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Title An Investigation of Cyanide Free Baths for the Electrolytic Deposition of Copper and Brass

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An investigation has been carried out to find, if possible, some combination of zinc and copper salts in solution, other than their complex cyanide solutions, from which the two metals could be deposited simultaneously in the form of brass.

The problem is considered from the standpoint of theoretical decomposition voltages of the elements taken separately in similar solutions and from the standpoint of empirical experimental data taken on actual depositions from solutions containing the two metals.

Solutions considered are: simple sulfate solutions with additions of other metallic sulfates, boric acid, sulfuric acid, and organic addition agents; thiocyanate solutions; alkaline tartrate solutions; and citrate solutions.

Some brass deposits were obtained from the sulfate solutions. The conditions, however, under which these deposits were formed excluded the possibilities of their industrial application.

The thiocyanate solutions were not extensively investigated since, from the work done, they seemed to lack potential possibilities for development into a feasible plating bath. Copper thiocyanate is very slightly soluble; hence it is quite evident that in such a solu-

tion there would be a precipitate present which is objectionable.

The most promising solutions studied were solutions containing copper and zinc sulfates, sodium tartrate and sodium hydroxide. These were the only solutions in which the cathode decomposition potential curves for similar solutions of zinc and copper showed any appreciable tendency toward convergence. Fairly good brass deposits were obtained from these solutions on sheet iron, copper, and platinum cathodes. The adherence of the deposits on stainless steel cathodes was very poor. One of the deposits obtained from a solution, containing 33.7 grams $Na_2 C_4 H_4 O_6 . 2 H_2O$ per liter to which sufficient NaOH was added to make it distinctly basic, was analyzed as 44.7% Zn and 55.3% Cu.

The chief difficulties with this bath were: 1. poor anode corrosion; 2. a precipitate formed on standing; 3. deposits were not proper color and not uniformly good on all surfaces; 4. the throwing power of the solution was not too good.

The citrate baths did not seem to adapt themselves to brass deposition.

A further investigation was carried out with ammoniacal copper tartrate solutions to learn if there were not some possibility of their use as strike baths for plating copper on iron. Good copper deposits were obtained from these solutions at fairly high efficiencies. There seemed to be some difficulty of salt formation at the anode. The problem was not completely investigated. Such solutions do, however, offer possibilities for strike plating iron with copper preliminary to the regular acid sulfate bath.

AN INVESTIGATION OF CYANIDE FREE BATHS FOR THE ELECTROLYTIC DEPOSITION OF COPPER AND BRASS

by

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Table of Contents

AN INVESTIGATION OF CYANIDE FREE BATHS FOR THE ELECTROLYTIC DEPOSITION OF COPPER AND BRASS

Introduction

Brass is universally deposited electrolytically on various other metals as an ornamental coating and, to a lesser extent, as a protective layer. All commercial brass plating, however, is done from an electrolyte consisting of the complex cyanide salts of copper and zinc with free cyanide in the form of sodium or potassium cyanide. This bath is operated in the alkaline range because of the instability of the cyanide salts in an acid solution and because of the very poisonous hydrogen cyanide gas, which is given off when a cyanide salt is treated with an acid. Although it is possible to obtain very good brass deposits from the cyanide electrolytes, there still seems to be more or less objection to the use of cyanides in modern large scale electrodeposition processes. (8) The chief objections are: first, the poisonous nature of the cyanides, especially under the condition that the acid, carried over from the pickling bath, would tend to liberate hydrogen cyanide; and, second, the cyanide bath is unstable and expensive. Many attempts have been made to find another bath which would be suitable for commercial plating. In the chemical literature can be found recurrent reports of these investigations, many of which hold out some promise for the problem.

