magniture, is often of fundamental importance to larger industries," and we as electro-platers know that there are few articles manufactured for the convenience, comfort, adornment or luxury of mankind or for the utilities of business which do not at some time during the course of manufacture, come within the scope of the electro-platers or finishers' art. The public who purchase or use the product have very little conception of the part that finishing plays in adding to the utility or salability of commodities. In order to present to the public an idea of the extent that the art of finishing applies to commodities in general and of the methods and equipment used in the various processes, the Dayton Branch, A. E. S., is putting on an educational exhibit of finished products, materials, processes and equipment used in the prevention of corrosion, preservation, beautification, etc., of metals, wood and other materials. This exposition will be an innovation along educational lines, as it is the first time that an exposition has ever been staged on the basis of the finish itself and making the process and equipment of secondary importance.

The local manufacturers, merchants and newspapers are giving their hearty commendation and encouragement to what they characterize as "something new, unique, interesting and well worth while" as an educational factor.

It is to be expected that the various branches of the A. E. S. will be intensely interested in the results of this venture of the Dayton Branch with the idea of using this means to illustrate the extent electro-plating enters into modern industry and caters to the comfort, convenience and welfare of the public.

‘Let your light so shine before men that they may see your good works.”

“Come and learn of us.”

THE IONIC THEORY AND ITS APPLICATION TO PLATING

By Oliver P. Watts, Assoc. Prof. University of Wisconsin

From the time when man first deposited metals from solution by means of the electric current he began to speculate concerning the mechanism of this action. Why does the current cause metal to be deposited, and why does it cause metal to be dissolved from the anode by a solution which, without the current, does not attack the material of the anode?

During the century that man has experimented in and studied the electrodeposition of metals three theories have been evolved, one after another, to account for the facts observed. It is only the last of these, the Theory of Electrolytic Dissociation or Ionic Theory, that will now be considered.

According to their behavior when subjected to an electromotive force substances may be classified as insulators or conductors. There is no sharp line of demarkation between these classes. There are many substances which are too poor conductors to serve usefully for carrying current, but whose resistivity is not high enough for them to be useful as insulators ,and they are therefore not usually included in either class. We are interested only in conductors. These are divided into two classes—metallic conductors, which are unchanged by the passage of current, and electrolytes, which undergo chemical change in proportion to the current which traverses them.

In order for a substance to conduct electrolytically it must be a chemical compound, and must be fluid. There are two ~~d~~Ways in which a compound may become an electrolyte—

by fusion, and by dissolving it in some solvent. Many liquid compounds, such as alcohol, chloroform and carbon bisulphide, are non-conductors; and many solid compounds either do not conduct when dissolved in any solvent, or conduct only in certain solvents. There are also a few compounds, some oxides, sulphides, silicides, etc., which conduct in the solid state without undergoing chemical change, and hence are classed with metallic, not with electrolytic conductors.

Since water is the most common solvent that yields conducting solutions, and is the only solvent used for plating baths, this discussion of the ionic theory will be confined to solutions in water.

Water itself does not conduct electricity usefully, and there are many compounds, e. g. soap, glycerine, and alcohol, which dissolve without rendering it a conductor. On the other hand the dissolving of acids, alkalies, and metallic salts in water render it conductive.

The conductivity of water is not increased to the same extent by the dissolving of equal amounts of different substances, nor by the dissolving of chemically equivalent quantities. Some substances are much more effective than others in imparting conductivity to water. The most effective are nitric, sulphuric, and hydrochloric acids, and sodium and potassium hydroxides.

The conductivity does not increase in proportion to the amount of any particular substance that is dissolved, but the rate of increase in conductivity falls off as the solution becomes more concentrated. In the case of substances which are extremely soluble, such as sulphuric acid, sodium hydroxide, and the chlorides of zinc, calcium and magnesium, as the concentration of the solution is increased a point is finally reached where the dissolving of more of the substance actually causes a diminution of conductivity instead of an increase. It follows that, while for most substances a saturated solution is the best conductor, in case of very soluble substances, such as those mentioned above, the maximum of conductivity is reached considerably before saturation. A 30 per cent. solution of sulphuric acid is the best conductor of all mixtures of sulphuric acid and water.

Solutions may be divided into two classes: Electrolytes, which conduct electricity, and non-electrolytes, which do not conduct. In 1887 Arthenius stated the Ionic Theory as follows: "In all aqueous solutions which are electrolytic conductors the molecules are to a certain extent dissociated by the act of solution into at least two parts, oppositely charged electrically, and it is only such dissociated molecules, or ions, that carry current. The undissociated molecules play no part in conduction.

This is a brief statement of the ionic theory. Note that only ions add to the conductivity of solutions, so that large amounts of salts that ionize only slightly may be added to a plating soltuion without much increase in conductivity. The per cent. of the dissolved molecules that are dissociated into ions depends on the material and the concentration of the solution. In very dilute solutions of good electrolytes, viz., the mineral acids, the alkalies and the sodium and potassium salts of the strong acids, dissociation is practically complete. In very concentrated solutions only a small per cent. of the dissolved substance is dissociated, which accounts for the poor conductivity of concentrated sulphuric acid, and of saturated solutions of zinc and calcium chlorides.

Conductivity of Plating Baths

The electrolytic refiner, who may be using from 1,000 to 2,000 horsepower, is always striving to secure the highest conductivity for his solution, but to the plater conductivity is of much less importance. The solution is the same in all the 1,000 tanks of the refinery, and any increase in conductivity of the electrolyte applies to every tank. The plater is operating many different solutions, and an improvement in the conductivity of his copper solution does not apply to the nickel tank. He must use a generator voltage high enough to drive the desired current through his highest resistance bath, so that any saving in voltage on his other solutions by lowering their resistance does not save a cent on the electric power bill. If his highest resistance solution requires six (6) volts to give the current needed, there is no saving in making additions of sulphuric acid, lye or salt to his other solutions to lower their resistance, for he must still keep his generator set for six volts on account of the high-resistance solution. The less amount of energy absorbed by the solutions whose resistances have been lowered is merely wasted in the rheostat. The only way he can make a saving in power is to give his attention to raising the conductivity of those solutions which have the highest resistance so that he may lower the voltage of the generator. The power output of the generator equals the product of its voltage by the amperes which it delivers, but the metal deposited depends on the amperes and not at all on the voltage, so that if a plater can improve the conductivity of his solutions so that he gets the same current at a 10 per cent. lower generator voltage he has made a saving of 10 per cent. in power.

What substances shall the plater add to his highest resistance solutions so that he may operate his plating room at a lower generator voltage? There are, as is well known to the plater, few soltuions that will stand the addition of mineral acids, the substances which have the greatest conductivity. The organic acids, acetic, citric, tartaric, oxalic, etc., are but slightly ionized at any concentration, and so are of no aid.

Only a few solutions will stand the addition of sodium hydroxide (lye), so that for general use there remain only salts of the metals. The best conducting of these are the chlorides, nitrates and sulphates of sodium, potassium and ammonium. Nitrates seem to have been avoided in plating baths, possibly because they are reduced by any hydrogen that may be liberated along with the metal deposited.

All of these are much better conductors than are salts of the heavy metals which are deposited from plating solutions, and hence they act as real conducting salts, i. e., they improve the conductivity. Salts of organic acids are so slightly ionized that they are of no value for conductivity.

When only one substance is being deposited, Faraday's law tells us that for the same current the quantity of any particular metal deposited is always the same, and for different metals the amounts are proportional to their chemical equivalents.

An electrolyte is like a theater with the number of tickets limited to the number of seats, and every seat occupied. In this electrolytic theater a patron surrenders his ticket only on leaving, and on condition that a newcomer at once takes it and enters. Every seat in the electrolytic theater is always filled. The atoms of the elements are the people, and the electrical charges are the tickets of admission and departure. The ions are people who have entered and still hold their tickets, but admission to the electrolyte differs from the usual custom of theaters in that, instead of charging different prices for a single ticket, some persons are required to show one, others two, and still others three tickets, i. e., for atoms to become ions some must have one electrical charge, others two, and still others three charges, according as the valence of that particular element is one, two or three.

So far as can be seen the dissolving of an atom of metal from the anode is simultaneous with the deposition of one at the cathode, i. e., when an ion wishes to leave the electrolytic theater, he makes application to the doorkeeper at the cathode, who takes his ticket, instantaneously sends it around through the cable to the negative pole of the dynamo, from which it is returned via the positive terminal to the anode and handed to an atom of metal there without loss of time, so that a new ion enters there to take the place of the one which gave up its charge at the cathode and became metal. For an atom of metal to enter the solution it must obtain in some way the proper number of electrical charges, and for metal to plate out of solution the metallic ion must dispose of its charge. It is not necessary, however, that the departing ion shall give its charge to the negative pole of a dynamo, storage battery, or voltaic cell, nor that the entering ion shall have received its charge from the positive pole of one of the above sources of electrical energy. An ion may give its charge directly to the atom of a different metal. This is seen on putting a piece of clean iron into a solution of copper sulphate. As soon as an ion of copper touches the piece of iron it hands over its two charges to an atom of iron, and escapes from solution as metallic copper, while an iron ion takes its place in the solution. This process will continue as long as copper ions can come in contact with the iron. The function of a dynamo in plating is to collect tickets at the cathode and so permit metal to go out of solution there, and to pass the tickets (electrical charges) around to the anode, so that metal may enter there.

So far only metallic ions, which carry positive charges, have been considered; but when the molecules of a dissolved substance ionize, for each positive charge carried on a metallic ion, there is an equal number of negative charges carried on the non-metallic part of the salt or acid that was ionized. Like the metal ions, the hydrogen ion is positively charged, and is liberated at the cathode. Negatively charged ions, on the other hand, move toward the anode, and are liberated there if they escape from soltuion at all. Opposite charges of electricity neutralize each other, so when a negatively charged ion is set free at the anode its charge neutralizes an equal number of positive charges from the dynamo, and there is a shortage of positive charges, which results in a deficiency of metal entering solution from the anode. In other words, the efficiency of solution of the anode is less than 100 per cent. Oxygen is the element whose deposition is usually the cause of low anode efficiency.

If there are many hydrogen ions in the solution, i. e., much of any strong acid present, there is a possibility that some of these hydrogen ions will hand their charges to the doorkeeper at the cathode and escape from solution along with the metal that is being deposited. In this event the current efficiency of deposition of metal is less than 100 per cent.

The plater knows by experience that solutions of zinc, iron and nickel cannot be strongly acidified without causing much of the current to be wasted in the deposition of hydrogen, or in terms of the ionic theory, many hydrogen ions cannot be present without their taking part in electrolysis and being deposited at the cathode. There is a preference for deposition of hydrogen instead of these metals. To solutions of copper, silver, platinum and gold much free acid may be added, i. e., many hydrogen ions may be present, without any serious deposition of hydrogen —the preference is for the discharge of the metallic ion rather than the hydrogen ion. The solutions of the precious metals referred to above are the chloride or nitrate as used by the refiner, not the cyanide solutions used by platers, in which the addition of acid would result in the liberation of hydrocyanic acid, with results fatal to the plater as well as to the character of the metal deposit.

How is it that large amounts of boric acid can be added to the nickel solution without causing a disastrous liberation of hydrogen? Boric acid is about the weakest of all acids. It has so little of the character of an acid that oculists use a solution of it as an eyewash. To a chemist the difference between a strong and a weak acid is that the former yields a large number of hydrogen ions when dissolved in water, while the per cent. of the weak acid that is dissociated is small, and the number of hydrogen ions is few. Although many pounds of boric acid are present in a nickel solution hydrogen ions are so few that they cannot be deposited to any serious extent in place of nickel ions. As soon as these few hydrogen ions are removed, however, more of the boric acid dissociates and so maintains that very small concentration of hydrogen ions which is desirable for a white nickel deposit.

We have seen how current enters the solution at the anode and how it leaves at the cathode, by atoms of metal taking electrical charges from the anode and becoming ions, and by ions that are touching the cathode giving up their charges to that electrode and attaching themselves to it as a metal deposit, and how the dynamo makes the action go on by collecting the positive charges from the cathode and passing them around to the anode so that new ions can enter the electrolyte. Within the solution the ions are marching like two armies of snails, the positively-charged, metallic ions toward the cathode, and the negatively-charged ones toward the anode. The passage of electricity through an electrolyte is then like the movement of mortar by a line of hodcarriers—man and mortar go along together until they reach their destination, in this case the electrodes. Different kinds of ions move at different speeds—if a motion so slow as theirs can be referred to as **speed**. This movement towards the electrodes is called the "migration of the ions", and its velocity is proportional to the voltage impressed. Hydrogen has by far the greatest velocity, 10.8

cm. per hour at 1 volt, while the migration velocity of the silver ion is 1.7 cm. The procession of the ions has been compared to an army of snails, but this is a slam on the speed of the world's champion slowcoach, for it would be a slow snail indeed that could crawl only its own length in an hour, which is about the distance traversed in that time by the ions of the metals usually deposited by platers.

The removal of metal causes the film of solution in contact with the cathode to have a lower density than the main body of electrolyte, and as a result it rises along the cathode. At the anode a layer of denser solution is formed by the dissolving of metal, and there is a downward motion of this stronger solution which can be plainly seen when plating is carried out in a tank of clear glass. In a still solution in which the electrodes extend only half way to the bottom, after an hour or two a distinct stratification of the solution can be seen, with a clearly-marked boundary between the dense solution at the bottom and the dilute one on top.

Migration of ions is so much slower than this motion of the solution due to changes in density at the electrodes, that most of the ions that pass into solution at the anode are carried bodily to the bottom of the plating tank instead of directly across to the cathode where they are needed. In order to keep up the metal content at the cathode the refiner circulates his solution continuously. Some day the plater may do the same, although at present for preventing such stratification he usually relies on the removal and insertion of successive batches of articles to be plated, and a thorough mixing at the end of the day.

The percent of the molecules of each dissolved salt which dissociates into ions depends on the material of the salt and on its concentration, so that the dissolving of more of any salt not only changes the number of molecules in the solution, but the number of ions as well. At the anodes of a plating bath only positively-charged ions enter the solution, but at the same time a stream of negatively-charged ions is migrating toward the anode, so that there is an accumulation of both positive and negative ions around the anode. This would soon result in the number of ions there becoming disproportionate to the number of molecules, if the excess of positive and negative ions did not at once unite with each other into molecules. Dissociation into ions, and recombination into molecules is constantly occurring at different places in the solution to maintain the proper ratio between numbers of ions and of molecules. It is generally agreed that every ion in the solution assists in carring current through the main body of the electrolyte, but that only those which pass into or out of solution at the electrodes transfer current between the solution and electrodes. This brings us to the conclusion that what happens at the electrodes depends at any particular moment only on the current density and the nature and concentration of materials that actually touch the electrodes. At the cathode of a plating solution there are always at least two possibilities,--the deposition of metal and the deposition of hydrogen; and, as has been pointed out above, there is a perference for the deposition of one of these. If there are plenty of ions of that one to carry out of solution all the current which passes, only that ion will be deposited; but if there is an insufficient number of these ions in contact with the cathode to carry all the current at that moment, then enough of the second ion will be deposited to supply the rest of the current. The relative concentration of the two ions will evidently be a factor in determining whether only one or both ions will be deposited. It is well-known that a larger current can be used in strong than in weak plating solutions. This is not only because the stronger solution contains more ions of the metal, but the undissociated molecules of the metallic salt act as a reservoir of ions. As ions of the metal are removed by deposition, not only are ions migrating to the cathode carrying the current, but molecules of the salt dissociate until the original ration between ions and undissociated molecules is restored. In spite of these two sources of metallic ions there would soon be a deficiency of them in actual contact with the cathode, were it not that diffusion brings them in from the full-strength solution just back of the layer that is in contact with the cathode. It is because of this that so much greater currents may be used in strong than in weak plating solutions. The value of motion-plating and stirring lies in their assisting diffusion in maintaining a supply of metal ions at the surface of the cathode.

The greatly increased current density which may be employed when a plating solution is heated is due to a lowering of the viscosity of the solution so that the ions move much faster, and to a more rapid diffusion of the molecules of the metallic salt. Convection currents caused by heating also assist in supplying metal at the cathode.

To summarize:

In aqueous solutions that conduct electricity, a certain per cent. of the molecules of the dissolved compounds have separated into at least two parts, oppositely charged electrically.

The number of charges carried by an ion is the same as its valence.

Conduction varies with the number of ions and the velocity of their migration.

Molecules take no part in conduction, but constitute a body of reserves that supplies new ions when the original ones are removed.

Positively charged ions, the metals and hydrogen, move toward and are deposited at the cathode; negatively charged ions migrate toward the anode.

As soon as an ion has given up its charge of electricity to an electrode it becomes the familiar chemical element, copper, silver, chlorine, etc.

An electrolyte is like a street car so crowded that not a single individual can enter until some one gets off. There is only one exception to this for electrolytes, viz., when there is in solution some ion that is capable of changing from a higher to a lower valence, like the change from a ferric to a ferrous salt. A solution of ferric chloride can dissolve iron, i. e. cause iron ions to go into solution without the aid of the electric current, and without any other ion being pushed out of solution.

METAL FINISHING

By R. J. Hazucha, Chicago Branch, A. E. S.

This paper is written for the purpose of pointing out the difficulties of a metal finishing foreman which are not always under his supervision and which are at times his chief troubles, rather than giving a detailed description of a definate plating or finishing problem. Metal finishing from a manufacturing standpoint is a necessary evil and seldom receives credit for the part it plays in the various industries. More than 50% of articles finished today are not only finished for selling purposes, but are also protected against corrosion, which means conservation of materials. When we begin to analyze finishing it becomes necessary to separate same into three groups, namely, Preparation, Application and Preservation.

Preparation of Parts for Finishing

One of the first steps in preparing parts for finishing is cleaning. All parts that come to the finishing department should be reasonably clean from heavy lubricating compounds, oils and machine chips. It is also a good policy to clean parts between machining operations, for it has a direct bearing on the life of the tools used in manufacturing the parts and on the cost of finishing. When parts are full of heavy lubricants, chips and grit adheres to them readily and when they put through the succeeding operations the tools become dull and scratched or the articles become full of small impressions which requires extra labor to remove; also when parts are full of oil and have to be cut down, it is a very difficult operation to perform economically on account of too much lubrication on the buff. Buffing compositions when properly selected to fit a certain class of work and definite peripheral speed of a buff, contain enough lubricant and binder to make them adhere to the buffs and perform their duty; but when additional lubricant is added in the form of heavy oils on the surface of the parts, the cutting officiency is immediately lowered, which means that more power, more buffs and more compositions are necessary to obtain satisfactory results. To illustrate this properly, let us consider a grinding wheel which, when properly dressed, gives good results. Let us now apply some heavy oil or light grease on the face of this wheel and we will reduce the cutting efficiency of this wheel at once about 40%. This holds true with cutting down, which is nothing else but grinding in mild form.

The second step in preparing parts for finishing is detail inspection. This can be accomplished much easier if the parts are cleaned and the reason for mentioning inspection

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EDITORIAL

ESSENTIALS TO PROGRESS

The American Electro-Platers' Society has but one aim and purpose, or reason for its existence, i. e., the advancement of knowledge in the science of electro-plating and finishing of metals. If the Society functions as it should, and as we all desire to see it, its activities must result in progress in the art and science of electro-depositing and finishing of metals. There are at least two definite things to be done to insure progress.

First, We must give wider circulation to known methods and laws that govern the successful cleaning, plating and coloring of our product.

Second, Through study, experiment and scientific research, we must discover and develop more efficient methods and in some cases entirely new methods of producing electrolitic deposit·

In this editorial we will draw attention to the essentials to progress as they apply to the item first mentioned above.

It is the history in the development of the race that when man had a job too big for himself alone, he learned that the thing he could not do was made possible through organization and co-operation with others, and it is to this end that the A. E. S. is organized. Since no one man can, in the short span of his existence, master all the different branches of this specific science, yet if the experiences of a group are recorded and circulated, knowledge of the science is advanced—in that the experience of many (one thousand in the case of A. E. S.) can become the basis of knowledge to each individual. Therefore, to function as we should and make progress, it is essential that our membership shall increase, and that a greater number of our membership shall record their experience for the benefit of all.

Use the REVIEW. That is what the REVIEW is for. Let others know the methods or process that has brought success to you in your special field, thus advance the science of electro-plating. Let it be known that we are out for 100 per cent. of the men and women who by reason of their experience and activity in electro-plating are eligible for membership in the A. E. S. The A. E. S. needs them and they need the A. E. S. still more.

RELATIONS OF ANODE AND CATHODE EFFICIENCIES

By Oliver P. Watts

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In plating solutions anodes have two distinct functions to perform: First, to distribute the current properly and uniformly to the objects which are being plated; and, second, to supply metal to the solution at exactly the same rate as it is being deposited. It is only with the second of these functions that this paper is concerned.

With the long experience of the past to draw on, it is a comparatively easy matter to make up a solution that will at the outset give a good deposit of any particular metal. The difficulty is to maintain the solution in such condition that it will continue to yield the same good deposit every day during months and years of use.

There are several influences at work which cause the composition of a plating bath to change with use. One is the drip from the work as it is removed from the solution. Where a bath is used to capacity every day the quantity of chemicals carried away on the objects plated is sufficient to weaken the bath materially ,and if these are not replaced from time to time, the solution will finally become so weak that the current density regularly used will cause a "burned" deposit. It should be noted that "drip" does not change the relative proportions of chemicals in the solution, but lowers the concentration of all of them by the same amount. In cyanide solutions the carbon dioxide of the air reacts slowly with cyanide and makes it necessary to add this chemical occasionally in order to maintain the original amount of free cyanide. Certain plating solutions give a better deposit if acidified to a particular degree; for example, the sulphates of zinc and copper. This acid reacts with the anodes dissolving metal from them, slowly in the case of copper, but rather rapidly with zinc, thus lowering the acidity and raising the metal content of the solution. The desired acid content can be restored by adding more acid, but the extra metal remains.

Before entering upon a detailed consideration of current efficiencies at the electrodes it may be well to define the term **current efficiency.** Farady's law states that the amount of chemical change which takes place at both anode and cathode is proportional to the strength of current, to the time, and to the chemical equivalent of the metal or other element concerned, 26.8 ampere hours being required to deposit at a cathode or to dissolve from an anode a gram-equivalent of any substance. (The gram-equivalent is that number of grams which is equal to the quotient of the atomic weight of an element divided by its valence. Tables of atomic weights and valences are usually given in text books on chemistry.) Faraday's law expresses the facts as found by hundreds of experiments, and one can no more expect to find exceptions to it than to the law of gravitation. When someone shows us a heavy body suspended in air without any visible means of support, we do not enthusiastically acknowledge his claim that he has discovered a means of preventing the action of gravitation, but we look for, and **always find,** the suspending wire, thread, or magnetic force, which is opposing gravity and preventing its pulling the object to the earth. So when someone, with more enthusiasm than judgment, announces that he has overcome Faraday's law, careful investigation will show that he has overlooked chemical corrosion, some other change produced in the electrolyte, or the simultaneous deposition of another element along with the metal which he is trying to deposit from the solution.