Thon and Pinilla (10) report that they obtained brass deposits from a thiocyanate solution. Sukhodskii, Kheifetz, and Chapurskii (9) used a basic tartrate solution from which thin deposits of brass were

formed. In a discussion at the meeting of the American Electrochemical Society, Dr. Colin G. Fink (8) stated that brass deposits had been obtained from sulfate solutions in his laboratory. Preliminary experiments in this laboratory showed the possibility of getting a thin brass deposit from sulfate solutions containing certain addition agents under carefully regulated current density and agitation. Other investigators have tried various baths without success. Bennett and Davison (2) carried on extensive investigations with various simple and complex salts using a rotating cathode without success. In his review of the literature on brass plating, Bennett (1) gives a suggested bath consisting of the acetates of zinc and copper and ammonium salts.

Likewise many attempts have been made to find non-cyanide baths for the electrodeposition of copper alone. A few of these indicate some possibility of commercial application and also further suggest some possibilities for brass plating from similar solutions. Brown and Mathers (4) recommended an electroplating bath containing Rochelle salts and sodium hydroxide for strike plating iron. Fink and Wong (6) have developed the "oxalato" bath which is highly recommended for this purpose. Brockman and Brewer (3) suggest the use of triethanolamine solutions for copper plating. Vuileumier (11) has investigated the electroplating of copper from ammonical solutions and finds that good deposits are obt ainable under certain conditions. Fedotiev (5) used a cuprous chloride solution for copper plating.

The purpose of this research was to investigate some of the possibilities of non-cyanide brass plating which have already been reported in the literature and to make a further investigation of the various factors which might influence the binary deposition of zinc and copper from solutions containing no cyanide complexes or free cyanide.

While working with ammonical tartrate solutions of zinc and copper, some very good deposits of copper were obtained. This suggested the use of such solutions for strike plating iron with copper. As a secondary purpose in this investigation the properties of such solutions were studied.

Theoretical

When any solution containing two or more different metallic ions is electrolyzed, co-deposition of these metals will occur if their single electrode potentials are equal or nearly equal and do not exceed the single electrode potential of hydrogen, provided no other factors but the single electrode potentials affect the simultaneous deposition of these metals. Hence the problem in the deposition of binary alloys resolves itself into bringing the single electrode potentials of the two dissimilar ions in solution close enough together for co-deposition to occur, and, at the same time, avoiding the liberation of too much hydrogen.

Metals found close together in the electrochemical series have decomposition voltages which are fairly close to each other, and the simultaneous deposition of such metals does not offer such a difficult technical problem. For example lead and tin have nearly equal potentials in fluoborate solutions, and lead-tin alloys are deposited from such baths with cathode current efficiencies over a wide range of conditions of nearly 100 per cent. In the case of the co-deposition of zinc and copper the condition is, however, much different.

It is found that the single electrode potentials for copper and zinc ions in their normal sulfate solutions are +0.34 and -0.76 volt respectively as compared to the hydrogen electrode. This shows a total difference of 1.1 volts. In order to obtain co-deposition of the two metals, it is, therefore, necessary to make the copper

more negative or the zinc more positive. Inspection of the well known Nernst equation:

$$E = E_o + \frac{R\,T}{n\,F} \ln \frac{a_2}{a_1}$$

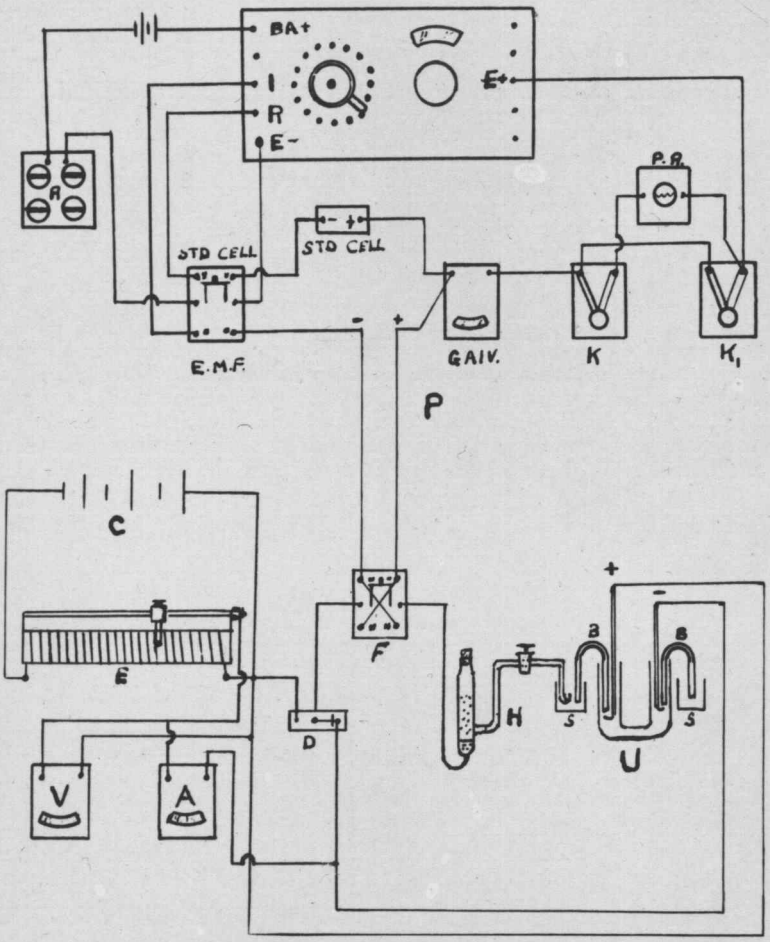
which gives the single electrode potential E for a metal in contact with any solution of its ions and in which E_o represents the normal electrode potential, R the gas constant, T the absolute temperature, n the valence of the ions, F the Faraday constant, a_1 the activity of the metal in the standard state, and a_2 the activity of the ions in the solution of given concentration (the activities may be replaced by the concentrations of the salt in dilute solutions since the degree of dissociation is large); shows that in the case of zinc and copper, since the valences are the same, the single electrode potentials of copper could be theoretically made to equal that of zinc at constant temperature by decreasing the concentration of the copper ions. On the basis of this equation a calculation shows that by decreasing the concentration of cupric ions to about 1×10^{-38} M, the single electrode potential of copper would equal the normal electrode potential of zinc. This is, of course, an extremely low concentration of ions. The decrease in metal concentration, by dilution, decreases also the conductivity. Both the low metal content and the low conductivity thus produced are undesirable. When metal content is low, there is no ready source for the renewal of the ions removed from about the cathode; these are practically all removed by the passage of only a small quantity of electricity. When the conductivity is low a great-

er amount of energy is consumed in the deposition of a given amount of metal. Therefore, the more satisfactory and practical method of controlling single electrode potentials is that of complex ion formation. Under such conditions there is only a low concentration of the metallic ion present at equilibrium, but it is possible to have a high concentration of the metal present contained in the complex ion. As the metal ions are removed by electrodeposition, more are formed immediately by the secondary dissociation of the complex ions so that there is not an impoverishment of ions around the cathode.

The simultaneous deposition of two metals, furthermore, is not determined by ion concentrations alone. Numerous other factors such as current density, temperature, over-voltage, polarization, complex equilibria, circulation, and addition agents will not only affect the deposition of the metals but likewise determine the composition of the resulting deposit. The current density effect may be due, partially, to the fact that the discharge potentials for all metals increase with increasing current density, although not all at the same ratio. At a constant current density, an increase in temperature produces a decrease in the discharge potentials of the metals. An increase in temperature also increases the rates of migration of the ions as well as increases diffusion. A rise in temperature decreases chemical polarization. Addition agents may affect the deposition of one metal and not the other, or there may be a decidedly different effect of the addition agents on the process of deposition. An excellent illustra-

tion of how these factors may influence the simultaneous deposition of the two metals is borne out in the work of Bennett and Davison(2) in which they were unable to get satisfactory deposits of brass on their rotating cathode from cyanide solutions, whereas on a still cathode good deposits are obtained from the same solutions.