Faraday's law does not state that one gram-equivalent of metal is deposited for every 26.8 ampere hours that pass through an electrolyte, but only that there is a total chemical change equal to one gram-equivalent at both anode and cathode. It is left for us to find out in each case whether it is one, or several different actions, that make up this total.

To illustrate: The atomic weight of iron is 56, and its valence in a solution of ferrous sulphate is 2, so the chemical equivalent of iron when plated out of a solution of ferrous sulphate is 28. On passing current through this solution it will be found that 26.8 ampere-hours deposit 28 grams of iron at the cathode and dissolves the same amount from anodes of pure iron. If we now add 20 c. c. of concentrated sulphuric acid to each liter of solution and pass the same amount of current, the result will be quite different. The increase in weight of the cathode will be perhaps only 18 grams, and the anode may have lost 30 grams. It looks at first sight as if Faraday's law no longer applied but let us look carefully! Suppose that we took three hours for electrolysis in the last case—we will let the cathode and anode hang in the solution another three hours with no current passing. A steady evolution of gas from each electrode tells us that some chemical change is taking place, and on weighing the electrodes again we find that each has lost 3 grams. This explains the loss of 31 grams by the anode during electrolysis—the current dissolved 28 grams, as Faraday's law predicted, and attack by the acid took away the other 3 grams. But what about the cathode, at which there was a deficit of 10 grams of iron? Had we watched the electrodes during the second electrolysis we would have seen a gas, hydrogen, coming from each electrode, and had the gas been collected it would have been found that 0.1 gram, the equivalent chemically of three grams of iron, was evolved from the anode, and 0.35 grams, equivalent to 10 grams of iron, at the cathode. The total action at each electrode is the same, and is that called for by Faraday's law. The dissolving of iron from the anode was 28 grams by the current and 3 grams by the acid. At the cathode we might have expected the deposit of 28 grams, but instead get 18 grams of iron, and hydrogen equivalent to 10 grams of iron.

Of the above hydrogen we know that .1 gram was set free by attack of the deposited iron by the acid, but how did we get the remaining 0.25 gram of hydrogen? This was deposited directly by the current. It is not at all uncommon to find hydrogen thus directly deposited along with a metal from plating solutions. This happens regularly in the cyanide copper solution and in brass plating baths, and in every case the total weight of metal plus hydrogen equals the amount of action called for by Faraday's law.

But the hydrogen or other gas liberated at the electrodes has no value to the plater, hence we reckon the efficiency of deposition or of solution on the per cent. of the current that is usefully employed in dissolving or depositing metal. If nothing but the metal desired is deposited at a cathode, and none of this is redissolved by acid, free cyanide, or other corroding agent, the amount of metal will equal that calculated from Faraday's law, and we say the current efficiency is 100 per cent. To find the efficiency of deposition or of anode corrosion, we have only to weigh the electrodes, electrolyze, keeping a careful record of time and current with instruments of guaranteed accuracy, and then weigh the electrodes again. If we divide the change in weight by the amount calculated for the number of ampere-hours used, the quotient will be the current efficiency.

We have seen how anode efficiency may exceed 100 per cent. Had we used a platinum anode its weight would have remained unchanged, and the anode efficiency would have been zero. Anode efficiency may, then, vary from zero for an entirely insoluble anode, to considerably over 100 per cent. Except for platinum plating, zero anode efficiency rarely met with in plating solutions. Cathode efficiency usually lies between 100 and 50 per cent., although it may fall to zero when nothing but gas is deposited. Addition of a large excess of free cyanide to a copper solution, or of much sulphuric acid to a nickel bath, will cause efficiency at the cathode to drop to zero. This is the result of the deposition of hydrogen in place of the metal, and not of corrosion by the cyanide or by the acid of metal already deposited. Efficiency at the cathode may be less than 100 per cent., either by attack of the metal by some corrosive agent, or by a portion of the current being spent in depositing a gas or in producing some chemical change other than deposition of metal.

Current efficiency in plating solutions is the per cent. which the metal actually deposited or dissolved is of that calculated by Faraday's law, assuming that all the current is spent in depositing or dissolving metal.

Effect of Unequal Current Efficiencies

It is evident from the wide divergence in composition of the solutions in successful use for depositing any particular metal, that it is not necessary for good results that fixed amounts of the different chemicals be used, or that they be used in a definite proportion to each other. There are, however, limits within which the ingredients of a solution for depositing any metal under certain conditions should lie, and when a solution has been made up to work well for some particular class of plating, it is very desirable to keep its composition unchanged. In order to do this it is not necessary that the current efficiency at both anode and cathode be 100 per cent., but only that they be equal—when metal will be added at the anode as fast as it is removed at the cathode.

If cathode efficiency is greater than efficiency at the anode metal is being removed from the solution faster than it is supplied, the solution is becoming weaker in metal, and if this continues for any considerable time, the solution may become so impoverished in metal that "burning" of the deposit results. Besides lessening the metal content, this inequality of anode and cathode efficiencies causes an increase in the concentration of the acid whose salt constitutes the bath, or of free cyanide if it is a cyanide solution. If efficiency at the anode exceeds that at the cathode the solution tends to become alkaline, and its free acid or free cyanide, if it contains any, is lessened in amount by combining with the excess metal.

The effect of increase of acidity in plating solutions varies greatly according to the metal that is being deposited. It is well known that there is a preference for the deposition of one of two metals that may be in the same solution. For example, if 10 oz. of copper sulphate and the same quantity of zinc sulphate be dissolved in a gallon of water and current be passed through the solution, only copper is deposited. Similarly, if copper sulphate and hydrogen sulphate (sulphuric acid) be dissolved together, the preference is for the deposition of copper. A copper sulphate bath may therefore be acidified very strongly without much falling off in efficiency of deposition at the cathode. Even a slight addition of sulphuric acid to a nickel solution causes a marked decrease of efficiency at the cathode, and a considerable addition causes the efficiency to drop to zero. When there is any choice offered for the deposition of either nickel or hydrogen the preference is to deposit hydrogen; therefore it requires the presence of but a small amount of a strong acid, like sulphuric or hydrochloric, to cause most of the current to be spent in depositing hydrogen instead of nickel.

It is only hydrogen in the ionic state that can be deposited instead of a metal. The general difference between a strong and a weak acid is that the former is highly dissociated into ions, or ionized, while the weak acid is but slightly ionized when dissolved in water. The weaker the acid the more of it may be added without cutting down efficiency at the cathode. Considerable amounts of acetic acid, and any quantity of the extremely weak boric acid may be added to a nickel bath without materially lessening the efficiency of deposition.

It is the general experience that nickel deposited from a slightly acid solution is whiter than that deposited from a strictly neutral soltuion, but the plater who tries to secure this desirable whiteness by addition of a strong acid like sulphuric is likely frequently to add too much acid and cause a great falling off in efficiency at the cathode, and also to get a brittle deposit. The value of the much-used boric acid consists in its ability to impart a slight acidity to the solution without the possibility of harm by the addition of an overdose.

In cyanide solutions free cyanide acts on current efficiency at the cathode like free acid in ordinary salt solutions; with some metals there is a marked lessening of current efficiency as the quantity of free cyanide is increased, while with other metals large amounts of cyanide may be added without any serious loss in efficiency. It all depends on whether the preference **in cyanide solutions** is for the deposition of the particular metal or for hydrogen. With copper and zinc the preference is for hydrogen, and if a considerable excess of cyanide be added efficiency at the cathode is greatly lowered. It does not take a very great amount of free cyanide to reduce the efficiency to zero, i. e., to completely prevent the deposition of copper from a cold solution. In the case of silver the preference is for deposition of metal, and large amounts of cyanide may be added without causing deposition of hydrogen at a current that did not cause its deposition before cyanide was added.

From a solution weak in metal a large current, i. e., too high a current density, will always cause deposition of hydrogen, and consequently a low current efficiency. It is important to keep this in mind, for, conversely, if it is desired to carry on deposition at a high rate metal must be supplied **at the cathode** as fast as needed by the high current. One way to assist in maintaining plenty of metal at the cathode is to use a solution which contains much metal at the outset, i. e., to employ a concentrated solution; another way is to heat the solution, thus increasing the rate of diffusion and at the same time setting up convection currents; a third and more effective way is to stir the solution vigorously. If the highest possible rate of deposition is desired all three methods should be combined by using a hot, concentrated solution which is vigorously stirred. By this combination the writer has made good nickel deposits at over 1800 amperes per square foot. The very general employment of "motion plating" for heavy silvering permits rapid deposition from baths too dilute to allow this without the aid of one of the three methods just mentioned for maintaining the supply of metal at the cathode. Predictions are unsafe things to indulge in, but the writer will venture one, viz.: that the day will come when, for some solutions at least, the plater will be using the methods of the electrolytic refiner, and will deposit his metal from a warm, highly concentrated solution, which is circulated and filtered continuously, and in which he will "go the refiner one better" by adding motion of the object being plated. Under these conditions plating will be done with a speed that now seems unbelievable, but which can be utilized only by some form of "mechanical plater" by which the time that each article is in the bath is fixed accurately.

Deposition of hydrogen along with some metals injures the quality of the deposit besides lessening its amount. This is the case with nickel, which absorbs some of the hydrogen, and is thereby rendered brittle and caused to curl from the foundation on which it is plated. Where there is a strong preference for deposition of metal rather than for hydrogen, for example, from solutions of silver cyanide and copper sulphate, the appearance of hydrogen indicates that the current density used is too high for the metal concentration of the solution; as a result of the use of too high a current the deposit is "burned." Because burning is accompanied by evolution of hydrogen many platers hold the erroneous idea that hydrogen is the cause of the burning. A consideration of the cyanide copper and brass solutions, where hydrogen is always evolved along with the deposition of metal, shows this view to be incorrect.

Control of Current Efficiency

Most solutions tend to be self-regulating in the matter of current efficiency, for if anode efficiency is less than efficiency at the cathode free acid or cyanide is being formed, and accumulation of either of these reduces efficiency of deposition and increases efficiency of anode corrosion. It is evident that in time increase of acid or cyanide will render the efficiencies at anode and cathode equal, when the composition of the solution will cease to change. The trouble is that in many solutions before this state of stability has been arrived at, the large excess of acid or cyanide has lowered the efficiency of deposition to a degree that cannot be endured, or may have spoiled the character of the deposit. Many solutions cannot, therefore, be left to correct themselves, in respect to the relation between anode and cathode efficiencies.

There is a general principle which applies to efficiency at the anode in all solutions, viz.; that increase of current density at the anode tends to lower the current efficiency, and lowering of current density raises current efficiency, if this is not already 100 per cent. Because of desiring a particular current on the objects being plated, it is frequently not feasible to change the current flowing through the bath, and the change of current density desired must be sought through a change in extent of anode surface.

If it is found that a nickel bath loses the desirable faint acidity above mentioned, it is because the efficiency at the anode exceeds that at the cathode, and metal is being dissolved faster than deposited. The remedy is to raise the current density at the anode, which can be done by removing a sufficient number of anodes. If, on the contrary, the nickel bath by use becomes too acid, the current efficiency at the anode is less than at the cathode, and the current density at the anode should be lowered by adding more anodes. The corrodibility of nickel anodes varies greatly, and it may happen that with all the anodes that the tank will hold there is still a production of acid; the remedy is to increase the corrosive power of the solution or to change to anodes which are more easily corroded. If the original solution contained only sulphates, its corrosive power may be increased by addition of a chloride; if this does not raise efficiency at the anode sufficiently other and more soluble anodes should be substituted. A temporary correction of acidity and restoration of the nickel content may be made by addition of nickel carbonate, but until the unequal efficiencies at the electrodes is corrected too great acidity will soon recur.

From the cyanide copper and brass solutions hydrogen is regularly deposited with the metal, indicating a current efficiency of deposition less than 100 per cent.; if current efficiency at the anode is greater than this, some of the necessary free cyanide is being used up, and the plater will soon be informed of this by the anodes becoming coated, and by the deposit becoming less bright. This condition may be remedied temporarily by adding more sodium cyanide. This increase of free cyanide raises the anode efficiency and acts still more powerfully in lowering efficiency at the cathode, both of which changes use up cyanide more rapidly than before, so it is only a short time before another dose of cyanide is needed. The proper relation between extent of anode and cathode surface is therefore very important in the brass or cyanide copper solution, but is difficult to secure, for too little anode surface causes the formation of a high-resistance film of metallic cyanide on the anodes. This is more troublesome in the brass than in the copper solution.

Since efficiency of deposition in the silver solution is affected but little by the amount of free cyanide present, this solution is very easy to regulate. The amount of free cyanide needed to give clean anode corrosion at any desired current density can be added without causing accumulation of metal in the bath. The wide limits within which free cyanide and all other constituents as well may be varied without preventing satisfactory operations is shown by the analyses of silver baths recently published in the Trans. of the Faraday Society, vol. 16, p. 524-33. A few of these solutions have been in use for 50 years, and many of them for 30 years.

Summary

1. Increase of current density tends to lower efficiency at both electrodes, but the amount of lowering varies greatly with different solutions, being affected by the metal concerned and by the amount of free acid or cyanide in the solution.

2. Lowering current density tends to raise current efficiency at both electrodes, if this is already less than 100 per cent.

3. Increase of free acid or cyanide tends to raise efficiency at the anode and to lower efficiency at the cathode, the extent of change varying greatly with the metal concerned, particularly efficiency at the cathode. Anode efficiency may exceed 100 per cent.

4. Increase of temperature or stirring tends to raise current efficiency at both electrodes toward a maximum of 100 per cent.

5. There is a natural tendency toward equality of current efficiency at anode and cathode. When the cathode efficiency is the greater, free acid or cyanide is on the increase an dthis tends to a lowering of cathode and a raising of anode efficiency; when anode efficiency is the larger, free acid or cyanide is being removed and the metal content is increasing, which tend to lower efficiency at the anode and to raise efficiency at the cathode. In some solutions this equalization of efficiencies is so slow that it cannot be left to take care of itself, because a poor deposit will result before equilibrium is reached.

6. A high metal content in the bath permits use of a high current density without abnormal falling off in cathode efficiency.

7. Even though the efficiency at both anode and cathode were 100 per cent., a much-used bath would finally become

too weak for use if only water were added to make up for evaporation and for the solution carried out on the objects plated. Metallic salts must be added to make up the loss. When efficiency at the anode exceeds that at the cathode it is usually only necessary to add acid or sodium cyanide, for the extra metal needed to maintain the solution is taken from the anodes.

UDYLITE PROCESS

In the June issue of the REVIEW, the organ of the American Electro-Platers' Society, there appears in article by Mr. C. H. Proctor on "Electrodeposition of Cadmium versus Zinc." In it he reviews to some considerable extent the causes of iron rusting and then goes on to describe the various methods which have been and are now employed to rust proof iron or steel articles.

After passing over galzanizing, electro-galvanizing and Sherardizing, which are known, and of great worth in the commercial world, he refers to other methods which are less known and employed. Some of these, which do not demand the deposit of a metal upon the surface of the iron or steel article to be rust proofed are in use today, the most common being the Parker Process, which consists in processing steel articles so that various phosphates, including that of iron, are made part of the surface of the article being treated. All of the mentioned methods in his paper have their part in industry and have various values for the exposure they undergo.

Just a year ago today three patents were granted to the Udylite Process Company for a rust proofing process which differed from these previously mentioned. The principle of this process was the depositing electrolytically of metallic Cadmium and an after baking or heating step. This causes the penetration and alloying of some of this metallic Cadmium which forms a thin skin underneath the top surface of the Cadmium and is integral with the skin and the base metal. As Mr. Proctor points out, these are apparently specific patents, and mentions particularly the use of these processes for protecting edged tools, springs, and piano wire. The patentees and the company to which they were assigned were fully aware that Cadmium plating had been

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A STUDY OF WATER-LINE CORROSION

BY

KENNETH M. WATSON and O. P. WATTS

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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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 waterline. 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.

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[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.

tention of our members either in their success or failure and we discuss and debate these findings at our meetings, impartially and without prejudice or levity, to a better understanding of our profession by our members. We hold annual conventions where three to five hundred men and women from all parts of the United States and Canada travel many miles each year to listen to the most eminent speakers and lecturers on electro-chemistry and the finishing of materials from the different universities, Bureau of Standards at Washington, D. C., and our membership. And do any of our visitors seek the usual recreation of these events. No, we are UNIQUE and seekers of education; we spend twelve to fifteen hours each day discussing and listening to debates on our profession to be of assistance to the progress of our industry and to be a part of it if possible.

I therefore say now to you gentlemen, who are qualified to become members of this great society, not to let the opportunity pass lightly or you may feel that in another decade you have lost another chance to have been better for having lived and when the grim reaper swings his sythe you can feel assured that you were a part of the wheat of life and not the chaff.

In conclusion, gentlemen, I wish to thank you all for your attention and especially the banquet committee for the efficient manner in which they have managed this annual event, and all the members who have so ably assisted me in the discharge of my official duties, and who have responded so cheerfully in all of our activities to the success of the entire American Electroplaters' Society, and this, my friends, is to me co-operation, UNIQUE, and its beauties and reward can be naught but Success, and I feel that the most excellent two formulas for foreman electroplaters in 1924 are to attend our convention at Milwaukee in June, get more education and a membership in the American Electroplaters' Society.

Ques. No. 1—Why is carbonate of soda added to a copper solution?

Ans. No. 1—To help increase the conductivity of the solution.

Ques. No. 2—What is a good stop off for use in preventing deposit in silver plating?

Ans. 2—Asphalt dissolved in turpentine with small addition of Koppell varnish was recommended. CHICAGO QUESTION BOX.

PITTING OF NICKEL PLATING

By Oliver P. Watts at Annual Banquet Chicago Branch, A. E. S.

January 25th, 1924.

"Passing the buck" is nowadays one of the most popular of indoor sports. All of us are ready to take full credit for our successes, but some of us want to shift the responsibility for our failures to other shoulders than our own. When about six weeks ago I was asked to speak tonight on the pitting of nickel plating, I had to confess that in my very limited experience with nickeling I had never had a case of pitting. "Lucky man," some of you will say; yet not so lucky for one who is to address a meeting of experienced platers on this subject! Naturally I demurred, but was assured that my complete inexperience was no bar to my speaking to you on this subject. What do you make out of that, coming from the chairman of your program committee?

As I had on various occasions already told you all that I **know** about plating, and many things that I only gussed at, it seemed to be a question of this subject or none at all. So, with the assurance of assistance from members of Chicago Branch, I accepted. Although I have used in experimenting all the time that I could beg, borrow or steal, I am still unable to give you a cure for pitting, and so stand before you like a school boy without his lesson, trying to shift the blame off on your program committee. You are in for a disappointing quarter of an hour. Put the blame where you think it belongs.

At the outset I wish to say that for the facts concerning pitting and for most of the samples exhibited, I am indebted to Messrs. F. J. Hanlon, F. C. Mesle, C. C. Martel, C. F. Nixon and O. E. Servis, without whose prompt and cordial co-operation it would have been impossible for me to speak on this subject at all.

Although pitting of nickel plate is of comparatively rare occurrence, considering the enormous amount of nickeling that is done, I am told that it is one of the most troublesome ailments in nickel plating. In attempting to find its cause the first thing is to learn with what other metals besides nickel pitting occurs. I have received only three replies on this point, too few to make my conclusions final, but they indicate that pitting has been found with nickel, iron, lead and cyanide copper solutions, while it is reported that pitting has never occurred with brass, silver and copper. Note that there is a conflict regarding copper. This will be referred to later.

During the war I encountered a bad case of pitting of lead plating, which was presented to you at the banquet in January and printed in the MONTHLY REVIEW for April, 1919. Hundreds of boosters were covered with pits like those shown in the picture here. The cause was traced to air, dissolved in the solution when it stood idle over night, and expelled when the solution became heated by the heavy current used in plating. Preheating the cold solution with steam stopped the trouble. Inspection of pitted nickel plate shows that this also is caused by the clinging of bubbles of gas to the metal surface during plating, but it has generally been thought that in this case the gas is hydrogen.

My first experiments were undertaken to determine whether the gas that causes pits in nickeling is air or hydrogen. Since the amount of gas is too small to be connected and tested readily, an indirect method was employed. A nickel solution, consisting of single sulphate, ammonium chloride and boric acid, was cooled nearly to the freezing point of water, and air blown through it for 15 minutes or more. An acid copper sulphate solution was treated similarly, both solutions were connected in series electrocally, and electrolyzed for 1 to 3 hours, while they were heating on a radiator or in a hot room. Pitting occurred in the nickel solution, but never in the copper solution. Had air been responsible for pitting this should have occurred in both solutions. If it were due to hydrogen pitting should occur just as found, only on the nickel; for at a reasonable current density hydrogen cannot be liberated from a strong solution of copper sulphate. Pitting also took place with this nickel solution without the cooling and heating. Other nickel solutions were made which did not give pitting under any conditions.

There are only two reasons that occur to me why air did not cause pitting in the copper solution, as it did in lead plating. The heating of the copper solution was from the outside, not evenly throughout the whole electrolyte by the current as with the lead solution, and the deposition of metal was much less rapid, so that air bubbles were not so promptly anchored in place by the building up of metal around them. Air bubbles were seen to collect on the sides of the glass jar in both the copper and nickel solutions, and some appeared on the cathodes, but did not stick to the copper long enough to cause pits.

It seems safe to conclude that hydrogen is the immediate physical cause of the pitting of nickel deposits as ordinarily met with. Pitting of any metal deposit by air bubbles may occur under such unusual conditions as caused it in the lead plating.

What causes the hydrogen bubbles? Here are the causes as given by two of those who were so kind as to write their experiences with pitting:

(a) The solution is too acid.
(b) It is too alkaline.
(c) The current density is too high.
(d) Imperfections on the surface of the metal.

Two members mentioned specific instances where starting a tank with new anodes caused pitting that persisted for several days. This is probably due to a skin on the anodes which resists corrosion, and the lessened efficiency at the anode produces acid which causes hydrogen to be deposited slowly. Slight grinding of the surfaces of the anodes before putting them in the tank should help to prevent this trouble.

Remedies

Certain precautions are obvious, such as keeping up the nickel content, keeping the acidity low, and avoiding too high a current density. Although the average current density may be low enough to avoid pitting on most of the object that is being plated, the unequal distribution of current that almost invariably occurs may give too high a current density on corners or edges, and so cause pitting at these places only. It is undoubtedly because of unequal distribution of current that the nickeling on some articles is pitted, while other objects beside them receive a perfect plate.

Imperfections in the surface of the article have been strongly emphasized by one member as a cause of pitting.