PLATE I



A Micro-ammeter
B Agar Salt Bridge
C Storage Battery
D Double Throw Switch
E Slidewire Resistance
F Current Reversing Switch
H Normal Calomel Half Cell
S Saturated KCl solution
U U-tube Containing Pt. Electrodes
V Voltmeter
P Leeds and Northrup Student Potentiometer

Experimental

The experimental part of this investigation was approached from two different angles. First, the single electrode potentials for the deposition of zinc and copper, taken separately from various solutions of their ions, were obtained. Plotting the data from these experiments shows whether there is any possibility for the cathode potentials' of zinc and copper in similar solutions becoming equal, or nearly equal. Of course, when the zinc and copper salts are mixed for the brass plating bath, the presence of one may exert some influence on the other; but, in general, a comparison of their respective decomposition potentials will throw some light on their behavior when placed together in a solution similar to the one used in the separate determination.

The second line of approach consisted of taking mixtures of the copper and zinc salts and attempting to get satisfactory brass deposits from them. Many different combinations were tried, and some of the typical ones are discussed in the following pages. Since the appearance, mainly color and smoothness, of brass plating is its most important property, this was used as the main criterion of the work done in this investigation. Other important characteristics referred to are: physical structure of deposit; its adherence to the cathode; and its chemical composition. Further points to have been investigated were the maintenance of bath composition, its cost, its throwing power, and its adaptability for various types of

work. No solution, however, was found which gave a deposit good enough to be adapted to these further studies.

The electrolytic method of analysis was used for determining the composition of the brass anodes and samples of plating analyzed. The brass was dissolved in nitric acid. This solution was evaporated to dryness on a water bath. The residue was treated with concentrated sulfuric acid and evaporated on a sand bath until white SO_3 fumes were liberated. The resulting paste, diluted with water, was electrolyzed until the copper was completely deposited. The electrodes were platinum and the current was supplied by a single cell of a lead storage battery. The electrolysis was operated at a temperature of from 70° to 80° C, materially decreasing the time required for the complete deposition of copper. Since there was no lead present, the zinc could be taken by difference, or the solution could be made alkaline with NaOH and the zinc deposited on the copper-plated platinum electrode by using 12 volts and a variable resistance by which the current could be adjusted from 0.5 amperes to 0.7 amperes.

The single electrode potentials were obtained by the method outlined by Müller (7). The wiring diagram for this set-up is given in Plate I. The potentiometer was a leeds and Northrup Student Potentiometer calibrated to 0.5 millivolt. The voltage was compared to an unsaturated cadmium standard cell with a given voltage of 1.0183 volts at 20° C. A normal calomel electrode was used as a reference electrode, and a saturated potassium chloride agar bridge

was used between the electrode in the U-tube and the arm of the calomel electrode. A double throw switch was included in the wiring so that the direction of the current could be reversed easily without making any disconnections. The variable potential drop was obtained by use of a slide wire resistance and a storage battery. In general platinum electrodes were used for determining the single electrode potentials. A stainless steel cathode was compared to the platinum cathode and showed very little difference in the decomposition voltage.

The platinum electrodes were made by sealing into glass No. 28 gauge platinum wire. The exposed wire was 1.66 cm. long, which was coiled into a round flat coil, having an exposed surface of 0.167 sq. cm.

The container for the electrolyte was a U-tube made from 16 mm. pyrex tubing. The bend was drawn out so as to be of smaller bore than the vertical arms. When making a run, the solution being studied was placed in the U-tube; the electrodes placed in position, always as nearly as possible to the same level in the tube; and one arm of the salt bridge placed as closely as possible to the platinum electrode. The electrodes were then short circuited for a short time to allow them to come to equilibrium. The electrode potentials were taken. Only one calomel cell was used, and it was moved from one side to the other in taking readings. The circuit was closed and a current passed through the cell. The potential drop across the cell was gradually increased.

An interval of five minutes was allowed between each successive reading in order to let the system come to equilibrium. All solutions were made up from C. P. grade materials.

Table I
Decomposition Potentials
of a N $ZnSO_4$ Solution

e_A	e_C	I	C. D.	V
0.456	0.459	0.0	0.000	0.0
0.459	0.310	0.0	0.000	0.2
0.781	0.164	2.0	0.012	0.6
1.100	0.022	3.0	0.018	1.0
1.254	-0.355	5.0	0.030	1.4
1.286	-0.766	8.0	0.048	1.8
1.344	-1.107	20.0	0.120	2.2
1.402	-1.112	50.0	0.300	2.3
1.465	-1.121	150.0	0.900	2.4
1.510	-1.125	250.0	1.500	2.5
1.574	-1.136	480.0	2.880	2.65

Explanation of Table:

e_A and e_C are potentials of the anode and cathode respectively as compared to the normal calomel electrode with the potentiometer; I is current flowing through the cell, measured in microamps.; C. D. is current density on the electrodes in milliamperes per sq. cm.; and V is the voltage drop across the cell as measured with the voltmeter.

Since the sulfates would be the cheapest and, in many ways, the most satisfactory salts to use, if possible; it was desirable to determine what effect the addition of alkali ions to the simple sulfates would have. Table I gives the data taken for the decomposition potential of N $ZnSO_4$ and Fig. 1 shows these data plotted, giving an example of a typical curve for determining decomposition potentials. Extrapolating the cathode and anode branches of these curves to zero

Fig. 1
Decomposition Potential Curve for N $ZnSO_4$
Circles Indicate Points on Curve for N $ZnSO_4$+N Na_2SO_4
Temperature 27°C

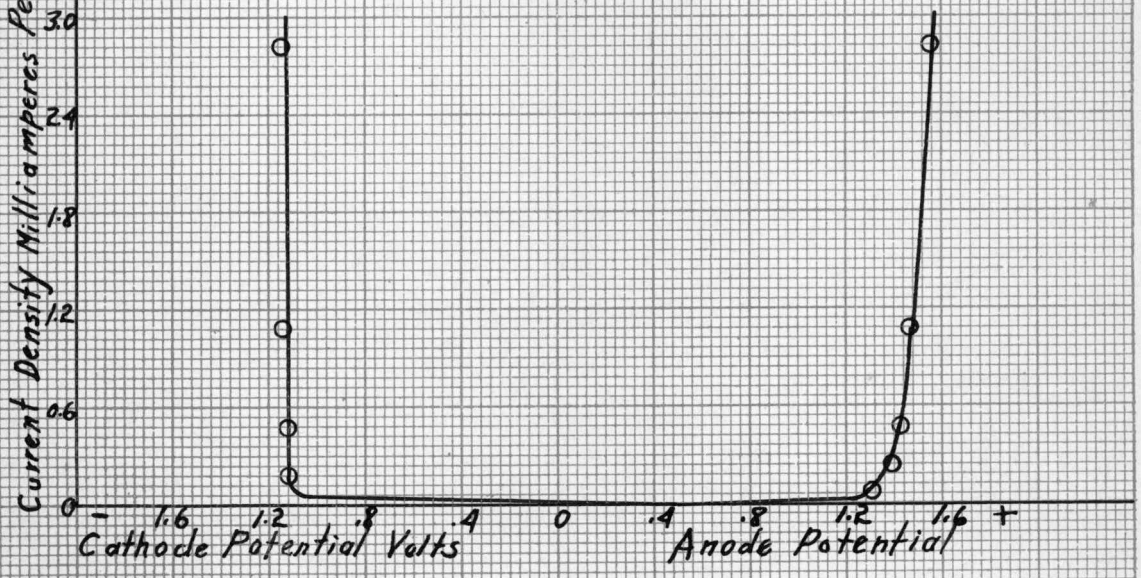
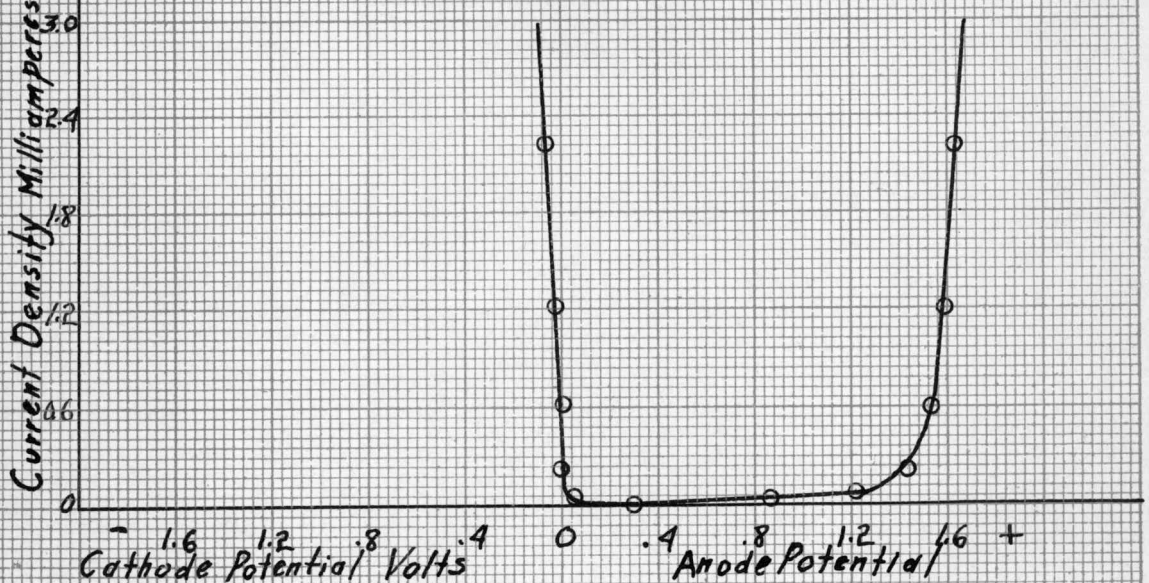