While this is probably not often a primary cause of pitting, causing pitting to occur from a solution that would not give pits if all objects in the tank had smooth surfaces, it may often determine where pitting will take place. Edges and corners always receive a higher current density than adjoining flat surfaces, and this will be true to some degree for microscopic scratches and pits on the surface of the metal. The location of gas pits along the edges of indentations is illustrated by the left-hand booster in the picture of pitting in lead plating, which has been passed around.

It is easy to see how a pit develops, once a bubble is formed and clings to the surface of the metal. Deposition beneath it is prevented, so a ring of metal is built up around the bubble, which tends to hold it from being dislodged, and so long as it can maintain its foothold it will absorb other bubbles that touch or bump against it. It is thus that the deep burrows were formed in the sample of electrolytic iron which I have in my hand. During deposition this was removed and rinsed under a faucet a half dozen times, but the bubbles of gas persisted through all this treatment. Once a deep pit is started you know how nearly impossible it would be to bridge over it by electro-deposition. Evidently the way to stop pits is to prevent their getting started.

One member states that pitting has repeatedly been cured by addition of epsom salts.

Since the pitting of nickel plate is usually due to hydrogen it might be assumed that the more hydrogen evolved the worse the pitting. This does not follow. In order to produce a pit the gas bubble must cling in one spot long enough for the metal deposit to build up around it to an appreciable degree. There is, therefore, little likelihood of pitting when there is a steady evolution of gas during plating, as in the brass and cyanide copper solutions. It is the slow evolution of gas, requiring 15 to 30 minutes for a bubble to form, that is dangerous. Even in the brass and cyanide copper solution, where normally a steady stream of hydrogen is evolved, there is a possibility that in deep cavities where the current density is very low deposition of hydrogen may be slow enough to cause pitting, provided the bubbles clinging there are not dislodged by gas rising from other portions of the object. The greater the amount of free cyanide present and the higher the current density the more rapid will be the evolution of hydrogen and the less the probability of pitting. It must be due to some difference in operating conditions that one of your members reports pitting in a hot cyanide copper solution, while I have used such a solution for occasional plating for several years without a single pit. My plating has been done at a high current density, 30 to 50 amperes per square foot, and on objects without deep cavities.

It would seem that one way to stop pitting in a nickel solution is to keep it acid enough to insure a steady evolution of hydrogen. While this will stop pitting, except possibly on portions of the surface where the current density is abnormally low, such as hollows, it would make the deposit so brittle that peeling would be likely to occur, and the remedy might be worse than the disease.

Two of my attempts to stop the deposition of hydrogen may be of interest to you, although neither proved to be practical. The first was to add to the nickel solution a depolarizer for hydrogen, that would oxidize this completely. Sodium nitrate was tried. It had the expected effect of removing every trace of hydrogen and there was no pitting; but it nearly stopped the deposition of nickel also, causing the efficiency of nickel deposition to drop from 93 to 0.5 per cent. The trouble is that the intrate not only exodizes the hydrogen that normally deposits, but invites a lot more hydrogen to plate out and be oxidized, so that nearly all the current is spent in depositing hydrogen instead ofnickel.

The other attempted remedy was the addition of a salt of a metal on which hydrogen is deposited with much greater difficulty than on nickel, that is a metal having a high overvoltage or discharge potential for hydrogen. The discharge potential of hydrogen is highest on mercury, so a small amount of mercuric chloride was added. It slightly lessened the deposition of hydrogen, but did not stop it. With the failure of these two medicines, both of which seemed promising from the electrochemical point of view, the only remedy at present seems to be that previously recommended, viz.: to keep the metal content up to full strength, the acidity low, and the current density low and uniform on all objects and their different parts.

The Effect of Density of Gas on the Volume Discharged from Orifice on Burner on Gas Stove

By

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ASSOCIATION HEADQUARTERS
445 WASHINGTON BUILDING
MADISON, WISCONSIN

THE EFFECT OF DENSITY OF GAS ON THE VOLUME DISCHARGED FROM ORIFICE ON BURNER ON GAS STOVE

By O. L. Kowalke and R. L. Rundorff

Chemical Engineering Department, University of Wisconsin

The suggestion to study the effects of density of manufactured gas on the flow out of the burner orifice of a top burner on a gas stove came through the discussions of papers before this Association on the experiences of various members in serving their customers under the revised standards for gas as ordered by the Railroad Commission in 1920. It was recognized that enlargement of orifices on burners was necessary if the gas delivered under the revised standard were of a higher density. No detailed data, however, were at hand to show how the volumes of gases delivered under various pressures varied with changes in density. The study of these variations was therefore deemed worth while.

The following method was employed. Gas of a known density (obtained from a container sufficiently large to insure an ample supply for each test) was measured in an American Meter Co. one-tenth cu. ft. wet test meter and made to pass through the orifice of a top burner of a gas stove with the burner in its regular position. The pressure of the gas in inches of water column was measured by means of a "U" gauge attached to a special connection just back of the burner cock. All volumes of gas measured were corrected for temperature and pressure and reported as volumes at 60°F and 30 inches of mercury. For each determination the gas was allowed to flow for 10 minutes as measured by a stop-watch.

The gas stove used in these tests was loaned by the Madison Gas & Electric Company to whom grateful acknowledgment is here made.

Perhaps the most interesting and puzzling task encountered in this study was the determination of the density of the gas. The first device was an effusion apparatus made after the suggestion given in Bur. Stand. Technologic Paper No. 94 and shown in Plate 1. wherein mercury was used as the fluid instead of water. Here the gas or air, previously dried over calcium chloride, was allowed to escape through an orifice 0.35 m. m., mean diameter, in a thin platinum sheet. The time required for a definite volume of gas or air to escape was noted with a stop-watch. The density of gas is then computed from the following formula:—

$$\frac{\text{density of gas}}{\text{density of air}} = \frac{t^2 \text{ (in seconds for gas)}}{t^2 \text{ (in seconds for air)}}$$

Care was taken to insure uniformity of temperature for both gas and air when making a determination and the mean of five determinations was employed as the correct value.

-Gas Effusion Apparatus-

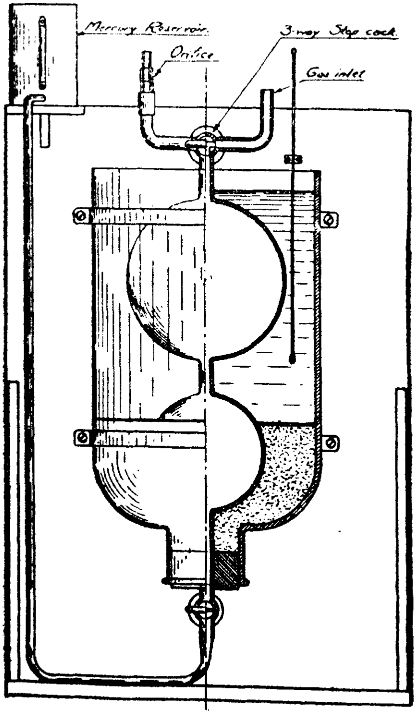

Plate 1

After the results of tests with air, carbon dioxide, and carbureted water gas were plotted on graph paper to show the variations in volumes of each of these gases with variations of pressure at the burner orifice, the reliability of density determinations with the effusion apparatus was seriously questioned. Repeated trials gave densities of:— 0.83 for carbureted water gas, 1.23 for carbon dioxide, and 0.75 for carbureted water gas diluted with 24% of hydrogen. The densities computed from gas analyses also showed rather widely different values. Furthermore the volumes of gases of various densities delivered through the burner orifice at the various pressures differed too widely from the computed volumes on the bases of the densities obtained by the effusion apparatus. It was quite apparent that a more reliable method for the determination of density would need to be found.

The second device used was a gas balance made after the description of J. R. Edwards, Bur. Stand. Tech. Paper No. 89 and shown here in Plate 2. Inside of a glass tube there is a sensitively mounted beam with a glass bulb sealed on one end; on the other end counterweights and a pointer are suitably mounted to balance the bulb. A scale is also mounted in the tube in such a position that the pointer on the beam moves freely in front of the graduations on the scale. A long "U" gauge suitably filled with mercury is connected with the glass tube in which the beam is mounted. The density of a gas is proportional to its pressure, and the buoyant force exerted upon a body suspended in a gas is proportional to the density and, therefore, to its pressure. Hence if the buoyant force exerted on a body is the same when suspended, successively in two or more gases, then the densities of the gases must be equal at these pressures. The density of two gases at normal pressure are inversely as the pressures when of equal buoyant force.

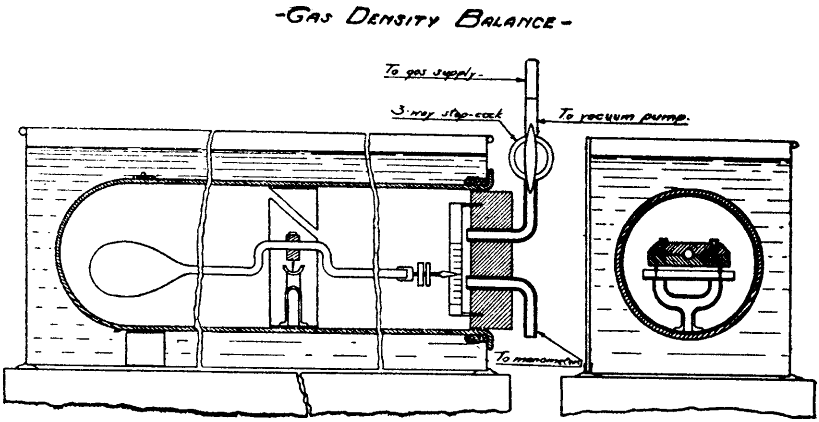

PLATE 2

The beam was first balanced with dry air in the balance case and the reading on the "U" gauge noted. The barometer reading was noted and the "U" guage pressure either added to or subtracted from the barometer pressure to determine the pressure of the buoyant air. The air was then evacuated and the gas under test, dried by calcium chloride, was admitted. The gas was then evacuated and flushed several times before the pressure in the balance case was adjusted to give the same buoyant force as air. At the point of equilibrim the "U" gauge was again read and the pressure added to or substracted from the barometer reading. The ratio of the pressures at the points of balance of the beam is the density of the gas. The average of three trials as described above was used for the density of the gas. Thus for carbureted water gas:—

Barometer ---------------- 740.0 m. m.
"U" for air -------------- 0.0
Pressure for air ------------------------- 740.0 m. m.
"U" for gas --------------- 271.7 m. m.
Pressure for gas = 740 + 271.7 = 1011.7 m. m.

$$\text{Density} = \frac{740.0}{1011.7} = 0.731.$$

In the following table are shown the results of determinations of density by the effusion method and by the gas density balance method.

Gas	Density — Effusion	Air=unity. Gas Balance
Hydrogen (com'l)	0.549	0.078
Carbureted water gas diluted with hydrogen	0.755	0.521
Carbureted W. Gas	0.837	0.682
Carbon dioxide	1.239	1.512

It is quite evident that this particular effusion apparatus does not give reliable data over a wide range of densities but might be sufficiently accurate for control work. The diameter of the orifice in the effusion apparatus was 0.35 m. m which is undoubtedly too large for the gases lighter than air and too small for gases heavier than air.

The burner orifice was of the type commonly used on gas stoves. A cap with an orifice in one end was screwed on over a pipe fitted with a sharp cone at the end. The apex of the cone fitted into the orifice of the cap so that by screwing the cap in or out the gas flow could be decreased or increased respectively. The orifice in the cap was really a channel whose dimensions are:—length = 0.084 inches, diameter = 0.118 inches, area = 0.010936 sq. in.

The results obtained in these tests are shown in graphical form in Plate 3. The volumes of gases delivered through the burner during a 10-minute interval are plotted as ordinates and the densities as abscissae for pressures of 1, 3, 5, 7, and 9 inches of water respectively.

Hydrogen was included in the gases tested, but the results were unreliable. It was practically impossible to get the piping tight to avoid loss of hydrogen, especially in the rubber tubing that had to be used on the gas meter. The data on hydrogen are therefore not included.

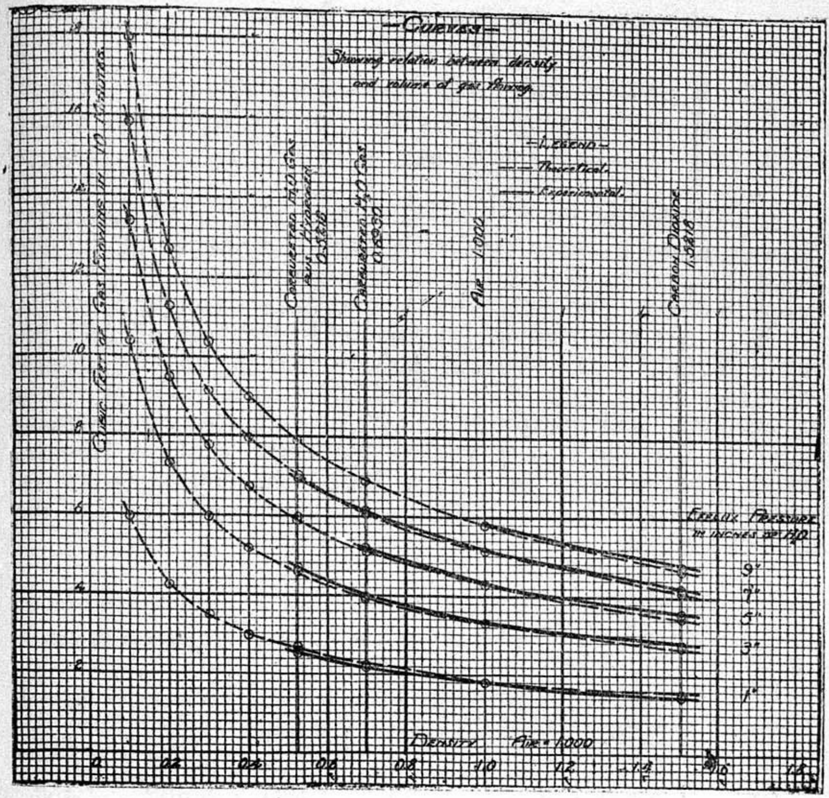

PLATE 3

The density of manufactured gas will vary from about 0.4 for coke oven or California oil gas to 0.7 for carbureted water gas. As can be seen from the graph, within the range from 0.4 to 0.7 the *rate* of *change* of slope is decidedly more rapid than for densities greater than 0.7. The higher the pressure the more rapidly does the volume delivered increase with changes toward the lighter density gases. Thus in a distribution system where the pressure does not exceed 3 inches of water, the change in volume of gas delivered by a change in density from 0.5 to 0.7 is smaller than in a system where the pressure is 9 inches of water.

The data shown in Plate 3 check very well with the theoretical volumes computed from the formula for the flow of gases from channel orifice:—

$$Q = 1658.5\ A\,K \sqrt{\frac{H}{d}}$$, (Bur. Stand. Tech. Paper 193.)

where:—

Q = cu. ft. gas flowing per hour.
A = Area of orifice in sq. in.
K = discharge coefficient for orifice.
H = discharge pressure at orifice in inches water.
d = density of the gas, (air = 1.0).

The discharge coefficient (K) was computed from the data obtained by passing air through the burner at various pressures. The average of determinations at 10 different pressures was the value used, and this was found to be 0.6264. Air was chosen for the determination of (K) because of the convenience and the fact that the data of several experimenters obtained at different times were in excellent agreement. The computed results are a little low for gases other than air but quite within the limits of experimental error. In the table below are listed the comparisons between the experimental values and those computed for the different gases.

Pressure inches of water	Carb. W. Gas diluted with hydrogen		Carb. Water Gas		Carbon dioxide	
	Observed	Computed	Observed	Computed	Observed	Computed
1	2.505	2.623	2.204	2.276	1.527	1.546
3	4.588	4.544	3.999	3.943	2.728	2.678
5	5.897	5.866	5.251	5.091	3.562	3.457
7	6.905	6.941	6.155	6.023	4.184	4.091
9	——	7.870	——	6.829	4.732	4.638

It thus appears that the flow of gases out of orifice on gas stoves can be determined accurately by applying the above formula. The reliability of the results will depend largely on the success in making accurate observations on the density of the gas.

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[FROM THE TRANSACTIONS OF THE AMERICAN ELECTROCHEMICAL SOCIETY, Volume XLV, 1924, being the Transactions of the Forty-fifth General Meeting, at Philadelphia, Pa., April 24, 25 and 26, 1924.]

A FURTHER STUDY OF THE DEZINCIFICATION OF BRASS

BY

CLEVELAND F. NIXON

A paper presented at the Forty-fifth General Meeting of the American Electrochemical Society, held in Philadelphia, Pa., April 25, 1924, Mr. S. Skowronski in the Chair.

A FURTHER STUDY OF THE DEZINCIFICATION OF BRASS.[1]

By Cleveland F. Nixon[2]

Abstract.

The presence of oxygen or of comparatively highly ionized copper in solution is necessary to initiate selective corrosion. The acetate, lactate, bromate, and perchlorate of copper do not promote dezincification. Brass is not the only alloy susceptible to "dezincification"; copper-aluminum (70-30), manganese-copper (25-75), and cadmium-magnesium (85.7-14.3) were found subject to selective corrosion. From experimental evidence it is concluded that, with the exception of 90 per cent, or more, copper alloys, the commercial brasses are subject to dezincification. Of the special alloy brasses tested arsenic brass and nickel brass are recommended for further study.

In a recent paper[3] Ralph B. Abrams explained the mechanism by which the dezincification of brass is accomplished. He came to the conclusion that the phenomenon of dezincification is not caused by the leaching out of the zinc, nor is it primarily the result of couples set up between the copper and zinc particles. Instead he found dezincification to be the result of the dissolving of the brass as a whole with the subsequent redeposition of the copper. Furthermore, he found that there is no dezincification whatsoever unless a membrane, either natural or artificial, is present to hold the copper-rich solution in contact with the brass.

It is the purpose of the present paper to build on the foundation Mr. Abrams has laid. Corrosion tests have been made upon the whole gamut of commercial brasses and bronzes, in an effort to discover a brass that is not susceptible to dezincification by sea

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[1] Manuscript received July 5, 1923.

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[3] Trans. Am. Electrochem. Soc., 42, 39 (1922).

water. Before taking up this phase of the investigation, however, it will be well to review some of the work done on 70-30 sheet brass from the same piece from which Mr. Abrams secured his specimens, and also on some specially made alloys, in order to bring out limitations of the rapid corrosion method, and to bring out more evidence in regard to the problem of selective corrosion.

ROLE OF OXYGEN IN DEZINCIFICATION.

The solutions used during the investigation, usually 150 to 250 cc. in volume, were contained in ordinary glass tumblers covered with watch glasses to minimize evaporation and to keep out dust. Since the type of corrosion which is particularly troublesome to users of brass is dezincification rather than corrosion as a whole, no attempt has been made to conduct quantitative tests.

The solutions given in Table I were boiled and sealed with oil to exclude oxygen.

TABLE I.

Action When Oxygen is Excluded.

Expt. No.	Time in days	Solution	Result
1	17	H_2SO_4—0.5*N* $CuSO_4$—0.5*N*	The dezincified specimen was covered with bright copper crystals and occasional areas of smooth brass skin. The dezincification was more extensive at the strained portion of the bent brass strip than at the unstrained portion.
2	17	HCl—0.5*N* $CuCl_2$—0.5*N*	Same as Exp. 1.
3	85	HCl—0.5*N* NaCl—0.5*N*	No dezincification whatsoever.

In experiment No. 3, at the end of 85 days, 5 cc. of hydrogen peroxide was introduced below the surface of the oil. Under this new condition appreciable dezincification occurred within 38 days. In other tumblers, using solution No. 3, it was found that the addition of only 1 g. cupric chloride or the bubbling of air through the solution produced a similar result.

Thus it is apparent that oxygen plays no part in the dezincification of brass in copper solutions, which is as would be expected. Copper is slowly deposited and brass, as such, goes into solution. In this respect the action resembles immersion plating.

However, in solutions which contain no copper, the action is different. The copper which is necessary to start dezincification is dissolved with an evolution of hydrogen. Since the discharge potential of hydrogen on brass is higher than the potential of brass itself, oxygen is needed as a depolarizer. Once started, however, the process of dezincification is capable of continuing without access of oxygen.

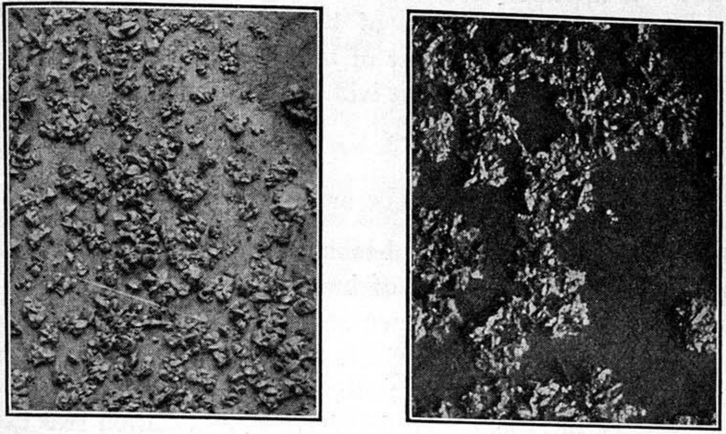

FIG. 1. FIG. 2.

Figures 1 and 2 show crystals of copper which form on the surface of brass during dezincification. These photographs are of samples of hard 70:30 brass, subjected to chemical corrosion in cupric chloride solution acidified by hydrochloric acid. The crystals consist of solid copper with a brilliant, metallic luster. Such crystals occur in both chemical and electrolytic dezincification of brass, in copper solution.

THE EFFECT OF VARIOUS COPPER SOLUTIONS.

Up to this time the only salts that had been used were the sulfate and the chloride. It was assumed that any soluble copper salt, since it is at least slightly ionized, would furnish copper to be deposited, and would therefore initiate dezincification.

To verify this assumption 70-30 sheet brass was subjected to the action of all the copper solutions available. Of these it was found, in addition to the sulfate and chloride, that the nitrate and the fluosilicate produce dezincification. But the acetate, cold or heated to 80° or 90°, the lactate, the acetate plus potassium bromate, and the perchlorate, all acidified with the corresponding acid, after 80 days, produced not the slightest trace of dezincification.

It was at first thought that this most unexpected difference in the effect of various copper solutions was due to a change of potential of copper with respect to brass, in the different solutions. Experiment showed that this was not the case; indeed the difference in potential between copper and brass is greater in acetate solution than in sulfate. It is noticeable that those salts which foster dezincification are, relatively speaking, excellent conductors, while those which do not dezincify brass are poor conductors. It appears, furthermore, that the degree of ionization influences selective corrosion of brass. Since copper may be plated electrolytically from any of these solutions, it is difficult to see why plating by immersion will not also take place when the opportunity to do so is offered.

THE SKIN OF BRASS.