Fig 2
Decomposition Potential Curve for ½N $CuSO_4$
Temperature 25°C



current, a potential drop of approximately 2.55 volts is obtained. This would represent the minimum voltage that would deposit zinc under the conditions of the experiment. The values plotted in this graph are compared to the normal calomel electrode and have not been corrected to the hydrogen electrode.

Table II
Decomposition Potentials for a
N $ZnSO_4$ + N Na_2SO_4 Solution

e_A	e_C	I	C.D.	V
0.381	0.381	0.0	0.000	0.0
1.087	0.006	2.0	0.012	1.0
1.254	-0.906	5.0	0.018	1.95
1.319	-1.113	12.0	0.072	2.2
1.385	-1.117	40.0	0.240	2.25
1.430	-1.122	80.0	0.480	2.3
1.483	-1.129	180.0	1.080	2.4
1.556	-1.141	470.0	2.820	2.55

Table II gives the data for a solution normal with respect to $ZnSo_4$ and normal with respect to Na_2 SO_4. The points on the curve for these data fall so close to those for normal Zn SO_4 alone that it is impossible to draw two separate curves on the same graph. In Fig 1, however, points from Table II have been indicated by circles on the curves from Table I. These curves indicate that the presence of the sodium ions in solutions of this concentration have very little effect on the decomposition voltage at low current densities. In more dilute solutions the influence that the presence of the sodium sulfate would have on the conductivity would perhaps have some effect on the potential required to obtain a given current density. A solution of half

normal Zn SO_4 was compared to the normal solution, and for a current density of 0.8 milliamperes per sq. cm. the cathode potential of the half normal solution was -1.123 volts as compared to -1.121 volts for the normal solution, and the anode potential for the half normal solution was +1.468 as compared to +1.465 for the normal solution. The difference here is very small, really no difference within the limits of experimental error. The results would indicate that the presence of the sodium ions or the difference in concentration of the zinc sulfate had very little effect on the decomposition voltage, within certain limits at least. These solutions were neutral.

Next the effect of change in the acidity of the solution was investigated. A solution of half normal Zn SO_4 was made distinctly acid to methyl orange and congo red with sulfuric acid. At a current density of 0.72 milliamperes per sq. cm. the cathode potential was 0.432 volt and the anode potential was +1.515 volts. It is seen here that the cathode potential has dropped sharply and the anode potential has increased somewhat over that of the neutral solution. A half normal solution of zinc sulfate was treated with concentrated sodium hydroxide solution until the zinc hydroxide first formed was just dissolved. The resulting solution was decidedly basic to phenolphthalein indicator. The cathode potential, for a current density of 0.72 milliampere per sq. cm. was -1.22 volts and the anode potential, +0.702 volt. Under these conditions the negative potential of the cathode has increased, and the positive potential has sharply decreased over that of the neutral solutions. There would be a

noticeable tendency for hydrogen evolution from such a solution. It is obvious from these experiments that the conditions favoring a lowering of the negative cathode potential are an increase in the acid concentration and the current density. An increase in the current density raises the hydrogen over-voltage and thus inhibits the liberation of hydrogen at the cathode. The hydrogen over-voltage drops markedly in an acid solution unless other factors are present to prevent it.

Solutions of copper sulfate were subjected to similar conditions. Table III gives decomposition potentials for a half normal $CuSO_4$ solution.

Table III
Decomposition Voltages for
Half Normal $CuSO_4$ Solution

e_A	e_C	I	C. D.	V
0.320	0.320	0	0.000	0.0
1.312	0.106	5	0.030	1.05
1.436	0.038	35	0.210	1.28
1.523	0.014	100	0.600	1.45
1.584	-0.020	210	1.260	1.65
1.6 +	-0.061	370	2.150	1.85

These data are plotted in Fig. 2. The cathode branch of this curve compared with that of Fig. 1 shows them to be much the same shape, although the magnitude of the cathode potential is much different--about 1.12 volts. The slopes of these curves would not indicate that there would be a convergence of them within any reasonable limits.

Table IV gives the data for a half normal $CuSO_4$ solution made distinctly acid with sulfuric acid. A comparison of these results with

Table II indicates that a difference in acidity has very little influence on the decomposition voltage of $CuSO_4$. This is quite different from what was observed in the case of zinc.

Table IV

Decomposition Voltages of Half Normal $CuSO_4$ in Acid Solution

e_A	e_C	I	C. D.	V
0.229	0.224	0	0.000	0.00
1.178	0.052	40	0.240	1.00
1.392	0.028	90	0.540	1.24
1.553	-0.020	200	1.200	1.45
1.6 +	-0.066	400	2.400	1.75

Table V shows the effect of temperature change on the decomposition voltage of half normal $CuSO_4$. In this table the potential applied on the electrodes is constant throughout the run. It can be seen that if the current density had been maintained constant that the change in cathode potential would have been greater than here indicated. The data here given are reversible, that is, for decreasing temperatures on the same solution, practically the same values were obtained as for increasing temperatures.

On the basis of these experiments a number of attempts were made to deposit zinc and copper simultaneously from an acid sulfate solution. A stainless steel cathode, made from sheet U. S. stainless steel No. 18, was used because of the ease with which the deposit could be dissolved from the surface with nitric acid without material-

ly affecting the electrode. A suitable platinum electrode was not

Table V
Effect of Temperature Change on
the Decomposition Voltages of
a Half N $CuSO_4$ Solution

Temp.	e_A	e_C	C. D. milliamps./cm.^{2}
26° C	1.396	-0.058	0.54
35°	1.388	-0.052	0.660
40°	1.387	-0.026	0.660
45°	1.389	-0.011	0.720
50°	1.388	+0.002	0.840
55°	1.389	+0.016	0.990
60°	1.385	+0.030	1.200
66°	1.361	+0.042	1.560
70°	1.354	+0.048	1.800

available. A half normal Cu SO_4 solution gave the same cathode potential at 2 milliamperes per sq. cm. current density with a stainless steel cathode as with a platinum cathode. A rectangular piece of steel with an exposed area of 0.696 sq. in or 4.5 sq. cm. was sealed into a glass tube with wax and connection was made with copper wire, soldered to the piece of steel. Similar electrodes made from commercial sheet brass, analyzed as 66% Cu and 34% Zn, were used as anodes. An anode was used on each side of the cathode. The solution was stirred with a mechanical stirrer consisting of a rotating glass rod. At low current densities copper deposits were obtained; at intermediate current densities loose non-adhering deposits, ranging in color from dark red to black, were obtained. At high current densities closely adhering zinc deposits covered with loose black deposits

were obtained.