Perhaps the most puzzling phenomenon encountered during this investigation was a thin skin of brass which appeared, with few exceptions, upon every specimen studied. As far as this skin is concerned, it is immaterial whether or not the solution used is chloride, sulfate, nitrate, or fluosilicate, whether copper is present in the solution or absent. To the above generalization two exceptions are to be noted—brass in cupric chloride plus potassium dichromate, and brass in cuprous chloride dissolved in a solution of magnesium chloride and hydrochloric acid. In these cases, corrosion as a whole as well as selective corrosion takes place. Where dezincification alone has occurred, and where the skin of brass is present, the original size and shape of the specimens are retained.

The skin itself is composed of shiny brass, sometimes easily peeled off and sometimes tightly adherent. It is very thin (estimated 0.0078 in. (0.02 mm.) or thinner) and is continuous except for places where crystals of copper occur. On some specimens crystals covered the entire surface exposed. These copper crystals grow up through small openings in the brass film and gradually spread over the surface; where the film has been thus covered it is usually eliminated by dezincification.

It has been suggested that this skin acts as a membrane which holds the copper solution in contact with the brass beneath, and so makes dezincification possible. But if this were true, the skin also should be destroyed, for such a corrosive solution may be expected to bore outward as well as in. The skin, it must be concluded, is, in electrical potential, or in some other unknown way, different from the rest of the brass.

SELECTIVE CORROSION OF ALLOYS OTHER THAN BRASS.

Monel Metal

Monel metal was subjected to the tests used in studying brass, namely chemical and electrolytic corrosion in acidified copper sulfate, acidified sea water, and acidified cupric chloride. In no case did selective corrosion take place, although the loss by ordinary corrosion was, in 224 days, 0.065 g. per sq. cm. in acidified sea water and 0.04 g. in copper sulfate. Monel metal undergoes no action comparable to the dezincification of brass, nor, it may be added, does German silver. These facts are easily explained by the fact that both Monel metal and German silver are lower in the scale of potentials than copper.

Special Alloys.

Several special alloys were made to determine whether or not the phenomenon of selective corrosion could be obtained with alloys other than brass. Theoretically, any solid solution made up of metals widely different in potential should, when placed in an appropriate solution, show "dezincification." As far as this conclusion was tested it proved to be true.

A copper-aluminum alloy containing 70 per cent copper and 30 per cent aluminum, though very brittle and highly crystalline, was found to be even more susceptible to selective corrosion than is brass. "De-aluminification" was induced by a solution of copper acetate and acetic acid. A manganese-copper alloy (25 per cent manganese and 75 per cent copper) was found to undergo selective corrosion in the same manner as does brass and aluminum-copper.

As a copper-free alloy which should undergo selective corrosion, an alloy of 85.7 per cent cadmium and 14.3 per cent magnesium was made. Two samples of this alloy, one unwrapped, the other swathed in several layers of filter paper were placed in an acidified solution of cadmium chloride and allowed to stand for 48 days, with the following result:

(a) The unwrapped specimen was found to be swelled completely out of shape. Originally, it was an inch (25 mm.) section of a half-inch (12.5 mm.) circular bar, but at the end of the experiment, it was almost spherical. Except for a small core of the original metal at the center, the entire mass was spongy, crumbly, black cadmium.

TABLE II.

High Copper Brasses and Bronzes.

Exp. No.	Time in Days	Composition Per cent	Dezincification	Remarks
1	17	Cu 90 Zn 10	None	Temper, soft; corrosion as a whole, considerable.
2	26	Cu 94.88 Zn 5.08 Pb trace Fe 0.04	None	Some corrosion.
3	33	Cu 92 Pb 8 Fe 0.25	None	Temper, soft (sheet). Specimen covered with layer of tightly adherent black copper oxide. Some corrosion.
4	33	Cu 92 Pb 8 Fe 0.25	None	Temper No. 6, hard (sheet). Specimen covered with layer of tightly adherent black copper oxide. Some corrosion.
5	48	Cu 88 Sn 10 Zn 2	None	Gun metal; this specimen was also run in acidified $CuSO_4$, and electrolytically in sea water, with the same effect. Slight corrosion.
6	46	Cu 90 Fe 2 Al 8	None	Ampco bronze (sheet). Much corrosion. Also run electrolytically with similar results.

(b) The original shape of the wrapped sample was preserved. On unwrapping, it was found that a few gray crystals had grown up through a small break in the paper, just as copper crystals grow up through the brass skin. The specimen itself was covered

TABLE III.

Copper-Zinc Brasses.

Exp. No.	Time in days	Composition Per cent	Temper and Form	Dezincification	Remarks
7	28	Cu 80 Zn 19.84 Fe 0.04 Pb 0.1	Hard sheet	None.	A black powder on the specimen, probably copper oxide. Some corrosion.
8	26	Cu 79.55 Zn 20.40	Soft rod	In sections.	Black powder on specimen.
9	26	Cu 79.00 Zn 20.95	Hard sheet	Thin, tightly adherent copper film.	No oxide or brass film on surface of specimen.
10	33	Cu 60.00 Zn 39.19 Fe 0.09	Soft sheet	Copper crystals and a loose, continuous jacket of copper.	The copper deposit readily peeled off, showing pitted yellow brass beneath.
11	33	Cu 61.00 Zn 38.88 Pb 0.07 Fe 0.05	Hard rod	Some.	The original surface of the brass is very resistant to corrosion. All the dezincification took place at the sawed ends.
12	33	Cu 61.50 Zn 38.24 Pb 0.21 Fe 0.09	Hard rod	Some at ends as before.	The specimen was also run in acidified $CuSO_4$. At the end of 63 days the piece was covered with dense copper crystals and brass skin, under which was considerable redeposited copper.
13	30	Cu 63.00 Zn 36.88 Pb 0.07 Fe 0.05	Hard tube	Unaffected save on outside edges.	Was also tested in acidified $CuSO_4$ solution with a result similar to that obtained in the case of Exp. 12. The copper solution was much paler blue at the end of the test than at the beginning.
14	30	Cu 65.50 Zn 34.23 Pb 0.21 Fe 0.06	Hard sheet	Copper crystals.	The brass skin was over about 0.02 mm. of re-deposited copper.
15	30	Cu 69.96 Zn 29.99	Hard rod	Fine crystals; very little dezincification.	
16	33	Cu 61.74 Zn 38.16 Pb 0.10 Fe 0.04	Soft rod	Faint trace on ends.	The protective action of the tough outer layer was particularly noticeable in this specimen.

with gray metallic crystals, and partially, by the original shiny surface. This shiny surface was only a film easily removed, showing a black amorphous material below.

Three things are noteworthy here. First, there is a skin effect, such as is observed in the dezincification of brass; second, the action is much more rapid than in the case of brass; and third, the effect of the membrane is to retard the action, rather than to speed it up as is the case with brass. This last may be explained only by assuming that the close packing of the redeposited metal enforced by the artificial membrane retarded the passage of solution into the metal. This reasoning, carried further, will explain why brass corrodes so much more slowly than the magnesium-cadmium alloy. Re-deposits of copper are, as a rule, quite dense and continuous; seepage through this material is necessarily, therefore, a slower process.

TABLE IV.

Leaded Brasses.

Exp. No.	Time in days	Composition Per cent.	Temper and form	Dezincification	Remarks
17	12	Cu 60.00 Zn 37.50 Pb 2.50		Dense continuous copper envelope.	Electrolytically as anode in sea water. Current density 0.3 amp./sq. ft. (0.03 amp./sq.dm.) No brass skin.
18	30	Cu 65.50 Zn 33.32 Pb 1.12	Hard sheet	Along edges, but only a few crystals on surface.	The tough outer layer of brass affords protection against corrosion.
19	30	Cu 67.75 Zn 31.06 Pb 1.13	Soft sheet	Along edges, but only a few crystals on surface.	Evidently the effect of heat treatment is here very slight.
20	32	Cu 63.75 Zn 34.19 Pb 2.00	Soft rod	Along edges, but only a few crystals on surface.	
21	32	Cu 63.75 Zn 34.19 Pb 2.00	Hard rod	No dezincification appreciable.	Here temper seems to have some influence.

Thus it may be seen that brass is by no means the only alloy which undergoes selective corrosion. However, all alloys which are subject to "dezincification" have one property in common. They may be said to contain within themselves the seeds of their own destruction. That is, one of the salts formed by corrosion turns about and attacks the original alloy.

TABLE V.

Commercial Tin-Brass.

Exp. No.	Time in days	Composition Per cent	Temper and Form	Dezincification	Remarks
22	83	Cu 60 Zn 39 Sn 1		Slight but uniform coat of copper over entire specimen.	Naval brass. Result verified by using as anode in sea water.
23	123	Cu 70 Zn 29 Sn 1	Light annealed	The merest trace of dezincification.	Admiralty brass. Result also checked by using as anode in sea water.
24	33	Cu 62 Zn 37 Sn 0.75 Fe 0.08	Hard tube	A few copper crystals on the surface of the metal, but that is all.	
25	30	Cu 62 Zn 37 Sn 0.75 Fe 0.08	Soft tube	Much of the specimen has completely corroded away, but especially toward the bottom of the piece there is considerable dezincification.	This specimen and specimen 24 are identical in composition. Annealing in this case effects an increase in dezincification.

COMMERCIAL BRASSES AND BRONZES.

All of the experiments recorded in Tables II, III, IV and V are chemical corrosion tests in a solution half normal to both hydrochloric acid and sodium chloride, unless otherwise stated.

It is seen from Table III that ordinary brasses succumb uniformly to dezincification.

It is evident from Table IV that, as far as dezincification is concerned, the presence of one or two per cent of lead is immaterial. The results recorded in Table IV, and for straight brasses, in Table III, are almost identical.

The tin brass stands up better, perhaps, than any of the other brasses, but still leaves much to be desired. There is no commercial brass that, from our tests, could be expected to stand up indefinitely without dezincification. The next step, therefore, was to attempt to secure an alloy that would resist dezincification. The first of these to be considered is nickel brass.

TABLE VI.

Nickel Brass.

Exp. No.	Time in days	Solution	Per cent Nickel	Dezincification
26	27	$0.5N HCl$; $0.5N NaCl$	4	None
27	27	Acidified $CuSO_4$	4	None
28	12	Electrolytically, as anode, in sea water	4	None
29	27	$0.5N HCl$; $0.5N NaCl$	8	None
30	27	Acidified $CuSO_4$	8	None
31	12	As anode in sea water	8	None

NICKEL BRASS.

Attention was drawn to nickel brass by the fact that German silver, (Ni 18 per cent, Cu 64 per cent, and Zn 18 per cent) resisted all efforts to bring about dezincification. Two alloys were therefore made with copper and zinc in the ratio of 60-40, one containing 6 per cent nickel, and the other 4 per cent nickel. These were subjected to chemical corrosion in the hydrochloric acid and salt solutions, with the results shown in Table VI.

These results are promising. Since there was not the slightest indication of dezincification in any case, it is probable that the percentage of nickel can be further cut down without altering the resistance of the alloy to dezincification. This will be an interesting alloy to study further.

SILICON BRASS.

It was thought that silicon might prevent the dezincification of brass. So two alloys, one containing 1 per cent and the other 2.5

per cent, of silicon were made from 70:30 brass and the element silicon. These alloys were tried out in all the standard solutions, both chemically and electrolytically, and appear to be on a par with tin-brass in regard to dezincification, except for this curious fact: for silicon brass, acid chloride solution is without effect while copper sulfate is very corrosive. In the case of the tin-brass this is reversed. The tin alloy is more susceptible to the action of the hydrochloric acid-salt solution, but withstands the action of sulfate solutions for days without visible change. Silicon brass should prove useful in sea water if its physical properties are acceptable.

ANTIMONY BRASS.

A brass containing less than 0.5 per cent of antimony was tested, but found to be of no value. Antimony in this quantity has practically no influence upon dezincification. The attempt to utilize antimony was inspired by the fact that arsenic brass proved to be so remarkably resistant.

TABLE VII.

Arsenic Brass.

Solution	Time in Days	Dezincification
0.5*N* NaCl 0.5*N* HCl	85	None
0.5*N* $CuSO_4$ 0.5*N* H_2SO_4	29	None
Acidified $CuSO_4$	32	None
Sea water, as anode	12	None

ARSENIC BRASS.

Following the suggestion of G. D. Bengaugh and R. May in a communicated discussion of Abrams' paper on the dezincification of brass, an alloy containing less than 0.3 per cent of arsenic was made up; the results, recorded in Table VII, were remarkable.

It is evident that arsenic plays a remarkable part here, as it does in many other cases. A slight addition of arsenic to a dilute solution of sulfuric acid will nearly stop the corrosion of iron in this solution. By dipping iron or steel into a solution of arsenic in dilute hydrochloric acid, deposition by immersion of copper from a solution of copper sulfate will be stopped.

From the above experiments it is apparent that a small fraction of one per cent of arsenic in brass will greatly retard, if not completely prevent, dezincification. While this beneficial effect is explainable where hydrogen is evolved in corrosion, in the case of brass the mechanism is not apparent.

In the preparation of this paper, indebtedness is acknowledged to E. D. Coleman, who started this investigation, to William Price, chief chemist of the Scovill Co., Waterbury, Conn., for his cooperation in furnishing samples of some thirty commercial brasses; and especially to Professor O. P. Watts, without whose suggestions and guidance this paper would never have been written.

CONCLUSION.

1. Oxygen or an appropriate copper salt in solution is essential to start the dezincification of brass.

2. Solutions of copper acetate and other slightly ionized salts do not incite the dezincification of brass.

3. Monel metal and German silver proved entirely resistant to selective corrosion. This finding is corroborated by experience. Monel has been used extensively and successfully for marine fittings.

4. The condition of the surface is an important factor in dezincification. Whether or not the surface offered to corrosion is the original cast or rolled surface, or has been recently fractured, filed or cold-worked, sometimes determines whether or not dezincification will occur.

5. Brass, though the only commercial alloy subject to dezincification, is by no means the only alloy susceptible to this type of corrosion.

6. The rate of dezincification is dependent to a considerable extent upon the porosity of the redeposited metal.

7. All alloys tested containing above 90 per cent of copper were not subject to dezincification, no matter what constituents made up the other 10 per cent.

8. In general, commercial brasses are all subject to dezincification; heat treatment and the presence or absence of the beta constituent are only minor details. Tin, however, slows down the action to a considerable extent.

9. Antimony brass is of little use in resisting dezincification; silicon is beneficial in slowing down selective corrosion in sea water; while nickel and arsenic brasses appear promising, and are worthy of special study.

DISCUSSION.

C. H. ELDRIDGE[4]: In the past year we made some observations that check Mr. Nixon's statement that other alloys besides brass are susceptible to this selective corrosion or dezincification. While working with specimens of ancient bronze and silver, for the Metropolitan Museum in New York, we studied two ancient bracelets covered with a hard, green, oxy-chloride crust and classified as bronze. On removing the crust we brought to light a smooth, white metallic core, which proved to be silver.

It seems that the copper, alloyed with the silver as a hardener, had migrated outward under the corrosive influences of the moist soil, and the final product was a spongy silver core covered with a high copper crust. One bracelet, when finished, was about the size of a lead pencil and was hard and strong. The other bracelet was completely decuperized, leaving a soft, spongy core of silver with no ductility or mechanical strength. I remember to my disappointment that I tried to bend it a little, but it snapped like a pipe stem. Thus we have two cases where sterling silver or copper-silver alloys will undergo selective corrosion.

COLIN G. FINK[5]: It is only by the removal of the green copper crust, by a new process which we devised, that we find the silver and observe that the copper in the alloy has moved outwards, leaving the silver behind. Whether or not the separation of the copper from the silver takes place in two stages, whether

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[4] Research Metallurgist, Metropolitan Museum of Art, New York City.

[5] Head, Division of Electrochemistry, Columbia Univ., New York City.

or not both the copper and the silver go into solution first and the silver is then precipitated out again, or whether it is merely the copper going into solution and forming the crust, we really do not know. Personally, I am inclined to believe that both metals go into solution and that metallic silver is precipitated out as a secondary reaction. At all events, as Mr. Eldridge said, the decuperization of our copper-silver alloy fits in nicely with Mr. Nixon's study of the dezincification of brass.

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

EFFECT OF REDUCED PRESSURE ON RATE OF CORROSION OF AMALGAMATED ZINC IN ACID AND IN ALKALI SOLUTIONS.[1]

By E. W. Greene and O. P. Watts.[2]

Abstract.

There is a definite acceleration of the corrosion of amalgamated zinc in sulfuric acid by a vacuum. This acceleration is effected either with or without air in the solution. There is a retardation of the corrosion of amalgamated zinc in sodium hydroxide by a vacuum. This retardation takes place with or without air in the solution, but is greatest with the air present. There is a retardation of the corrosion of lead in acetic acid by a vacuum. This retardation is effected with or without air in the initial solution, but is greatest with the air excluded.

Carhart,[3] in his book on "Primary Batteries," makes this statement: "When amalgamated zinc is plunged in water, acidified with one-twentieth of its volume of sulfuric 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 air, bubbles again adhere to the plate, and the chemical action is arrested." He considered this as evidence that a vacuum accelerates corrosion by removing a film of polarizing hydrogen.

In investigating the corrosion of metals by acids, O. P. Watts and N. D. Whipple[4] questioned the statement of Carhart, and in order to disprove it they tested the relative corrosion of several metals under a vacuum and at atmospheric pressure. In every

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[1] Manuscript received July 2, 1924.

[2] University of Wisconsin, Madison, Wis.

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

[4] Trans. Am. Electrochem. Soc., 32, 257 (1917).

case they found that the effect of the vacuum was to retard corrosion. The results of these experiments are reproduced in Table I, as they directly bear on the subject in hand. In explaining their results these investigators attributed the retarding effect of the vacuum as being due to the removal of depolarizing air from the solution. They did not, however, test amalgamated zinc, about which Carhart had made his statement.

TABLE I.

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

In vacuum, 2.4 to 3.5 cm. of mercury.

No.	Reagents Used	Loss in g.
107	Fe N H_2SO_4 190 cc.	0.7332
108	Fe N H_2SO_4 190 cc., 0.25 g. Na_3AsO_4	0.0083
109	Pb N CH_3COOH 190 cc.	0.0374
110	Cu N H_2SO_4 190 cc.	0.0044
111	Zn N NaOH 190 cc.	0.0101

At Atmospheric Pressure.

No.	Reagents Used	Loss in g.
112	Fe N H_2SO_4 190 cc.	1.6266
113	Fe N H_2SO_4 190 cc., 0.25 g. Na_3AsO_4	0.0287
114	Pb N CH_3COOH 190 cc.	0.0841
115	Cu N H_2SO_4 190 cc.	0.0208
116	Zn N NaOH 190 cc.	0.0772

In these investigations it was recognized that possibly both Carhart and the later experimenters were right, and that the vacuum might produce two opposite effects on the rate of corrosion: (1) Accelerate corrosion by partially removing the adhering film of polarizing hydrogen; (2) Retard corrosion by removing the depolarizing oxygen from the solution.

If oxygen was removed from the corroding solution by boiling, and was kept out by a layer of oil on the surface of the solution, the retarding effect of the vacuum would be eliminated, and the vacuum should accelerate corrosion by removing the hydrogen.

Accordingly, in the first set of data four specimens were put in boiled $2N$ H_2SO_4, and the surface of the acid was covered with 0.125 to 0.250 in. (3.18 to 6.35 mm.) of gas-engine lubricating oil. Two of these were put under the vacuum obtained from a laboratory filter pump, and two were left under atmospheric pressure. At the same time the total effect of the vacuum was investigated by placing four specimens in unboiled acid with no oil on the surface, and putting two of these in the vacuum, and leaving two at atmospheric pressure. Amalgamated zinc was used, because this had not been used by recent investigators, and because it was referred to by Carhart. The result is shown in Table II.

TABLE II.

Corrosion of Amalgamated Zinc by 2N Sulfuric Acid.

Temp. 25° C., time 116 hr. Zinc slightly amalgamated electrolytically, area 7.5 sq. cm. Volume of acid 300 cc.

No.	Pressure	Treatment	Covering	Loss in g.
1	Atmosphere	None	None	0.3882
2	Atmosphere	None	None	0.3886
3	10 cm. Hg	None	None	0.3991
4	10 cm. Hg	None	None	0.3854
5	Atmosphere	Boiled	Oil	0.0545
6	Atmosphere	Boiled	Oil	0.0300
7	10 cm. Hg	Boiled	Oil	0.0678
8	10 cm. Hg	Boiled	Oil	0.0989

Specimens 1, 2, 3, 4 show a slight acceleration of corrosion under the vacuum, but within experimental error. It must be concluded that the vacuum either has no effect, or that the accelerating and retarding effects counterbalance each other.

In the case of the specimens where the air was removed by boiling (5, 6, 7, 8) the vacuum causes from 24 per cent to 230 per cent more corrosion. Therefore, it would seem that the effect of the vacuum on the hydrogen film was such as to increase the corrosion.

In the first test it was noticed that some of the specimens were corroding unevenly—bubbles of hydrogen gas were unevenly distributed over the surface. This may have been due to insufficient amalgamation. The second test was run on the same specimens amalgamated by rubbing the mercury in. In this second test two specimens were put in boiled acid with no oil on the surface, and put under the vacuum to determine the effect of the oil. See Table III.

A comparison of specimens 9 and 10 with 15 and 16 shows that even under the vacuum the effect of the oil in keeping out oxygen and preventing its depolarizing action is great. Specimens 11 and 12 show that the resulting effect of the vacuum is to increase corrosion. It should be noted that the corrosion is greater under the vacuum, even in the case of the boiled specimens 9 and 10. The effect of the vacuum when the air is excluded from the solution by oil is uncertain, because specimens 13, 14, 15 and 16 lead to no conclusions. The large discrepancy between specimens 15 and 16 could not be accounted for, unless there was faulty amalgamation of 16.

TABLE III.

Corrosion of Amalgamated Zinc by 2N Sulfuric Acid.

Condition as in Table II, except that the zinc was amalgamated by rubbing with mercury, and the time was 142 hr. and the vacuum only 18 cm. of mercury.

No.	Pressure	Treatment	Covering	Loss in g.
9	18 cm. Hg	Boiled	None	0.6988
10	18 cm. Hg	Boiled	None	0.6611
11	Atmosphere	None	None	0.5603
12	18 cm. Hg	None	None	0.7628
13	Atmosphere	Boiled	Oil	0.0118
14	Atmosphere	Boiled	Oil	0.0158
15	18 cm. Hg	Boiled	Oil	0.0094
16	18 cm. Hg	Boiled	Oil	0.0155

At this point it was decided to use a pure metal, such as lead, for the purpose of obtaining more uniform results, and to see if the results checked those obtained with the amalgamated zinc. Pure "test lead" in thin sheets was used. The object of the thin sheets was to increase the accuracy by increasing the proportion of surface to weight. As the effect of the vacuum with no air present was the principal result wanted, twelve specimens were put in boiled acid with oil. Four more were used in unboiled acid to determine the effect of the vacuum alone. The results are shown in Table IV.

The result of this test are exactly opposite to the experiments with amalgamated zinc, and as they are remarkably uniform they may be considered fairly reliable. Instead of increasing corrosion, as in specimens 5 and 6, the effect of the vacuum alone is about the same as boiling the solution and then excluding the air by oil, *viz.*, a reduction of corrosion to 35 per cent. The placing

TABLE IV.

Effect of Diminished Pressure on Corrosion of Lead by N Acetic Acid.

Temp. 16-29° C. Time 285 hr. Surface exposed 37 sq. cm. Volume of acid 300 cc.

No.	Pressure	Treatment	Covering	Loss in g.
17	Atmosphere	Boiled	Oil	0.1261
18	Atmosphere	Boiled	Oil	0.1061
19	Atmosphere	Boiled	Oil	0.1062
20	Atmosphere	Boiled	Oil	0.1040
21	Atmosphere	Boiled	Oil	0.1096
22	Atmosphere	Boiled	Oil	0.1058
23	10 cm. Hg	Boiled	Oil	0.0108
24	10 cm. Hg	Boiled	Oil	0.0124
25	10 cm. Hg	Boiled	Oil	0.0145
26	10 cm. Hg	Boiled	Oil	0.0145
27	10 cm. Hg	Boiled	Oil	0.0187
28	10 cm. Hg	Boiled	Oil	0.0165
29	Atmosphere	None	None	0.2734
30	Atmosphere	None	None	0.3285
31	10 cm. Hg	None	None	0.1175
32	10 cm. Hg	None	None	0.1017

TABLE V.

Effect of Diminished Pressure on Corrosion of Amalgamated Zinc in N Sodium Hydroxide.

Temp. 16-29° C. Time 285 hr. Surface exposed 15 sq. cm. Volume of solution 300 cc.

No.	Pressure	Treatment	Covering	Loss in g.
33	Atmosphere	Boiled	Oil	0.0200
34	Atmosphere	Boiled	Oil	0.0210
35	10 cm. Hg	Boiled	Oil	0.0080
36	10 cm. Hg	Boiled	Oil	0.0063
37	Atmosphere	None	None	0.0451
38	Atmosphere	None	None	0.0448
39	10 cm. Hg	None	None	0.0142
40	10 cm. Hg	None	None	0.0126

of this last solution under a vacuum reduces corrosion still further to only 4 per cent of its initial value.

In order to determine if this effect of a vacuum is confined to acids only, amalgamated zinc specimens were corroded in normal alkali. The results, which are recorded in Table V, do not agree

TABLE VI.

Effect of Time on Corrosion of Amalgamated Zinc in 2N Sulfuric Acid.

Time 107 hr. Temp. 18-24° C. Surface exposed 15 sq. cm.

No.	Pressure	Treatment	Covering	Loss in g.
41	Atmosphere	Boiled	None	0.0707
42	Atmosphere	Boiled	None	0.0812
43	Atmosphere	Boiled	None	0.1127
44	Atmosphere	Boiled	None	0.0851
45	10 cm. Hg	Boiled	None	0.1075
46	10 cm. Hg	Boiled	None	0.3066
47	10 cm. Hg	Boiled	None	0.1448
48	10 cm. Hg	Boiled	None	0.1147

TABLE VII.

Effect of Time on Corrosion of Amalgamated Zinc in 2N Sulfuric Acid.

Time 43 hr. Temp. 18-27° C. Other conditions as in Table VI.

No.	Pressure	Treatment	Covering	Loss in g.
49	Atmosphere	Boiled	None	0.0279
50	Atmosphere	Boiled	None	0.0316
51	Atmosphere	Boiled	None	0.0330
52	Atmosphere	Boiled	None	0.0294
53	11 cm. Hg	Boiled	None	0.0320
54	11 cm. Hg	Boiled	None	0.0373
55	11 cm. Hg	Boiled	None	0.0350
56	11 cm. Hg	Boiled	None	0.0367

with those obtained with amalgamated zinc in acid. With unboiled solutions the vacuum reduces corrosion 30 per cent, and is more effective than boiling and covering the solution with oil. The combined effect of boiling, covering with oil and subjecting to reduced pressure is to lower corrosion to only 1.6 per cent of the loss in the original solution.

Two other tests were run on the amalgamated zinc specimens in acid, boiled and with no oil on the surface, the object being to check the results shown by specimens 9, 10, 11 and 12, namely, that the corrosion of amalgamated zinc is accelerated by the vacuum. These results appear in Tables VI and VII, and verify the results mentioned above. The test recorded in Table VII was run for a comparatively short time to see if cutting down the amount of corrosion would render the results more uniform.

The experiment recorded in Table VI (omitting specimen 46) shows 58 per cent more corrosion under the vacuum than at atmospheric pressure. The experiment recorded in Table VII shows 15 per cent more corrosion under vacuum. The rate of corrosion has evidently increased with time. This may be due either to increase of surface as the specimen becomes roughened by corrosion, or to diffusion of mercury from the surface into the zinc, which was 0.165 cm. (0.065 in.) thick, so that the concentration of the protective mercury on the surface became less, or to the combined effect of both of these actions.

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

THE CORROSION OF IRON ALLOYS BY COPPER SULFATE SOLUTION.[1]

By C. M. KURTZ and R. J. ZAUMEYER.[2]

INTRODUCTION.

By OLIVER P. WATTS.

A number of years ago, when a specimen of duriron first came into the hands of the writer, one of the first tests of its resistance to corrosion was to see if a bright and adherent electroplate could be obtained on it from an acidified solution of copper sulfate. Although iron and steel are so vigorously attacked by this solution that a good electroplate is not obtainable, the duriron sample was as readily plated as if it had been brass or copper. A few years later when stainless steel came on the market the writer found this also to be unattacked by a solution of copper sulfate. This simple test thus served to differentiate these two materials of known resistance to corrosion from the long list of alloy steels.

It was therefore thought that the application of this test to a large number of iron alloys might serve to divide the alloying elements into two groups, those which confer distinct resistance to corrosion, and those which are unpromising, and may be rejected when attempting to render iron resistant by alloying. Such tests were carried out by two seniors in the chemical engineering department of the University of Wisconsin three years ago, but the results were not published at the time, because of the hope that a series of corrosion tests of the same alloys in acids could be carried out. As there is no prospect that this can be done in the immediate future, their report is now presented as a possible aid to those who are experimenting to render iron and steel resistant to corrosion by alloying.

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[1] Manuscript received July 2, 1924.

[2] Dept. of Chem. Engineering, Univ. of Wisconsin, Madison, Wis.

A striking feature of the tests was the effect of even the smallest speck of fire-scale (black oxide) on the surface or in crevices, which invariably served as a starting point for the deposition of copper. This indicates the reason for the insistence by manufacturers of stainless steel upon a perfect surface, free from flaws. Another salient fact is the superiority of chromium over all other alloying elements, so far as used in these alloys. Invar, an iron alloy containing 36 per cent of nickel, is reported to be resistant to rusting and corrosion, yet the writer has spent much time during the past year in the attempt to find some element that can be added to invar and prevent its destruction by corrosion in a certain commercial use, without impairing its unique temperature coefficient of expansion. The copper sulfate test, which requires over 45 per cent of nickel alloyed with iron for effective resistance, proves to be a more reliable guide in this case than the published and supposed-to-be authoritative statements about invar.

While some of the authors' conclusions rest on a narrow foundation, and may be disproved by later and more extensive experiments, the data which they present are of permanent value. It should be noted that these tests were applied only to forgeable alloys of iron.

ABSTRACT.

Samples of 400 different forgeable iron alloys were subjected to the copper sulfate test. Those alloys containing chromium appeared the most resistant. Silicon was also found to be very effective. With certain alloys corrosion resistance was greater after heating the samples to redness and quenching in water. Tests at 93° C. were practically the same as those at room temperature.

[C. G. F.]

There are several methods in use at the present time for testing the corrodibility of alloys. The commonest one is the sulfuric acid test, which consists in immersing the specimen in the acid for several hours and determining the loss in weight. Another test is the salt spray test. In this, the specimen is enclosed for a number of days in a small box in which the atmosphere is kept saturated with a solution of sodium chloride. As in the acid test, the loss in weight serves as an indication of the corrodibility. The third method, the one which was employed in this series of tests, is the immersion of the specimen in the solution of copper sulfate. It is a well-known fact that iron and some of its alloys, when immersed in a solution of copper sulfate, will cause copper to deposit on the surface of the metal. On the other hand, it has been found that certain other alloys, such as duriron and stainless steel, which are unusually resistant to corrosion, do not deposit copper from a sulfate solution. The application of this test to many different alloys should afford a means of determining the combinations and proportions of different elements which are likely to yield corrosion-resisting materials. This test has one decided advantage over those mentioned above, in that it gives almost immediate results.

During the course of 'the investigation, nearly four hundred alloys prepared from electrolytic iron were subjected to the copper sulfate test. These alloys had been made up a number of years before, in an investigation financed by the Carnegie Institution, for the purpose of obtaining data concerning certain physical properties. Most of the specimens were forgings which had been made from such small ingots that a considerable amount of scale had become included in the metal at the time of forging. A small portion of each specimen was ground free from scale, and a drop of copper sulfate placed on a part of the clean surface. The solution used was exactly normal in copper sulfate and about 0.07 *N* in sulfuric acid. Those specimens on which copper deposited readily were discarded, and those on which no copper deposited were set aside for further treatment. Those on which copper deposited slowly, and which were apparently on the border line, were saved for special heat treatment.

Of all the alloys tested, those containing chromium appeared to be the most resistant. When chromium was the only added constituent, at least 10 per cent was required to resist the action of copper sulfate. Silicon was also found to be very effective. Nickel is effective provided there is 6 per cent or more chromium present. Ten per cent nickel made a 7 per cent chromium alloy resistant. In another case, 14 per cent nickel was found to be effective with a 6 per cent chromium and 1.5 per cent silicon. This would indicate that if there is 6 per cent chromium present,

TABLE I.

Action of Copper Sulfate on Alloys Containing Chromium.

Composition (Per Cent)				Other Elements (Per Cent)	Action		
No.	Cr	Si	Ni		I	II	III
133H	0.5	0.5	..	....	D	..	..
133I	1	0.5	..	....	D	..	..
137A	1	...	..	....	D	..	..
133A	2	0.6	..	....	D	..	..
137B	2	...	..	....	D	..	..
144Z	2	...	10	....	D	..	..
150B	2	...	..	10 W, 10 Mo, 0.5 V. 0.40 C	D	D	..
155U	2	...	..	10 W	D	..	..
133J	3	0.5	..	....	D	..	..
133D	3	0.8	..	....	D	..	..
156F	3	...	8	....	D	..	..
133E	4	1.1	..	....	D	..	..
137C	4	...	..	....	D	..	..
136M	5	1.0	..	4 Mo, 3 Mn	D	D	..
133B	5	1.4	..	....	D	..	..
133X	5	1.5	..	12 Mn	D	..	..
136O	5	1.5	..	4 Mo, 12 Mn	D	D	..
160J	5	...	..	0.3 V	D	..	..
160H	5	...	..	0.5 V	D	..	..
160K	5	...	..	1. V	D	..	..
163A	5	...	..	2 W, 0.60C	D	D	..
163G	5	...	..	5 W, 0.60 C	D	..	..
154E	5	...	10	....	D	D	..
133K	6	0.4	..	....	D	..	..
133L	6	0.4	..	....	D	..	..
136A	6	1.5	14	....	ND	..	ND
147Z	6	1.3	..	....	D	D	..
133F	6	1.7	..	....	D	D	..
133T	6	4	..	....	D	D	..
136D	6	...	..	....	D	..	..
148A	6	...	..	18 W, 0.3 V, 0.40 C	ND	..	D
154F	7	...	10	....	ND	..	ND
163B	7	...	..	3 W, 2 Mo	D	ND	..
126B	7.2	3	..	9 W	ND	..	ND
137E	8	...	..	....	D	D	..
133M	8	1	..	....	D	ND	..
136R	8	1	20	....	ND	..	ND
133C	8	2.3	..	....	D	ND	..
133Q	8	4.5	..	? C	D	D	..
121C	9.7	1.9	..	0.31 C	ND	..	..
144U	10	...	..	....	ND	..	ND
146H	10	...	..	....	ND	..	..
154H	10	1	10	....	ND	..	ND
1-30-20	10	1.5	..	10 W, 5 Mo	ND	..	..
111S	10	2	..	....	ND	..	ND
155K	10	2	..	0.3 V, 0.60 C	D dep slowly (CHA)	D dep slowly (CHA)	D- slowly

TABLE I—*Continued*

Action of Copper Sulfate on Alloys Containing Chromium.

Composition (Per Cent)				Other Elements (Per Cent)	Action		
No.	Cr	Si	Ni		I	II	III
137L	10	2	..	2 Ti	ND	..	..
146L	10	2	20	....	ND	..	ND
146Z	10	2	..	20 W	ND	..	..
156P	*10*	*2*	..	2 W, 2 Mo, 0.3 V	ND	..	ND
154I	10	2	10	....	ND	..	ND
122E	10	3	..	....	ND	..	ND
126A	10	3	..	5 W	ND	..	ND
113Q	*10*	*4*	..	....	ND	..	ND
112A	*10*	*5*	..	....	ND	..	ND
133R	10	6	..	....	ND	..	ND
154A	10	...	8	....	ND	..	ND
154B	10	...	12	....	ND	..	ND
156H	10	...	..	2 W, 0.3 V, ? C	ND	..	Slow
156I	10	...	..	2 W, 0.3 V, 0.60 C	D	ND	D
156J	10	...	..	2 W, 0.3 V, 0.60 C	D	ND	..
155R	10	...	..	5 Mo	ND	..	ND
155V	10	...	..	10 W	ND	ND	ND
155S	10	...	..	10 Mo	ND	..	..
154K	10	...	10	1.0 C	D	D	D
155L	10	...	..	0.3 V, 0.65 C	D	ND	..
160I	10	...	..	0.3 V	ND	..	ND
160G	10	...	..	0.5 V	ND	..	ND
163O	10	...	..	1.0 V	ND	..	D
156G	10	...	..	2 W, 2 Mo, ? C	Spots	ND	..
141C	10.3	2	..	1.0 V, 0.30 C	ND	..	Spots
136G	13	...	..	....	ND	..	..
133O	13	0.5	..	....	ND	..	..
133N	13	1.8	..	....	ND	..	ND
133G	13	3.6	..	....	ND	..	ND
133U	13	5.5	..	....	ND	..	ND
141E	15	2	..	....	ND	..	ND
5-25-20C	15	1	1	0.3 Mn, 1.0 C	ND	..	..
137H	16.2	...	..	....	ND	..	..
136H	17	...	1.5	....	ND	..	ND
137S	20	1	10	0.3 V	ND	..	..
136L	20	1	..	3 Mn	ND	..	ND
141G	21.4	1	..	1.0 V, 3 Mn	ND	..	..
141B	21.8	...	..	....	ND	..	ND
136U	30	...	..	....	ND	..	ND

the addition of 3 to 4 per cent of nickel is equivalent to 1 per cent chromium. Tungsten, added to 6 per cent chromium, is also effective. Eighteen per cent tungsten, together with 6 per cent chromium, produced an alloy which was apparently on the border line, showing that 4.5 per cent of tungsten is equivalent to 1 per cent of chromium. This is further supported by the fact that 9 per cent tungsten added to an alloy containing 7.2 per cent chromium and 3 per cent silicon made it resistant, whereas it would have deposited copper without the tungsten. Molybdenum was found to have practically no effect when the chromium content was below 10 per cent, but the addition of 5 to 10 per cent of molybdenum to a 10 per cent chromium alloy greatly improved its resistance to the action of copper sulfate. The presence of carbon had a decided effect upon the corrodibility. Up to 0.31 per cent it was found to be harmless, but larger amounts caused copper to deposit. Small amounts of vanadium, 0.3 to 1 per cent, seemed to have no effect whatever.

A number of specimens which appeared to be on the border line, and also a few containing from 0.4 to 1 per cent carbon, were heated to a bright red heat for twenty minutes in a gas muffle and then quenched in cold water. As a result, a large percentage of those which had deposited copper in the first test were rendered resistant to the action of the sulfate solution. All of the 10 per cent chromium alloys containing up to 0.65 per cent carbon, which had at first been acted upon by the sulfate, resisted its action after the heat treatment. An alloy containing 8 per cent chromium and only 1 per cent silicon, which had deposited copper in the first test, was made resistant. This treatment was also found to improve the protecting action of tungsten and molybdenum, for a 7 per cent chromium alloy containing 3 per cent tungsten and 2 per cent molybdenum was effectively cured by quenching.

To test the effect of annealing, most of the specimens which had resisted the action of the copper sulfate in the first test, were heated to a bright red heat in a gas muffle for about half an hour, and allowed to cool slowly with the furnace. The subsequent test showed that those which, by their composition, were near the border line, had been rendered slightly less resistant. In three such cases there was from 0.3 to 1 per cent vanadium present. Those alloys containing from 0.4 to 0.65 per cent carbon, which had been previously quenched, were found to have lost their resistant qualities after annealing. The results of these three tests are given in Table I. The column headed I shows the results of the test on the specimens as received. Column II shows

TABLE II.

Alloys on which Copper Deposited.

No. of Specimens	Composition	
	Per Cent	Per Cent
40	Cu 0.4 to 10	
2	V 0.3 to 0.4	
65	Ni 0.25 to 45	
6	Co 0.5 to 6	
8	Sn 1.0 to 10	
15	As 0.25 to 10	
9	Ag 1.0 to 10	
2	Pb 3.0	
6	Mo 5.0 to 16	
8	Bi 1.0 to 10	
7	Mn 0.25 to 10	
3	Se 0.25 to 1.3	
2	Al 2.3 to 2.5	
13	W 2.0 to 20	
22	Si 0.25 to 7	
10	Monel 2.0 to 20	
14	Cu 0.5 to 20	and Si 0.25 to 6.7
12	Mn 5.0 to 15	and Cu 0.5 to 3
14	Cu 1.0 to 10	and Al 0.5 to 4
2	Sn 1.5 to 3	and Si 1.0 to 4
2	Sn 2.0 to 4	and Al 1.0
3	Mo 2.0 to 10	and Mn 1.0 to 2
6	Mo 4.0 to 16	and V 0.5 to 1
5	Ni 2.0 to 6	and Cu 0.7 to 2
3	Ni 5.0 to 10	and V 0.5 to 3
3	Cu 3.0 to 5	and As 1.0 to 4
5	W 4.0 to 7	and V 0.3 to 0.4
4	Mo 5.0 to 10	and Ni 10 to 20
1	Mo 5.0	and W 5
4	Ni 0.5 to 15	and W 3 to 5
1	Mo 10.0	and Si 4
1	Sn 3.0	and Cu 1 + Al 1
1	Ni 3.0	and Mo 7.7 + Si 2

TABLE III.

Effect of Copper Sulfate on Alloys of Fe and Ni.

No.	Per Cent Ni	Action
150U	45	Slow deposit
154T	50	No deposit
173W	90	No deposit
173X	95	No deposit

the results of quenching, and column III, of annealing. D means that copper deposited, and ND means no deposit.

After the above experiments had been practically completed, a letter was received from a well-known steel company which specializes in corrosion-resistant alloys, in which they stated that, according to their experience, the copper sulfate test was unreliable, as the results were likely to vary with small changes of temperature and the length of time of immersion. They stated that they had found specimens which were resistant to copper sulfate at 70° F. (21° C.) to deposit at a temperature only two degrees higher.

In order to check these statements, all the specimens which had been found to be resistant at room temperature, approximately 70° F. (31° C.) were heated to 100° F. (38° C.), but the results did not differ in the least from those of the first test. The specimens were then heated to 200° F. (93° C.) and tested a third time. However, the results in every case were identical with those of the first two tests.

In order to ascertain the effect of time, all the specimens from the temperature test were ground free from scale for a distance of two inches from the end, and immersed in copper sulfate solution in such a way that only the clean surface came in contact with the solution. They were allowed to stand for five days, observations being taken at frequent intervals. Many of the specimens did not deposit copper at all, and on those which did, the deposit started, in every case, from microscopic cracks or scale inclusions, and spread from these points.

Had it been possible to obtain specimens which were perfectly free from imperfections, it is probable that there would have been no deposit whatever. The time test brought out one or two points of interest, which would otherwise have been passed by unnoticed. Two alloys, one containing 10 per cent chromium and the other containing 10 per cent chromium and 5 per cent molybdenum, were acted upon to an equal degree, while the alloy containing 10 per cent chromium and 10 per cent molybdenum was not attacked at all, showing that unless molybdenum is present in amounts greater than 5 per cent, it has practically no effect. In several cases the alloy was somewhat corroded at the end of the fifth day, and a black coating had formed, although the characteristic red color of copper was lacking. Judging by these results, then, it would appear that time and temperature are not important factors in the copper sulfate test.

CONCLUSIONS.

1. When only chromium is alloyed with electrolytic iron, it must form at least 10 per cent of the alloy in order to make it resistant to the action of copper sulfate.

2. A 6 per cent chromium alloy may be made resistant by: (a) addition of 18 per cent tungsten; (b) addition of 14 per cent nickel. With 6 per cent chromium present, 4.5 per cent tungsten or 3 to 4 per cent nickel is equivalent to 1 per cent chromium.

3. A 7 per cent chromium alloy can be made resistant by: (a) addition of 10 per cent nickel, or 3.5 per cent nickel is equivalent to 1 per cent chromium; (b) by addition of 3 per cent silicon and 9 per cent tungsten; (c) addition of 3 per cent tungsten, and 2 per cent molybdenum, heating to bright red heat for twenty minutes and quenching in cold water.

4. An 8 per cent chromium alloy can be made resistant by: (a) addition of 1 per cent silicon and heat treatment as described above; (b) addition of 14 per cent nickel.

5. A 10 per cent chromium alloy is not affected by amounts of carbon less than 0.31 per cent, but from 0.4 to 0.65 per cent carbon causes copper to deposit. This can be prevented by heat treatment. One per cent carbon causes a deposit which cannot be prevented by heat treatment, even when 10 per cent nickel is present. Alloys containing carbon, which were resistant after quenching, became non-resistant after annealing. With 15 per cent chromium, 1 per cent carbon does not cause a deposit.

6. If a resistant alloy is near the border line with respect to chromium and silicon content, 1 per cent vanadium will cause a deposit after annealing.

7. If only nickel is alloyed with electrolytic iron, it does not begin to resist corrosion until the nickel content reaches at least 45 per cent.

8. The temperature at which the specimen is tested seems to have no effect.

9. The length of time of immersion seems to have no decided effect beyond that expected, of increasing the amount of deposit and rendering it darker in color.

10. Five per cent molybdenum added to a 10 per cent chromium alloy apparently has no effect, although 10 per cent molybdenum has a protecting action.

11. Manganese seems to have no effect whatever.

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TESTS FOR GRADING CORROSION-RESISTING ALLOYS

BY

WM. E. ERICKSON AND L. A. KIRST

A paper presented at the Forty-sixth General Meeting of the American Electrochemical Society, held in Detroit, Mich., October 2, 1924, Dr. Saklatwalla in the Chair.

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, p. 319.

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 accompanying 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.

B. D. SAKLATWALLA[6]: It appears to me that the acid radical should be considered a factor. We are comparing a sulfate solution with a chloride solution and a nitrate solution and are totally disregarding the acid radical phase. Prof. Watts, how pure were the metals you used? Some of these metals are obtainable commercially in a much purer condition than others, and very small amounts of impurities have a decided effect on the results.

O. P. WATTS: In regard to the question of chromium, it was the Goldschmidt (Al reduced oxide) variety. We bought it in Germany before the war. The tungsten was a bar of General Electric Co's pressed tungsten. The molybdenum was the Goldschmidt brand. The silicon was the Carborundum Company's "commercially pure silicon," probably containing around 97 per cent silicon.

COLIN G. FINK[7]: In other words, in all of your metals there is at least a half per cent of impurity.

O. P. WATTS: Yes, in the case of silicon, of course, much more than that. The effect of the acid radical is brought out in the case of duriron, which will resist sulfuric acid satisfactorily, but is attacked by hydrochloric acid; in applying these tests the acid radical has to be taken into consideration.

A. L. FERGUSON[8]: The title of the paper refers to corrosion-resisting alloys, and, as I understand from the discussion, pure metals were used in the tests, I do not see the connection between the tests applied to pure metals and their application in the case of alloys.

O. P. WATTS: The tests were carried out on this list of about 40 alloys, which Kurtz and Zaumeyer found to be resistant in the

[6] Vanadium Corp. of America, Bridgeville, Pa.

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

[8] Asst. Prof. of Physical Chemistry, Univ. of Michigan, Ann Arbor, Mich.

copper sulfate test. In the main they were alloys of iron with 8 per cent or more of chromium, and also in many cases molybdenum, nickel, copper and other non-ferrous alloys were included in the lists, besides those that Kurtz and Zaumeyer had already tested. Then these few elements specifically mentioned were tried in addition to this list of alloys, so that the test of the elements is merely a little supplementary matter.

R. J. McKAY[9]: I would like to corroborate the statements on the effect of different acid radicals. Our experience in corrosion testing has shown that results with nickel alloys using sulfuric acid cannot possibly be applied to hydrochloric acid, even though concentration, temperature and other conditions are identical. The difference in corrosion loss is much greater between these two mineral acids than that between two such acids as acetic and oxalic.

[9] Supt. of Technical Service, International Nickel Co., New York.

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THE GRANULAR RESISTOR FURNACE

BY

O. P. WATTS

THE GRANULAR RESISTOR FURNACE*

BY O. P. WATTS

USES

The granular resistor furnace is useful for heating tubes and crucibles to temperatures attainable only by the electric furnace, and where greater uniformity of heat is required than can be obtained by an arc. It is a most convenient method of melting metals and alloys in amounts of 100 to 1000 grams, and for carrying out high temperature reactions on a small scale.

CONSTRUCTION

On a fireproof table or floor, a layer of firebrick is supported on other bricks laid on edge, so that there are channels for air cooling. On this is laid a layer of magnesia brick of the length and width of the furance desired; a row of the same bricks is laid on edge to form the sides of a rectangular box, with the ends left open for insertion of electrodes. Firebrick are now laid along the sides to hold the magnesia brick in place, and carbon electrodes, preferably rectangular, are inserted in the ends. If crucibles are to be lifted from the furnace for pouring the metal, the channel should be about 3/4″ wider than the largest crucible used, but the area of cross section of the furnace should be kept as small as possible to lessen the current required, and the crucibles should be set about 2″ apart lengthwise of the furnace. If the charges are to be allowed to cool in the furnace, the crucibles may be set an inch apart lengthwise, and several rows may be placed in the furnace if desired. If the electrodes that lead current into the furnace are much smaller than the resistor, a "spreader" of carbon or graphite should be placed across the interior end of the electrode so that the current will spread uniformly in the resistor, instead of passing only through that portion immediately in front of the electrodes.

CRUCIBLES

For low temperatures fireclay or black-lead crucibles may be used, but for melting pure iron and other high temperature processes these are destroyed by the reducing action of the hot carbon, and only

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* One of a series of reports prepared at the request of the Committee on Research Methods and Technique appointed by the Division of Physical Sciences of the National Research Council. It is the purpose of these reports to present in brief outline a summary, more or less critical, of the methods which may be employed in various kinds of Physical measurements. See Editorial in this Journal *9*, p. 410, 1924.

crucibles machined from graphite electrodes are suitable. For metals which take up carbon when melted, graphite crucibles must be lined with magnesia. This should be calcined as strongly as possible, or better fused in the electric arc, crushed, and ground to a fine powder, which is dampened with water and tamped into the crucible around a form of wood, which is then withdrawn. The crucible and lining are dried slowly for 8 to 10 hours, placed in the furnace, covered with a graphite lid cut from an electrode of the same size as the crucible, completely covered with resistor carbon, and heated for 1 to 2 hours at a maximum temperature of 2000°C, and allowed to cool in the furnace over night. The linings should be stone-like in appearance. They may be used in the crucible in which baked, or removed and stored for future use in similar crucibles, but cannot be used without the protective case of graphite, as when white-hot magnesia has too little strength to stand handling.

Graphite crucibles tend to short-circuit the resistor, and hence develop a hot spot where current enters the crucible; they are, however, such good conductors of heat that this rarely does any harm. If the crucible is an insulator, the hottest spots are on its sides, where the cross section of the resistor is least, and since such crucibles are poor heat-conductors, it may be necessary to arrange for a uniform thickness of resistor on all sides of the crucible.

THE RESISTOR

Granular carbon or graphite may be used, but the latter has the disadvantage of a low resistivity which necessitates a much greater amperage to heat the furnace in which it is used. Resistor may be bought of any manufacturer of carbon electrodes, or may be made from coke or scraps of carbon or graphite electrodes by crushing and screening. For particles of fairly uniform size the finer the particle the higher the resistance. Dust lowers resistance by filling the voids, so that where the amperage is limited it is well to screen the resistor after using it a few times. For small furnaces the resistor should be finer than for large ones. Through 12 mesh and held on 20 is a convenient size for laboratory furnaces. When especially high resistance is desired carborundum may be added to the carbon.

VOLTAGE AND POWER REQUIREMENTS

Because of the large negative temperature coefficient of granular carbon, voltage regulation from 110 to 40, in steps of 20 to 30 volts, is desirable. The desired regulation is simply secured by having several points of connection to an auto-transformer, or to the secondary of a standard transformer, and changing one furnace cable from one to another of these when it is desired to raise or lower the power input.

For rapid heating of a furnace 20″ long, 3 1/2″ wide and 7″ deep for melting pure iron in three crucibles 3″ in diam. and 6″ high, 40 to 60 K.W. is desirable, although, by taking more time, a maximum of 40 K.W. would suffice. In a furnace 53″×12″×9″ deep, 36 crucibles each 3″ in diam. and 6″ high have been heated hot enough to melt electrolytic iron in six hours with an average of 50 K.W. and a maximum of 70 K.W. for moments. The metal was not poured, but left to cool in the furnace, and the crucibles were completely buried in the resistor in this case.

OPERATION

The crucibles are placed in the furnace as already specified, covered with Acheson graphite covers if they are to be completely buried, or with pieces of magnesia brick or fireclay if the metal is to be poured into molds. The resistor is then poured in to the desired depth, and left to lie loosely, except where it makes contact with the electrodes, at which point it may be tamped. Should the furnace fail to heat rapidly enough at the maximum voltage, magnesia bricks may be laid on the ends of the resistor and pressed down; as a last resort the resistor may be tamped between the crucibles.

Care should be taken that the furnace does not heat too rapidly, for there is a tendency for current to flow in the lower part of the resistor where pressure is greatest, and this may become so hot that the bottoms of the magnesia linings are destroyed before warning is given by looking at the top of the furnace. Rapid reduction of magnesia by carbon begins at 2030°C.[1]

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[1] D. S. Grenfell. Tr. Amer. Electrochem. S. *27*, 231.

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	1.7%
	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
A. Stansfield
E. M. Baker.

American Electrochemical Society,
Columbia University,
New York City.

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EFFECTS OF NITRATES ON CURRENT EFFICIENCY OF PLATING SOLUTIONS

BY

P. A. NICHOL AND O. P. WATTS

A paper presented at the Forty-eighth General Meeting of the American Electrochemical Society, held in Chattanooga, Tenn., September 24, 1925, President F. M. Becket in the Chair.

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.
[2] Senior in Chemical Engineering, Univ. of Wisconsin, Madison, Wis.
[3] Professor, Chemical Engineering, Univ. of Wisconsin.

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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DISCUSSION.

WM. BLUM[5]: These results are consistent with those in a paper by F. C. Mathers and E. G. Sturdevant[6], who noted the effect of

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

[6] Trans. Am. Electrochem. Soc., 30, 135 (1916).

nitrates in nickel solutions. In a recent paper by H. E. Haring[7], it was shown that hydrogen peroxide also decreases the cathode efficiency in nickel solutions, especially at low current densities.

In order to predict the effect of an oxidizing agent upon metal deposition in any given solution, it is necessary to consider not the static, but the dynamic potentials involved. Thus the equilibrium standard potentials for reduction of H_2O_2 , $HMnO_4$ $HCrO_4$ and HNO_3 are respectively (according to Allmand-Ellingham "Applied Electrochemistry") +1.8, 1.5, 1.3 and 0.95 v. For the deposition of silver from nitrate solution, the equilibrium potential is +0.80 v., and from cyanide solution about —0.4 v. For copper from the sulfate solution it is +0.34 v, for lead from nitrate —0.14 v. and for nickel from sulfate about —0.25 v. Merely from the fact that all of these static potentials for metal deposition are much more negative than those for the reduction of oxidizing agents, we might (erroneously) assume that in the presence of these oxidizing agents no metal could be deposited, which is the case only for very low current densities.

The fact that at higher current densities, metal is deposited with increasing efficiency shows that the electrolytic reduction of oxidizing agents must involve much greater polarization than does the metal deposition. If these polarization curves were determined it would probably be possible to predict and explain such results as were obtained in this paper by Messrs. Nichols and Watts.

Such data as I referred to above are only true for certain hydrogen ion concentrations, and therefore the pH of any one of these solutions might have changed enormously the cathode efficiency in the presence of nitric acid.

O. P. WATTS (*Communicated*): The experiments indicate that any considerable amount of nitrate in the nickel sulfate, double or single, the zinc sulfate and the ferrous ammonium sulfate plating solutions will cause the efficiency of metal deposition to drop nearly to zero; that nitrate causes a considerable, but not fatal, diminution of efficiency in the cyanide copper and silver baths; but that nitrate may be added to the lead fluosilicate solution, used for plating as well as for refining, and to the copper sulfate solu-

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[7] Trans. Am. Electrochem. Soc., 46, 107 (1924).

tion, without seriously lowering their efficiency. It is probable that the presence of nitrates will also seriously interfere with the operation of the cyanide zinc, cyanide cadmium, and brass baths.

The higher efficiency of the silver nitrate solution as compared with the cyanide containing nitrate is not entirely a matter of metal ion concentration. This would seem an adequate explanation for this particular case, and the relative concentration of metal and nitrate ions is probably a factor to be reckoned with, as is also current density. But the addition of nitrate to a nickel bath, in which there was a fairly *high* concentration of nickel ions, had a tremendously greater effect in lowering the efficiency of deposition than in the case cited, where the silver ion concentration was very small. There is evidently some other and more important factor involved than the relative or absolute concentrations of the metallic and nitrate ions.

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The Thomas Gas Calorimeter[1]

Factors Affecting Its Precision, Flexibility, and Reliability

By R. A. Ragatz and O. L. Kowalke

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Description of Thomas Calorimeter

THE Thomas gas calorimeter is designed to give automatically and continuously a record of the heating value of a gas. In general, the instrument may be described as a continuous-flow calorimeter, in which gas is burned at a steady rate and the heat of combustion is absorbed by a stream of air flowing countercurrent to the products of combustion. Figures 1 and 2 show its construction and operation. Three meters, geared together and driven by the same motor, are immersed in a large tank in which a constant water level is maintained by means of a bucket pump and weir over-flow. One of these meters measures the gas whose heating value is to be determined, another measures the air to be used in absorbing the heat of combustion, and a third meter measures the air necessary for combustion.

The gas to be tested, supplied preferably at a pressure of 3 to 6 inches of water, is admitted to the calorimeter through a pressure-reducing orifice, and enters a small expansion chamber. On the cover of this chamber is a bleeder flame, which consumes gas at a rate sufficient to clear the supply pipe and prevent any considerable time lag in the heating values registered, and also serves to reduce the gas pressure on the inlet side of the gas meter to atmospheric.

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[1] Presented under the title "Factors Affecting the Precision, Flexibility, and Reliability of the Thomas Recording Gas Calorimeter" before the Division of Gas and Fuel Chemistry at the 71st Meeting of the American Chemical Society, Tulsa, Okla., April 5 to 9, 1926.

Upon leaving the gas meter the gas is delivered to a chamber, where it is thoroughly mixed with the necessary primary air for combustion, supplied by the combustion air meter. The mixture of gas and air is then delivered to the burner unit, where it rises through a central tube and is burned at the top, forming a small flame. Secondary air to insure complete combustion is admitted to the flame from the combustion air meter through a second tube concentric with the first. The products of combustion are deflected downward and pass through the annular space between the secondary air tube and a third tube, the heat interchanger. As the products of combustion pass downward they give up their heat to a stream of air which is flowing in the opposite direction along the outside surface of the heat-interchanging tube. The products of combustion and the heat-absorbing air travel in entirely separate ducts and are not mixed with one another. The transfer of heat from the products of combustion to the heat-absorbing air is so efficient that the products of combustion are discharged from the bottom of the burner unit at a temperature very nearly that of the incoming heat-absorbing air. The water condensed from the products of combustion is removed by a drain leading to the water storage tank.

The meter supplying air to the burner unit for absorbing heat delivers it in a definite ratio with respect to the volume of gas supplied. An electrical resistance thermometer located near the outlet of this air meter gives the temperature of the heat-absorbing air as it enters the burner unit. The temperature of the heat-absorbing air after passing upwards through the heat interchanger, and after having absorbed the heat from the products of combustion, is measured by a second electrical resistance thermometer. The heat-absorbing air is discharged at the top of the burner unit.

Figure 2 shows diagrammatically how the recording system operates. Two resistance thermometers, T_1 and T_2, one measuring the temperature of the heat-absorbing air delivered to the burner unit and the other measuring the temperature of the heat-absorbing air after being heated by the products of combustion, are in adjacent legs of a Wheatstone bridge. The recorder mechanism automatically keeps the bridge in balance by shifting the point of contact, *S*. The position of this point of contact when the bridge is balanced depends upon the temperature difference between the two resistance thermometers, which in turn depends upon the heating value of the gas being burned. That is, the higher the heating value of the gas the greater will be the difference in temperature and resistance between the thermometers located at the inlet and the outlet for the heat absorbing air.

By making a graphical record of the positions of the points of contact, *S*, the Thomas calorimeter gives a continuous record of the total heating value of the gas supplied to the calorimeter, expressed in B. t. u. per cubic foot at standard

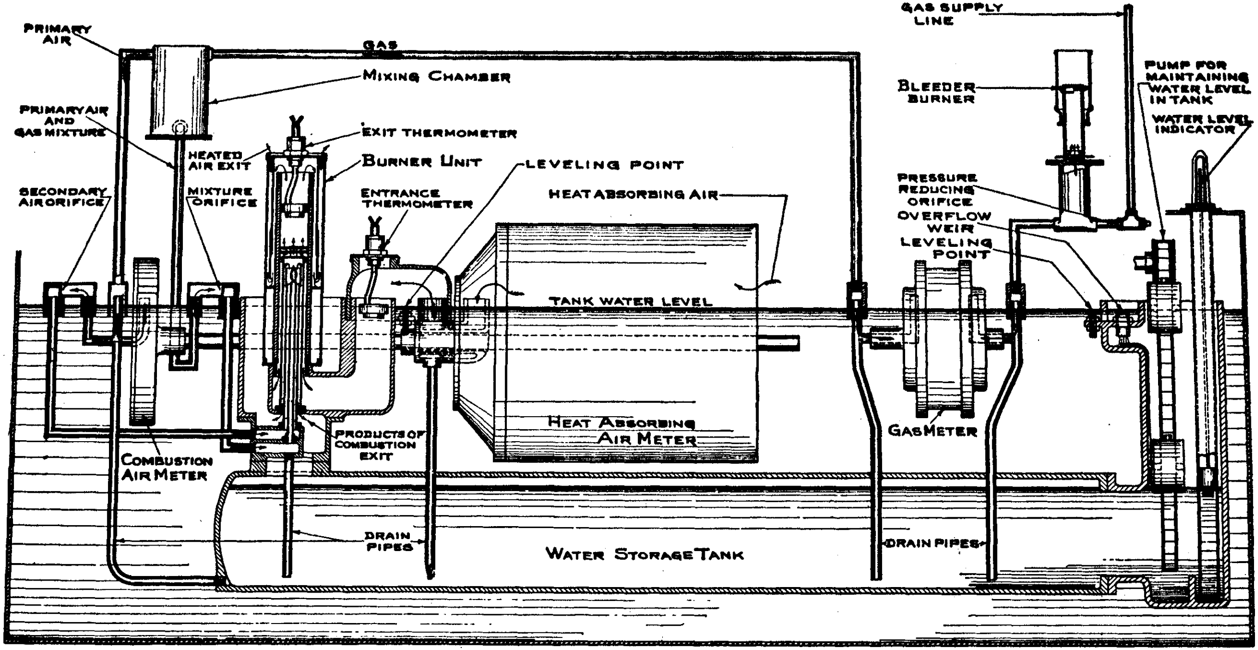

Figure 1—Arrangement of Piping and Meters in Tank Unit

conditions—namely, 60° F., a barometric pressure of 30 inches of mercury, and the gas saturated with water vapor. The reading indicated is always the total heating value of 1 cubic foot of gas at standard conditions, irrespective of the actual barometric pressure or tank temperature.

The use of air as the heat-absorbing medium makes it theoretically possible to design a continuous-flow gas calorimeter whose indications would be independent of variations in temperature, barometric pressure, or meter speed, and would be a function only of the heating value of the gas. If the meters of the Thomas calorimeter were operating in a fluid having negligible vapor pressure, and if both the gas and the heat-absorbing air were free of water vapor, the temperature rise of the heat-absorbing air would be independent of meter speed, barometric pressure, or of the initial temperature of the heat-absorbing air, assuming the burner unit to have an efficiency of 100 per cent. This would be true because both the mass of combustible and the mass of heat-absorbing air delivered to the burner unit would be affected to exactly the same extent by variations in meter speed, barometric pressure, and tank temperature. But the meters of the Thomas calorimeter operate in water, which has an appreciable vapor pressure, and the presence of water vapor in the gas and in the heat-absorbing air complicates the theory somewhat. It may be shown that under these conditions the temperature rise of the heat-absorbing air is not only a function of the heating value of the gas, but is dependent to a slight extent upon barometric pressure and to a more pronounced extent upon the initial temperature of the heat-absorbing air. However, the nickel wire selected for the resistance thermometers has a resistance-temperature relationship which compensates for these effects quite exactly. The manufacturers guarantee the instrument to be accurate within 1 per cent, irrespective of the barometric pressure and the tank temperature, provided the latter is between the limits 55° and 90° F.

Heating Value Comparisons between the Thomas and Junkers Calorimeters

At the present time the calorimeter of the Junkers type is accepted by the gas industry as the standard instrument for determining the heating value of gas. The results of a number of comparisons between the Thomas and Junkers calorimeters are given in Table I. Both instruments were operated simultaneously on gas stored in a 65 cu. ft. gas holder, thereby avoiding uncertainties due to variations in heating value during a test. The Thomas calorimeter was operated as recommended by the manufacturers, while the Junkers calorimeter was operated according to the recommendations of the Bureau of Standards.[2,3]

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[2] Waidner and Mueller, *Bur. Standards, Tech. Paper* **36.**

[3] *Ibid., Circ.* **48** and **65.**

Table I—Comparisons between Thomas and Junkers Calorimeters

Test	Heating Value		Difference	Per cent difference	Gas used in test
	Junkers	Thomas			
1	524	523	−1	−0.19	*A*
2	531	532	+1	+0.19	*A*
3	533	532	−1	−0.19	*A*
4	528	531	+3	+0.57	*A*
5	525	523	−2	−0.38	*A*
6	537	543	+6	+1.12	*A*
7	537	544	+7	+1.30	*A*
8	540	543	+3	+0.56	*A*
9	545	547	+2	+0.37	*A*
10	547	548	+1	+0.18	*A*
11	543	545	+2	+0.37	*A*
12	541	544	+3	+0.55	*A*
13	542	544	+2	+0.37	*A*
14	525	531	+6	+1.14	*A*
15	526	530	+4	+0.76	*A*
16	528	524	−4	−0.76	*A*
17	463	460	−3	−0.65	*D*
18	448	450	+2	+0.45	*C*
19	448	449	+1	+0.22	*C*
20	448	448	0	0.00	*C*
21	580	576	−4	−0.69	*B*
22	580	579	−1	−0.17	*B*
23	581	577	−4	−0.69	*B*
24	581	577	−4	−0.69	*B*
25	503	506	+3	+0.60	*A*
26	503	505	+2	+0.40	*A*
27	503	505	+2	+0.40	*A*
28	504	505	+1	+0.20	*A*
29	504	505	+1	+0.20	*A*
30	505	504	−1	−0.20	*A*
31	503	505	+2	+0.40	*A*
32	504	504	0	0.00	*A*
33	504	505	+1	+0.20	*A*
34	504	506	+2	+0.40	*A*
35	504	508	+4	+0.79	*A*
36	508	512	+4	+0.79	*A*
37	509	514	+5	+0.98	*A*
38	511	513	+2	+0.39	*A*
39	513	513	0	0.00	*A*
40	510	514	+4	+0.78	*A*
41	511	515	+4	+0.78	*A*
		Average difference		0.49	

Most of the comparisons were made on carbureted water gas without altering the composition, but several comparisons were also made on carbureted water gas diluted with hydrogen or carbon dioxide, or enriched with Blau gas. Analyses of the different gases are given in Table II.

Table II—Analyses of Gas Used in Tests

(Figures in per cent)

A—Carbureted water gas
B—Gas enriched with Blau gas
C—Gas diluted with carbon dioxide
D—Gas diluted with hydrogen

Gas	*A*	*B*	*C*	*D*
Carbon dioxide	4.3	4.4	17.8	2.9
Illuminants	10.4	12.2	8.7	7.1
Oxygen	1.3	1.3	0.9	1.1
Carbon monoxide	27.8	26.5	24.1	20.1
Hydrogen	30.9	29.0	27.1	50.8
Methane	11.0	10.8	9.0	5.9
Ethane	1.1	2.1	1.2	1.6
Nitrogen	13.2	13.7	11.2	10.5
	100.0	100.0	100.0	100.0

The average difference between the heating values obtained with the two instruments is 0.5 per cent, which indicates that the manufacturer's guarantee of an accuracy of 1 per cent is fulfilled. The differences between the heating values given by the two instruments are not necessarily errors in the Thomas calorimeter, since errors may enter into the operation of the Junkers calorimeter, even when following the best practice. Relative to the accuracy attainable with the Junkers type of calorimeter, Waidner and Mueller[2] say:

> Experience has shown that, if due attention is given to the precautions that have been shown to be of importance, an accuracy better than 0.5 per cent is attainable, and in ordinary routine testing an experienced observer should obtain results accurate to within about 1 per cent.

Lag of Thomas Calorimeter in Recording Changes of Heating Value

The lag of the Thomas calorimeter was investigated by operating on carbureted water gas taken from the mains, and then switching to the holder which contained gas of either higher or lower heating value as shown in Table II. Three lag tests were run on each type of gas and the average results are given in Table III.

Table III—Summary of Lag Tests

Per cent of total change recorded	Time in minutes after switching to holder		
	B[a]	*C*[a]	*D*[a]
10	4.6	5.0	5.1
20	5.0	5.6	5.6
30	5.5	6.0	6.1
40	6.0	6.5	6.6
50	6.4	7.1	7.1
60	6.8	7.7	7.7
70	7.5	8.5	8.7
80	8.1	9.4	10.0
90	9.7	12.2	14.3
95	11.8	19.3	23.5
100	30	60	60
Total change registered, B. t. u.	51	87	73
Average time for first response, minutes	4.0	4.1	4.5

[a] Gas in holder.

Effect of Rapidly Varying Room Temperature

It was thought desirable to determine whether or not the readings of the calorimeter were affected by rapid variations of temperature such as might be caused by leaving open the door of the room in which the calorimeter is installed. The calorimeter was operated at normal room temperature on gas supplied from the holder till the reading became steady, then the window of the laboratory was opened and kept so for one hour. The results as given in Table IV show that the change registered is approximately 0.1 B. t. u. per degree Fahrenheit drop in room temperature.

Table IV—Effect of Rapid Variations in Room Temperature

Test	Drop in room temperature ° F.	Change registered by Thomas calorimeter B. t. u.
1	17	0
2	23	2
3	32	3
4	34	4

Effect of Pressure of Gas Supplied

In operating the Thomas calorimeter it is important that the pressure at the inlet side of the gas meter be constant and very nearly atmospheric. Changes in gage pressure at the inlet of the gas meter will change the volume of gas delivered to the burner unit owing to change of water level within the meter, and will therefore affect the heating values recorded.

It was considered desirable to determine whether or not the arrangement for reducing the gas pressure to atmospheric is efficient enough to take care of any considerable variations in line pressure, and give a constant pressure at the meter inlet. The calorimeter was operated on gas from the holder till the reading became steady. The line pressure of the gas supplied was then varied from 2 to 8 inches of water by increments of 2 inches, and the calorimeter was allowed to operate for 45 minutes at each increment. The pressure of the gas at the inlet of the gas meter was measured by means of an inclined water gage. No change was observed in the heating value recorded, as the pressure of the gas supplied varied from 2 to 8 inches of water. The readings taken on the inclined gage showed that the pressure at the inlet to the gas meter was 0.003 inch water column and that it was the same for all line pressures between 2 and 8 inches of water column.

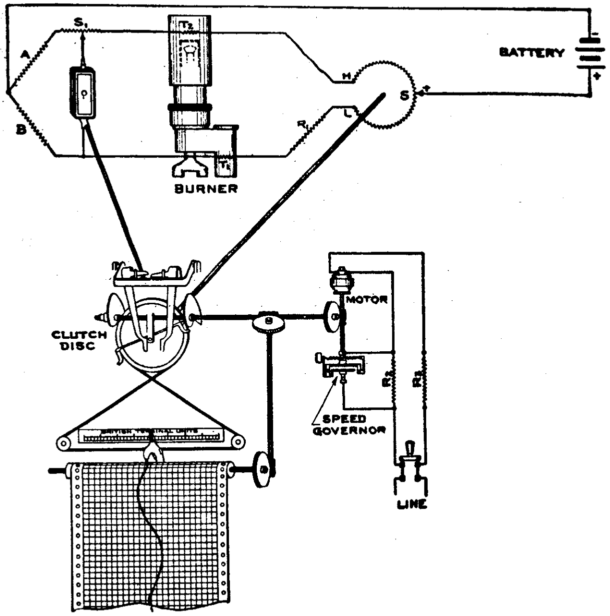

Figure 2—Wiring Arrangement

Effect of Atmospheric Humidity

If the gas and the air delivered by the three meters operating in the tank of the Thomas calorimeter leave the meters completely saturated, humidity should have no effect on the readings. The humidity of the air in the room was varied from 29 to 88 per cent and the calorimeter operated throughout the test on gas from the holder, but no change in heating value was recorded. This indicates that the gas and the air delivered by their respective meters are completely saturated.

Performance

The first model tested at the Chemical Engineering laboratories of the University of Wisconsin was installed in January, 1922, and was operated continuously over a period of 5 months. In February, 1923, a new model embodying certain changes was installed and the tests described in this paper were performed on the improved model.

Since its installation, the improved model has been in operation for periods of time which total about 2 years and 2 months. A certain amount of routine attention and a few minor replacements have been necessary to keep the instrument in good condition. The tube for secondary air is subjected to extremely corrosive conditions from the products of combustion. It was found that this part, owing to failure from corrosion, had to be replaced approximately every 6 months. At the present time secondary air tubes of Pyrex glass are being tested to determine their suitability to replace the metal tubes now employed. The heat interchanger has suffered some on account of corrosion from the products of combustion, but it is still in use. The flexible metal hose connection from the gas pressure reducing chamber to the gas meter was replaced by a solid pipe connection. On all the new models the solid pipe connection is standard construction.

The data obtained in these researches on several models submitted by the manufacturer have been factors in changes of design which have improved the precision obtainable.

their platers, to each spend for example $100 to find out if they can apply the results to their own plant, with possibly great savings? Of course if the plater and manufacturer are satisfied that their present practice cannot be improved, there is no necessity for research. The best way to let us know that you want more research, is to use, so far as possible, the results already obtained.

DR. WM. BLUM,
Associate Editor.

THROWING POWER

(An address before Chicago Branch, American Electroplaters' Society, Jan. 29, 1927.)

By Oliver P. Watts

The old saying, "The used key is always bright," applies to other than merely physical things. It applies particularly to our knowledge. Forty years ago I could read Greek, with much difficulty and a dictionary. Today I don't know the whole of the alphabet, and frequently find myself "stumped" by some one of the two or three letters, which to the more erudite, tell the name of the fraternity or sorority which inhabits the latest addition to the group of magnificent buildings which house so many of my students. At about the same time I was supposed to be extra proficient in the calculus. Today calculus is all Greek to me, and I have merely a bowing acquaintance with the integral sign. It isn't only the unused tool that rusts. By disuse any power or attribute that we may possess is lost.

So, while I have nothing new to tell you on the subject of throwing power, it may perhaps be profitable that we spend a few minutes on the general principles of this important, but until recently, utterly neglected subject.

If you were required to plate both inside and out a hundred brass tubes three or four inches long and a half inch inside diameter would you choose the sulphate or the cyanide solution for plating, supposing that you had both ready for use? The electrotyper and maker of phonograph records, who deposit ten pounds of copper to one deposited by the average plater, invariably use the sulphate solution; yet you would choose the cyanide solution because of its superior throwing power.

Why should the two solutions behave so differently in this respect? If the cyanide solution is capable of depositing copper way up inside the tube, where we would expect little or no current to flow, why does the sulphate solution utterly fail to do the same? Ohm's law tells that the current flow varies directly as the em.m.f. or voltage, and inversely as the resistance. But the voltage between the anodes and any part of the cathode is practically the same, and if the composition and concentration of the plating solution is uniform, the resistance to different parts of an object will be proportional to their distances from the anodes. So far it seems as if the flow of current to different objects or to different parts of the same object should always be in inverse proportion to their distances from the anodes, and that all solutions should have exactly the same throwing power—quite contrary to our observations in plating.

G. Gore, in his book on electrodeposition, published a half-century ago, notes that in addition to the ohmic resistance of solutions, which varies uniformly with the distance, there is some special obstacle to the passage of current, residing at the contact of electrode and electrolyte. To this he gave the name "transfer resistance." One factor which contributes to this transfer resistance is the difference in composition between the film in contact with the electrodes and the main body of solution. At the cathode metal is being removed, and consequently the film of solution here is weaker, and at the anode where metal is dissolving the film is more concentrated in metal than the main body of solution. These changes in concentration alter the potentials of both anode and cathode in such a way as to oppose the flow of current, and this opposition increases with rise in current density. Under ten amperes per square foot this change in potential of the cathode seldom exceeds 0.03 volts, so that this change in concentration is not a very important factor in throwing power. A more important factor in altering the potential of the cathode is the hydrogen often deposited along with metal from many plating solutions. The total alteration of potential or polarization of the cathode at current densities now used may in extreme cases amount to as much as a volt, a considerable portion of the total voltage across the solution.

With certain solutions the cathode polarization changes but slightly, while with others it increases greatly with increase of current density. It is this latter property, the increase in cathode polarization with rise of current density, which imparts throwing power to a plating solution. If the voltage be represented by E, the total polarization at both electrodes by P, the current by I, and the resistance to the part of the cathode under consideration by R, then

$$E = P + IR$$

Only that portion of the voltage not offset by polarization is effective in sending current through the solution. Let us consider two portions of cathode surface, one of which is three times as far from the nearest anode as the other. More current flows to the near than to the far surface, but if the polarization is not affected by current density, the voltage effective in sending current to each surface is the same, and since R is proportional to the distances, the currents will be in the same ratio. If, however, P increases considerably with rise in current density, the polarization on the near surface will be much larger than on the far surface, and consequently the voltage remaining to send current to the near surface will be smaller than that acting on the far surface. The result is that the far surface gets a larger share of current than the relative distances warrant.

Another and most important factor in throwing power is current efficiency. If the current efficiency of each particular plating solution were the same at all current densities, the weights of metal deposited on near and on far parts would be proportional to current distribution; but the current efficiency varies, in some cases greatly, with changes in current density. In the cyanide copper solution an increase in current density causes a notable falling off in current efficiency, indicated by a great increase in evolution of hydrogen. This is favorable to throwing power, for at the near surface, where the current is greater, a larger per cent of it is wasted in deposition of hydrogen. In the nickel solution an increase in current density causes a rise in current efficiency, which is unfavorable to throwing power. If you must cover a hollow article with nickel, use a small current for a long time rather than a large current for a short time.

It is evident from the equation that the relative magnitude of polarization and IR-drop across the solution is important. If IR is very large compared to P, the changes in P due to differences in current density will have little effect on current distribution, and hence on throwing power; but if P is large compared to IR its changes will profoundly influence the amounts of current flowing to near and far portions of the cathode.

All other conditions remaining unchanged, throwing power can be increased by increase of polarization or by lowering of resistance. It does not follow, however, that solutions of low resistance have the best, or even good, throwing power. One of the lowest-resistance solutions in use by platers is the acid copper sulphate solution, notable for its poor throwing power. Since hydrogen is not deposited from this solution at currents used in plating, the only polarization at the cathode is that due to removal of copper from the cathode film, and while this is proportional to the current, its total is too small to impart good throwing power. The statement that hydrogen is not deposited from this solution is only another way of saying that its current efficiency does not fall off at current densities used in plating, so its very poor throwing power is accounted for.

It often happens that a change which influences favorably one of the three factors, resistance, polarization and current efficiency, may produce in the others a greater change unfavorable to throwing power. For example heating a solution always lowers its resistance, which taken alone improves throwing power; but it also lessens polarization and increases current efficiency, unless this was already 100 per cent, and both of these changes lower throwing power. For a more scientific and detailed discussion of throwing power you are referred to the papers by Dr. Blum, Haring and Thompson in Vol. 44, 46 and 47 of the American Electrochemical Society.

In 1917 I began the testing of throwing power by rolling tubes of thin sheet metal and finding how far inside the tube different plating solutions would deposit metal. By using tubes of different diameter and length it was hoped to classify plating solutions according to their throwing power. It was soon found that the ordinary plating solutions fell into two classes: cyanide solutions of good throwing power, and all other solutions tested of relatively poor throwing power, with no connecting link between. This investigation was interrupted by the war, and not resumed until two years ago, when an attempt was made to investigate and improve the throwing power of several solutions.

It was found that the addition of large amounts of aluminum chloride ($AlCl_3 \cdot 6H_2O$) to nickel sulphate solution imparted surprising throwing power. To prevent the precipitation of aluminum hydrate it is necessary to add citric acid before bringing the pH value to 5.7 by ammonia. In all cases the preliminary testing was done by plating tubes, and only the best solutions were measured on a Bureau of Standards throwing power box, kindly loaned for that purpose by Dr. Blum. As used the ratio of cathode distances was five to one, and the current was 0.5 ampere per square decimeter of cross section of the solution, or 4.9 amperes per square foot.

Some results are:

Single	Sulphate	$AlCl_3 \cdot 6H_2O$		Citric Acid		Throwing Power
G/l	Oz/gal.	G/l	Oz/gal.	G/l	Oz/gal.	
25	3.3	63	8.4	22	3	17%
25	3.3	125	16.7	45	6	28
25	3.3	250	33.3	90	12	40
Nickel	Chloride					
25	3.3	0	0	0	0	–7
25	3.3	65	8.7	32	4.3	18
25	3.3	125	16.7	65	8.7	32.5
25	3.3	250	33.3	125	16.7	35.3
100	7.3	250	33.3	125	16.7	26

At the same current density the special high sodium sulphate nickel solution of M. R. Thompson has a throwing power of only fifteen per cent. Thompson's solution carries 140 grams of single sulphate per liter, and is intended for rapid plating. It would be expected that a solution containing only 25 grams per liter of single sulphate would be limited to extremely slow plating, but this solution has been used at one ampere per square decimeter cross section of box, and an actual density of 0.96 amperes per square decimeter on the near cathode, for a half hour without a trace of burning. This is not recommended as a practical plating solution, on account of the cost of citric acid and trouble from precipitation of aluminum hydrate; but the facts have been presented to show that it is possible for a nickel solution to have a throwing power fully equal to that of the usual cyanide copper solution. With the knowledge that this is possible, the attainment of a practical solution of equal throwing power should be only a matter of persistent, though perhaps lengthy, experimenting.

In experiments with the zinc sulphate solution, notable for its poor throwing power, aluminum chloride which had proved so beneficial in the nickel solution was of no advantage, but ammonium citrate was a great help to throwing power. A solution containing 120 grams per liter (16 oz. per gallon) of crystallized zinc sulphate and 15 grams (2 oz.) of citric acid had a throwing power of 27.5 percent when neutralized by ammonia to a pH value of 6.0.

A cyanide copper solution which had a resistivity of 16.4 ohms per centimeter cube at 20 degrees centrigrade and a throwing power of 32.6, on addition of 50 grams caustic potash and 20 grams per liter of caustic soda, had a resistivity of 5.5 and a throwing power of 56 percent, the highest attained in any of my experiments. In three minutes this solution plated the inside of a tube 6½ inches long and 3/16 inch inside diameter, when one end of the tube was placed against the side of the tank so that current could enter the tube at one end only. Since the term percent is used in expressing throwing power it is but natural to think of any value much below 100 percent as something very inferior. This is not so. In computing throwing power by the Bureau of Standards formula for a five to one distance ratio a throwing power of 80 percent would necessitate that the same weight of metal be deposited on the far as on the near cathode—an impossibility. It would seem that the maximum throwing power attainable will be well under 80 percent.

The throwing power of the nickel, zinc and copper sulphate solutions was unfavorably affected by very slight increases in acidity, so that this will require careful watching if these solutions are to be kept up to the best throwing power of which they are capable.

If a study of throwing power will, as seems likely, produce a more uniform thickness of plating than is at present obtained, this will result in several economies. For the same service now secured a less weight of metal can be used, which means less labor, power and time required for plating. These economies will not be realized, however, without much experimenting and the accumulation of a knowledge of the effects of different conditions and chemicals on the various factors whose combination gives to each solution its particular throwing power. These factors have been pointed out by

Dr. Blum and his assistants at the Bureau of Standards.

For the plater who wishes to keep a check on the throwing power of his plating solutions, or to try the effect of addition of different chemicals, but who does not have a throwing power box, the method of plating tubes is recommended. Two, or at most three, steel rods around which to roll the sheet metal is all the equipment needed. By varying the length of tube as well as the diameter, it is possible to differentiate between the throwing power of all solutions. Thin sheet copper is used to make the tubes. For testing copper solutions this should be very lightly nickeled before rolling into a tube. For silver solutions, which deposit their metal on copper "by immersion," thin sheet iron should be used instead of copper. By stopping one end of the tube excessive length of tube may be avoided even in testing so good a throwing solution as the cyanide copper.

SCIENCE AND COMMON SENSE

By A. P. Munning*

Address delivered before open meeting, Newark (N. J.) Branch.

Francis Bacon, probably the first philosopher to distinguish that knowledge unapplied to action was superfluous knowledge, made the statement as far back as 1592 "that crafty men condemn studies, simple men admire them and wise men use them."

If we will apply these words to our everyday work and play, we will profit much more than in the endeavor which seems to permeate the whole universe of trying to combine into one poor brain all of the scientific data and nostrums and cure-alls which are being urged upon us.

It is with these thoughts in mind that I am going to try and show my appreciation of the honor bestowed upon me by Mr. H. A. Smith, in asking me to say a few words at random to you tonight.

The art or the lack of art of electroplating prior to the beginning of your society is well known to most everyone. At about that time, 1911, the industry began to absorb some of the basic underlying principles of other industries, because men coming into it had the courage to work, not on past

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*President A. P. Munning Co.

[FROM THE TRANSACTIONS OF THE AMERICAN ELECTROCHEMICAL SOCIETY, Volume LII, 1927, being the Transactions of the Fifty-second General Meeting, on the Northwestern Trip, September 4 to 20, 1927.]

ANODES FOR CHROMIUM PLATING

By

O. P. WATTS

Printed in U. S. A.

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.

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.

Chemical Engineering Laboratories,
University of Wisconsin.

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.

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EDITORIAL

This being the first month of the new year, in which many of our members have much spare time and many of the boys go ahunting for pleasure and profit, some in the wilderness of the forests for the Easter bunnies, and some in the public libraries for the hidden secrets of KNOWLEDGE. Others hunt in the Plating rooms for the year's mistakes and ways to correct them. The writer suggests a few of the following thoughts to the members hoping to overcome the sights, of Crepe, Mortgages and Chilblains, the usual rewards of HUNTERS partially equipped.

When starting out to hunt, whether it be for game or knowledge or mistakes in the Plating room, the first thing to know is WHAT you are hunting for. This requires EXPERIENCE. And to be able to bag the game we must also have a knowledge of the Tools required by the HUNTER.

In the Parlance of DAD LISCOMB, we see two (2) hunters. Both have the tools and the knowledge about hunting. The big fellow has a gun as good as the little fellow has and both work side by side in the Plating room and talk hunting in many of their idle moments. The little fellow frequently went after Mr. Rabbit, but the big fellow only talked about it. So one day, after much bickering, they both decided to hunt together.

So they loaded their guns and took the dogs and went into the field where the rabbits were numerous—and BANG went the little fellow's gun, and a nice juicy rabbit for Sunday dinner was the result and again spoke the gun of the little fellow and another rabbit bit the snow. As no sound had come from the big fellow's gun we scurried across the field to find out the reason and there we find the big fellow filling his pipe and the rabbits sliding by to try and dodge the little fellow's gun (of observation or investigation) and the rabbits (or opportunities) not only going, but GONE.

To the little fellow's inquiry of why didn't you shoot, the intelligent comeback was "Well, I am waiting for him to sit up." And as Dad would say, "There you are."

Now, brother hunters in the plating industry, why be fearful that the high school boy with his chemistry, and the polisher that has ambitions to fit himself for the job of plater. If when hunting with the gun of knowledge backed up with the experience that is yours, and the many experiences of our members as published in our REVIEW which is yours also to improve upon, and preserve your game preserve from poachers. Somewhere the writer saw a slang expression, the coat and pants do all the work but the vest gets all the gravy. Why not put on the VEST of Study and Knowledge and get all the GRAVY.

Dear members, you may think that the day of the experienced plater executive is on the wane, but on the contrary it is just commencing and his VALUE is on the increase with each day, but the time has come when "HE must KNOW."

ANODES FOR CHROMIUM PLATING

Address to American Electro-Platers Society and American Electrochemical Society, at Detroit, Dec. 14, 1927

By Dr. O. P. Watts, Wisconsin University

Several weeks ago I received a telegram asking if I would come to Detroit and speak at this meeting on anodes for chromium plating. I had made two brief visits to Detroit in as many years and wanted to come again, extend my all-too-slight acquaintance with its gigantic industries, and get further inspiration to continue research in my two chosen lines, electroplating, and the corrosion and protection of metals and alloys. You who live here cannot possibly feel the stimulus which an outsider gets on coming into this atmosphere of accomplishment, where more progress is made in industry in a year than occurs elsewhere in ten years. Of course I wire "Yes."

At the outset I want it understood that in chromium plating I am only a laboratory worker, who never saw any commercial chromium plating except the plating of two radiator shells, an exhibit which a friend staged for me here in Detroit on one of the visits to which I have referred. So I am here, not as an expert on chromium plating, but as I see it, merely to introduce that important subject for a general discussion, which will constitute the really valuable part of the evening's program.

The experiments which I shall report were all made with the chromic acid solution, and all statements are to be understood as applying to that solution only. If I may digress from the announced topic of anodes, I should like first to discuss chromium deposition. The chromic acid solution is peculiar both in its constitution and in its operation. Its constitution is peculiar in that the solution is a powerful oxidizing agent, and that nearly all chromium is hexavalent, less than one per cent being in the trivalent form, to which it is believed that hexavalent chromium must be reduced before it can be deposited as metal. The chromic acid solution is peculiar in operation in that a tremendous current density must be maintained at every point where chromium is to be deposited, and that the throwing power is far poorer than that of any other plating solution. The effect of valence in electrodeposition is simple. The common valence for metals is 1, 2 and 3, these numbers indicating the relative amounts of electricity carried by one atom of any metal having that valence. It therefore requires twice as much electric current to deposit at the cathode or to dissolve from an anode one atom of a divalent metal as is required for one atom of a mono-valent metal (valence = 1.), and so for other valences. A few metals can exist in solution with more than one valence, e. g., iron, chromium and copper. One way of changing the valence of such metals in solution is to add electric charges at the anode or to take them away (reduce the valence) at the cathode. Such action uses up electric current just as dissolving metal from an anode or depositing it at a cathode does. For a metal to dissolve at an anode each atom entering solution must be given a number of electric charges equal to its valence, and when it is deposited it must give up to the cathode the same electric charges. This is merely one way of stating Faraday's law.

In Sargent's solution, which I used, there were 32 ounces of chromium tri-oxide in which chromium has a valence of six, and only half an ounce of chromium sulphate, in which chromium has a valence of three. Let us speculate on what probably happens when current is passed through this solution. In doing this I am only expressing my opinions, based on the general principles of electrolysis, and not stating facts proved by experiments and analysis of this solution. The action is similar to that of a solution of ferric chloride, where iron has the higher of its two valences, three, instead of the valence two, as in ferrous salts. Many years ago I directed a student to electrolyze a solution of 13 oz. per gallon of ferric chloride at 10 amperes per square foot with iron electrodes. He found corrosion of the anode to greatly exceed 100 per cent, and instead of a gain in weight for the cathode, it actually lost weight, i. e., the efficiency of deposition was less than zero. At the cathode the entire current was spent in reducing the iron from the ferric to the ferrous state (changing its valence from three to two), so no iron could be deposited. In addition the cathode was corroded by the ferric chloride solution just as would have happened to any sheet of iron hung in the solution without any electric connection. At the anode the efficiency of the electrolytic corrosion was 100 per cent, and added to this was the corrosive action of the ferric chloride, which goes on whether current is passing or not.

Had a much larger current been used, iron would have been deposited, but this would occur only when the ferric chloride in the film touching the cathode had been reduced to ferrous, and its corrosive action thus stopped. If, when the current density is just high enough to cause deposition of iron, a mechanical stirrer be introduced, corrosion instead of deposition will result. The stirring brings in from the main body of solution so much ferric chloride that once more all current is used up in reducing this, and no iron is deposited.

At the anode iron dissolves as ferrous chloride, so that with continued operation the concentration of ferrous chloride increases and that of ferric chloride diminishes, the efficiency of deposition increases, and of anode corrosion diminishes, until each becomes 100 per cent. If the soluble iron anode be replaced by a large insoluble carbon anode, metal no longer enters the solution, but ferrous chloride that, by natural circulation or by stirring comes into contact with the anode, is changed to the ferric state. Any current left over after this is accomplished, evolves chlorine at the anode.

If two carbon electrodes are placed close together in a fairly concentrated solution containing about equal quantities of ferrous and ferric chlorides, a very considerable current can pass without any deposition of either metal or hydrogen at the cathode, or evolution of chlorine at the anode. At the cathode the entire current is spent in reducing the ferric iron to ferrous, and at the anode it is employed in raising the valence of the ferrous iron from two to three. The same action will occur even if the electrodes are far apart, provided a mechanical stirrer is used to prevent exhaustion of ferric chloride at the cathode and of ferrous chloride at the anode.

Now let us turn to the chromium plating solution. Here we have a concentrated solution with practically all the chromium in the state of highest valence, six. We should expect no deposition of metal until nearly all chromium in the film in contact with the cathode has been reduced to the lower valence, so at low and moderate current densities no deposit of metal can be looked for. But why the hydrogen, that deposits as soon as the current density has become high enough to deposit metal? It is like the hydrogen that is deposited along with nickel when a small addition of sulphuric acid is made to the nickel bath. Chromium trioxide (CrO_3) is the anhydride of chromic acid (H_2Cr_4), just as sulphur trioxide (SO_3) is the anhydride of sulphuric acid (H_2SO_4). The reaction of each anhydride with a single molecule of water (H_2O), forms the acid. Just as the sulphuric acid supplies hydrogen to be plated out along with the nickel, so the chromic acid supplies hydrogen to deposit with the chromium. The more sulphuric acid added to the nickel solution the more hydrogen and the less nickel there is deposited.

Faraday's law is that at both anode and cathode a total of chemical changes must occur equivalent to the current, and no exception to this is known. Three different changes are going on at the same time at the cathode in a chromium plating solution, reduction of the valence of chromium from six to three, deposition of hydrogen, and deposition of metal. The sum total of these accounts for the whole current flowing. If with a constant current we increase the amount of any one of these changes, one or both of the other changes must necessarily be diminished. This principle is beautifully shown when plating with cadmium from cyanide solution. At low current density no hydrogen accompanies deposition of metal, i. e., the efficiency is 100 per cent. Increase the current and hydrogen begins to be deposited along with cadmium, because in each second of time there is not enough cadmium brought by diffusion into contact with the cathode for this larger current to be entirely occupied in depositing cadmium; so the deficiency in cadmium has to be made up by deposition of the only other substance that can be deposited at cathodes from this solution, viz., hydrogen. Now bob the cathode up and down in the solution as if you were fishing for cod. The evolution of hydrogen ceases. You are continually moving the cathode into fresh solution where there is plenty of metal to carry all current to the cathode, so hydrogen is no longer deposited, and the efficiency of metal deposition is 100 per cent even at the higher current.

This is what is accomplished by "motion planting," long used in the deposition of silver, in order that a weak solution of this precious metal may be made to deposit silver as fast, without burning, as a much stronger still solution can do. Whenever so much current is driven through a solution that there is not enough metal in contact with the cathode at all times to carry the whole current to the cathode, the balance of the current deposits hydrogen. The only exception to this is where a part of all the current may be used in the reduction of some metal in the solution from a high to a lower valence, as pointed out for ferric chloride and the chromic acid solution.

At the anode similarly, all current not employed in dissolving metal or in raising the valence of metal already in solution (what chemists call oxidizing the metal to a higher valence), evolves oxygen, chlorine, etc., depending on the solution.

It is evident why motion of the cathode or stirring the solution can entirely prevent the deposition of chromium, as you know it does, unless you increase the current at the same time that you stir the solution. The motion brings into contact with the cathode enough chromic acid so that the entire current is used in reducing this to a lower valence, and consequently there is no deposition of chromium. The higher the temperature, the higher must be the current density to secure any deposition of chromium. Why? Because rise of temperature lowers viscosity, and so increases the rate of natural diffusion of all dissolved substances; this, like gentle stirring, brings the high-valence chromium to the cathode faster than before. A high current density is thus required in order that, after all this extra chromic acid has been reduced, some current may still be left over to deposit chromium.

It is on the same principle that you warm the nickel and cyanide copper solutions, to allow the use of an extra high current density. Burning occurs because there is not enough metal in the film of solution touching the cathode, and not, as some people erroneously think, because hydrogen is evolved. As previously explained, evolution of hydrogen is often an indication that there is a lack of sufficient metal at the cathode, hence it is not strange that some should have mistaken a symptom for the cause of the disease. Heating accelerates diffusion, and thus brings into the cathode from the main body of solution enough extra metal so that the current density, and hence the speed of plating may be increased without burning. Hydrogen in chromium plating indicates how much current is wasted in depositing a substance that is useless, except as it may serve as a tenuous hook on which to hang patents. It is worse than a waste, for it causes vigorous stirring at the cathode surface, where stirring has the greatest effect in diminishing the efficiency of chromium deposition. Anything that cuts down the liberation of hydrogen will therefore have a double effect in increasing the efficiency of deposition of chromium.

Anodes

My remarks on anodes for chromium plating are based on small-scale experiments in the laboratory, run 24 hours a day, with electrode removal only at long intervals. Since the solutions were covered, the loss by spray was negligible, and because of the infrequent removal of cathodes, the solution carried out on these was but a small fraction of that so lost in commercial plating. As a result of these differences commercial solutions need replenishing with chromic acid sooner than mine, and the injurious effects which resulted from the use of most anode materials will be slower to appear in commercial solutions, since a considerable part of the anode products are carried out with the solution lost.

As commonly used in plating solution anodes serve two distinct purposes. They lead in and distribute current to the articles to be plated, and also supply metal to replace that which is deposited. Practice in chromium plating has differed from the normal in the use of anodes only to distribute current, the metal taken from the solution being replaced by additions of chromic acid at suitable intervals. There have been two reasons for this: First, the difficulty of obtaining chromium anodes; second, the greater cost of supplying chromium from anodes instead of by chromic acid.

So far as I have observed, the materials which have been recommended for anodes are chromium, lead, steel or iron, and several grades of chrome steel. Of these only chromium supplies the necessary metal to the solution. Besides testing all of these and several commercial alloys noted for their resistance to corrosion, I made a few special alloys in order to find the effect of certain other elements which have been found resistant to ordinary chemical corrosion.

Chromium

The chromium anodes were free from carbon and iron, and corroded very smoothly and uniformly without the production of sludge. Efficiencies are based on a valence of six for chromium. The efficiency of deposition was 12 per cent at the start, 9.2 per cent after 48 hours, and only 2 per cent at the end of 131 hours. Were there no loss of solution the final chromium content would have been 377 per cent of what it was at the start. Besides lowering the efficiency of deposition, other effects of this tremendous gain in chromium were serious increases in the viscosity and electrical resistance of the solution. Bright deposits were no longer obtainable, and treeing on the edges of cathodes was a regular occurrence. Chromium anodes are not suitable for continued use in the chromic acid solution because chromium is dissolved so much faster than it is deposited.

Lead

The lead was coated with peroxide by use as anode in dilute sulphuric acid before placing it in the chromium solution. Electrolysis was continued for 342 hours with no addition except water, when 70 per cent of the chromium originally in the solution had been deposited. The freshly made solution had a cathode efficiency of 3.8 per cent, which rose to a maximum of 22 per cent at the end of five days, and had fallen to 12.3 per cent at the end of the test. Since current density affects the efficiency of deposition, similar effects are not to be expected unless solutions are run at about the same current density, 112 amperes per square foot. A tendency to treeing was noticed when their chromium content had become very low, and deposits were then less bright than at the start. Addition of 8 oz. of chromic acid per gallon restored the original brightness of deposit. So far as keeping the solution in good condition is concerned, lead anodes are eminently satisfactory, and in this continuous operation there was no difficulty from insulating coatings of lead chromate, which are so troublesome in the intermittent operation of commercial solutions.

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 on the Sargent solution. Both steel and Armco iron anodes became covered with a brown coating, presumably manganese dioxide from the manganese which they contained, and were very slowly corroded. The efficiency of corrosion diminished with time, falling from 2.4 per cent at the start to 0.3 per cent at the end of 340 hours. The average rate of corrosion was 0.0084 grams per ampere hour. After continued use of the iron anode several injurious effects were noted: the rate of deposition was only seven-tenths that from a similar solution with lead anodes, the resistance was doubled, a brownish film very difficult of removal formed over the chromium plate, and the tendency to treeing was greater than with lead anodes. As a result of the higher resistance the temperature of the solution was higher by 180° F. than when the anode was lead. This difference in temperature is undoubtedly partly responsible for the lower efficiency of deposition found in this solution.

Because of the greater loss of solution by spray and by drip from articles plated, these effects of iron or steel anodes will be much slower to appear in commercial plating solutions. If the amount of solution carried out on "the work" is extremely great because of large surfaces plated and extremely short period of plating, it is conceivable that the iron content might never reach the harmful concentration. I would like to have reports on *whether* or *not* the above effects of steel anodes have been observed, with the volume of solution, period of plating, and how long the solution has been in use.

Silicon-Iron

Duriron, an iron-silicon alloy containing about 15 per cent of silicon, is noted for its resistance to corrosion. An alloy of 16 per cent of silicon with pure iron was made. This lost 0.0135 grams per ampere hour, about twice the corrosion of steel.

Nickel

Like iron, nickel tends to become passive in oxidizing solutions, hence it was thought that this might prove more satisfactory than iron, for any nickel which might dissolve should not cut down efficiency of deposition of chromium by using up current in changes of valence at anode and cathode, as iron does. For a period of 130 hours the rate of corrosion was 0.0624 grams per ampere hour, entirely too great for service as anode. The deposits of chromium soon became worthless.

Ferrochromium

Chrome steel, especially that of high chromium content, has often been recommended for anodes. Commercial ferrochromium, probably about 64 per cent chromium, quickly spoiled the deposit and the solution.

Stainless Steel

Stainless steel (13 per cent chromium and 0.3 per cent carbon) corroded at the high rate of 0.43 grams per ampere hour, and is a failure as anode. Chromium is a distinctly harmful ingredient of steel for use as anode in chromium plating.

Nichrome

The nickel-chromium alloys are esteemed for their resistance to corrosion by acids, so a strip of such alloy (20%Cr) was tried. This lost 0.66 grams per ampere hour, over double the loss of pure chromium, and 16 times the rate of deposition of chromium. This alloy proved an utter failure as anode, and it is probable that any addition of chromium to nickel only makes it worse as an anode, as for iron.

The unexpected and freaky behavior of the chromium plating solution in deposition, with which you are doubtless, to your sorrow, acquainted, extends to its corrosion of anodes, for in it many materials of great reputation for resistance to acids have failed utterly as anodes. The choice of anode material seems to lie between lead, with its habit of becoming coated with insulating lead chromate, and steel, which may bring about premature spoiling of the plating solution. It is a choice between two evils. * * * At the last minute I have a report from Dr. Becker of the Vacuum Can Co. that in the complete absence of sulphate, chloride, fluoride, etc., the ions which destroy passivity and promote corrosion of iron and steel anodes have been operated for four months without visible corrosion, and that no iron is found in solution. If this promise is confirmed by further experience steel will undoubtedly replace lead completely as an anode material.

PAPER ON RESEARCH, DEVELOPMENT AND STANDARDIZATION OF FINISHING PROCESSES AND METHODS

Presented by C. VanDerau

Annual Convention of American Electro-Platers' Society,
Toledo, Ohio, July 1, 1927

Up to the last few years, electro-plating and finishing has been known as more or less of an art, being done by skilled craftsmen.

evident that the zinc in some manner didn't come over, of course. When adding ammonia it would come over, and there is a question of how long it would continue to come over until he put in the zinc. If we would use less ammonia and use rather an amount of caustic soda we would find that we would keep our anodes cleaner and free from zinc. I think that if Mr. Goodsell had made additions of caustic potash they would have found that the zinc would soon have come out with the use of caustic soda.

MORE PERFECT METAL DEPOSITS

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Whether electroplating be done for protection or for ornament, it is desirable that the metal coating be perfect, free from holes through which moisture may get at the underlying metal and corrode or tarnish it. Then, too, adhesion must be sufficient to prevent separation of the coating under whatever service may reasonably be expected from the plated article. Adhesion of the deposit is largely a matter of the finish of the metal surface, and the perfection of cleaning this, and will not be discussed further.

Except when the thickness is utterly inadequate, the failure of electroplating occurs in tiny spots, not over extended areas. The points of failure may be either spots not covered by the metal deposit, or thin places in the plate which soon become worn through or corroded in service. In a study of the relation between thickness of deposit on steel and the frequency of pin holes, made twelve years ago, it was found that in general the thicker the deposit, the fewer the holes, and the longer the period of exposure required to produce rust. As a result of these tests it was recommended that metal deposits over steel be made thicker than was the commercial practice at that time. But deposits of copper or nickel heavy enough to protect steel out of doors must be so thick as to be impractical, and we are still accepting nickel-plated steel which rusts on long exposure.

Could these thin spots or "pin holes" be eliminated, electroplating would furnish almost indefinite protection to steel in ordinary usage. There is no problem in plating more important than this, and if I can be instrumental in starting a campaign for better metal deposits by the prevention of these thin spots or pin holes in electro-plate, I shall feel that I have performed a real and lasting service to the plating industry.

The final solution of this important problem will doubtless require extended laboratory investigation; but in the meantime platers may do much to improve metal deposits, even though perfect electroplate is not yet attainable. Madsen claims to produce perfect nickelplate, but never having tested or even seen any samples, I am unable to confirm or deny this claim. More perfect metal deposits can be secured by giving special attention to the solution and to the surface on which the plate is deposited.

The first thing for you folks to do is to get everybody who is working on plating to have this in mind and make observations on the effect of finishes in his plating conditions which may lead to less of these pin holes in electroplating. As to the causes of these pin holes I can only guess. I shall try to point out some of those which I think are probably the cause of them. There may be other things which I don't know anything about.

One thing which should certainly receive attention is the solution. Undoubtedly a great many of these pin holes come about from solid particles suspended in the solution which get on the face of the article being plated and make the thin spot very live on the face. It would be fine if we could remove suspended particles entirely from the plating solution. It is customary to leave a settling space in the bottom of the plating tank, and that disposes of a large amount of the sediment in the tank. With the high-speed production we have now-a-days, however, that is going to stir up a solution. And in many cases no doubt the settling space is not adequate and you have a great deal of that slime stirred up in your solution settling on your articles and producing bad pin holes on your plate. Continuous and rapid filtration is being used by some platers. That is certainly a step in the right direction. In two (2) installations that I have seen, in neither was the filtration rapid enough to keep the solution even approximately free from solid particles, although the filtration was doubtless a help toward better deposits. Of course sediment must be taken care of at a very reasonable rate. So many companies now regularly test their plated products for imperfect plating that it should be comparatively easy to learn whether or not more rapid and efficient filtration lessens the number of pinholes and imperfections.

I think, also, clearer solutions is one thing to aim at. I don't think we will ever attain an absolutely clear solution. But I think you men right here are the ones to tell what can be done in that way. Of course it can be tested in the laboratory, but to find out how much sediment you can get rid of practically without too much cost is something that will have to be settled in the plating room. And I hope that you men who take to filtering your solutions will observe the effect upon your plating—to what extent it makes an improvement on the pinholes in your plate. Now-a-days the big companies require that plated articles should be subjected to acid or some other corrosive material to find out how that plate is going to stand up. So it will be comparatively easy to compare the results of this plate through the result of filtration with the result without it, and in this way we will get at the true facts. And you have a chance at your meetings here to bring in the results and discuss them. Ten and fifteen men bringing in their results and exchanging their ideas will get ahead much faster than one or two men working by themselves. So I think it is highly important that you platers make such observations and believe it will result in great improvement.

I believe that there is little use in producing a solution perfectly clear from sediment without at the same time looking at another source of pinholes and imperfections: that is the surface of the metal upon which you are depositing. I have seen samples of metal that are being plated that are absolutely unfit for plating. The results were calculated to discredit all electro-plating in the eyes of the public. I had some samples of trunk wear sent to me some years ago to see what was the matter because they were having rust spots all over. For one thing they weren't putting on very much brass and for another thing the steel was absolutely unfit to plate in the condition in which they were plating. Examination showed that the surface of many pieces were deeply pitted from the removal of very heavy scale which had been rolled into the steel during manufacture. To make a bad matter worse, the ball burnishing of the steel before plating had rolled the edges of the deeper pits over to form caverns which there was no possibility of completely plating. The spots of bare steel in these formed voltaic cells with the brass plate surrounding them, and produced rusting with unusual rapidity. A sample of stainless steel from a well-known steel company was fully as badly pitted by the rolling of bits of scale into the steel. These were exceptionally bad cases, but even the pits in ordinary sheet steel may prove too deep and irregular for a poor-throwing solution to cover. I mention that as an example of what platers are sometimes asked to do. I think the best thing in that case is to tell the party supplying the steel that there is no possibility of doing the work satisfactorily. If plated, the result will discredit electro-plating.

In most cases, of course, you polish your steel surface more or less before plating, and it might be supposed that this would destroy any effect of pits in the original steel; but unless the polishing operations cut down to the level of the bottom of the deepest pits, there is still a likelihood that a poor-throwing solution, such as nickel, may fail to give a good deposit in the depressions. It is hardly to be expected that you could cover up those pits so that the plating would stand up without rusting.

Is there not a possibility that sometimes even in the finishing with emery that the scratches or grooves formed with the emery are too much to expect nickel to put a water-tight covering over those things?

I have been looking at nickel before and after plating with a binocular microscope. I use that because it is a wonderful improvement over the ordinary microscope and with the ordinary microscope you simply see down into the crevice and see that there is a whole down there, and that is all. But with this binocular microscope you can see the whole thing. Some of the big companies may have such a binocular microscope as a part of the equipment in some other part of the plant, and if you could examine your metal once in a while it would be a revelation to you to see the surface you have to plate and the result of the plating also. Of course it isn't necessary to have such a binocular microscope. It is a wonderful instrument, but even with a high-powered magnifier you can tell a great deal about the condition of metal surfaces. If you are not using that in your work I advise each one of you to purchase for a dollar or so one of these magnifiers and examine the metal before and after plating. It will be an education to you and will lead to greater improvement in the results of your plating. You will be able to tell some of the powers higher up that the metal is not fit to plate or that the finishing operations are not so good as you can make them and you can alter such operations so that you are producing a surface where there is more than a 50-50 chance of covering up the metal that you are trying to cover.

There is one topic that I wish to touch upon before leaving this subject, and that is the metal of zinc. Both the researches of the men responsible for the development of the electrolytic recovery of zinc, and the experience of the operators of the process show that very minute traces of certain metals in the zinc solution have extremely injurious effects upon the throwing power of the solution, the efficiency of deposition and the quality of the deposit, and that minute impurities in the deposited zinc greatly lessen its durability. It follows that the protection afforded by zinc plating may be much enhanced by the deposition of a purer zinc than is usually obtained in electroplating. This can be secured by starting with a pure solution and using only anodes of the highest quality.

I might say it took 25 to 30 years of experimenting before men got so that they could cover metals electrolytically. It has resulted in a 150-ton plant in Great Falls, Montana, and a lot of smaller plants elsewhere. They found that the reason men hadn't succeeded before was that the zinc solutions were not pure enough. Impurity cuts down the current efficiency and greatly lessens the throwing power and also affects the deposit unfavorably. They also found beyond any dispute that the purity of a deposit of zinc is an enormous factor in its durability, and that is the point that I want to emphasize more than any other. There is an enormous difference in the rate of corrosion of the high purity zinc and the ordinary zinc that we see. Several years ago I bought a zinc solution highly recommended and it did plate pretty well, but I found iron rust settled out of it until it seemed there wasn't anything else but iron rust. That solution had too much iron in it.

Two things to be remembered in connection with zinc are:

1. Keep your solution pure that you may get good throwing power and a high current efficiency, and

2. Your anodes should also be pure or you will defeat the object.

I believe the efficiency of electro-galvanizing can be enormously increased by getting pure zinc deposits, not 99% nor 99.9%, but 99.999%, and it will last four or five times as long as the 99% will last. There is no metal solution in which purity counts nearly so much in the nature of the deposit as in zinc.

This brief summary of some of the commonest failures of electroplating should serve to call attention to the remedies for the failures—properly filtered solutions, pure anodes, perfectly finished metal for receiving the deposit. With attention given to these three requisites, the quality of electro-plate should be greatly improved.