Table VI

Voltage as indicated by voltmeter	Anode Current Density amps./sq. cm.	Cathode Current Density amps./sq. cm.	Nature of Deposit
6	0.125	0.278	adherent, fine gray deposit covered with spongy black deposit
4	0.090	0.200	adherent gray deposit, not as good as previous one, covered with considerable loose black material
3	0.070	0.155	adherent gray deposit covered with loose black deposit
2.2	0.040	0.089	loose black deposit, brown in spots, underneath which was a very small gray deposit
1.5	0.020	0.045	loose dark red deposit not adherent at all
	2% H_2 SO_4 added		
3	0.050	0.111	loose red deposit
6	0.31	0.69	considerable loose black deposit over fine grayish-black adhering deposit

Table VI gives in tabular form the results of one of these runs, which is typical of a large number of others made under various conditions. The solution contained 200 grams $ZnSO_4 \cdot 6H_2O$ and 4 grams $CuSO_4 \cdot 5H_2O$ per liter of water. All results are for 25° C. The time allowed for each deposition was five minutes.

Addition of Na_2SO_4, $Al_2(SO_4)_3$, or $(NH_4)_2SO_4$ did not improve the deposits. These data bear out the information obtained from the work on decomposition potentials, but do not give promise of brass deposits from such solutions.

A brassy appearing deposit was obtained from a solution containing 4 grams of copper and 2 grams of zinc as sulfates per liter, made slightly acid with sulfuric acid, and saturated with boric acid. The current density was varied between 0.5 and 1.0 amper per sq. in., and the electrodes were agitated by hand. By carefully watching the electrode the nature of the deposit could be somewhat controlled by the amount of agitation. There was always a considerable amount of loose black deposit along with the adhering deposit. One of these deposits was analyzed by the method outlined; it had a composition of 81% copper and 19% zinc. The deposit was so small that too much credence could not be placed on the analysis. At low current densities copper only was deposited. Because of the extremely low current efficiency and the variable factors of agitation and current density, the solution did not seem satisfactory.

The thiocyanate solutions recommended by Thon and Pinilla were

investigated. Since the zinc and copper thiocyanate salts were not available in this laboratory, other salts were used and the amount of KSCN increased enough to convert these into the thiocyanates. A solution consisting of 366 grams of $Zn\ Cl_2 . 6\ H_2O$, 580 grams KSCN, and 1.25 grams $Cu\ SO_4 . 5\ H_2O$ per liter was electrolyzed with brass anodes and a stainless steel cathode at room temperature and at a cathode current density of 0.445- 0.89 milliamperes per sq. cm. A black non-adhering deposit was formed.

Zinc sulfate instead of zinc chloride was used. The electrolyte, in this case, consisted of 403.5 grams $Zn\ SO_4 . 6\ H_2O$, 580 grams KSCN, and 1.25 grams $Cu\ SO_4 . 5\ H_2O$. A large amount of white crystalline precipitate was formed in this case. This was presumable $K_2\ SO_4$, as it was soluble in excess water but not in acid. The solution was electrolyzed at a cathode current density of 0.445 - 0.89 milliamperes per sq. cm. The deposit was black and non-adherent. This solution did not seem to be too promising because of the insolubility of the copper thiocyanate. Even in a saturated solution, the copper concentration in solution would be very low. This is, as already pointed out, undesirable in plating solutions. Due to these inherently unavoidable difficulties, this method was not investigated further.

The tartrate solutions were next investigated. Fig. 3 gives the curves obtained when the cathode decomposition potentials were plotted against current densities for solutions half normal with respect to zinc and copper sulfates, normal with respect to sodium

Fig. 3

Cathode Potentials for Electrolysis of Solutions of $\frac{1}{2}$N $ZnSO_4$ and $\frac{1}{2}$N $CuSO_4$ in N $Na_2C_4H_4O_6$ Made Alkaline with NaOH

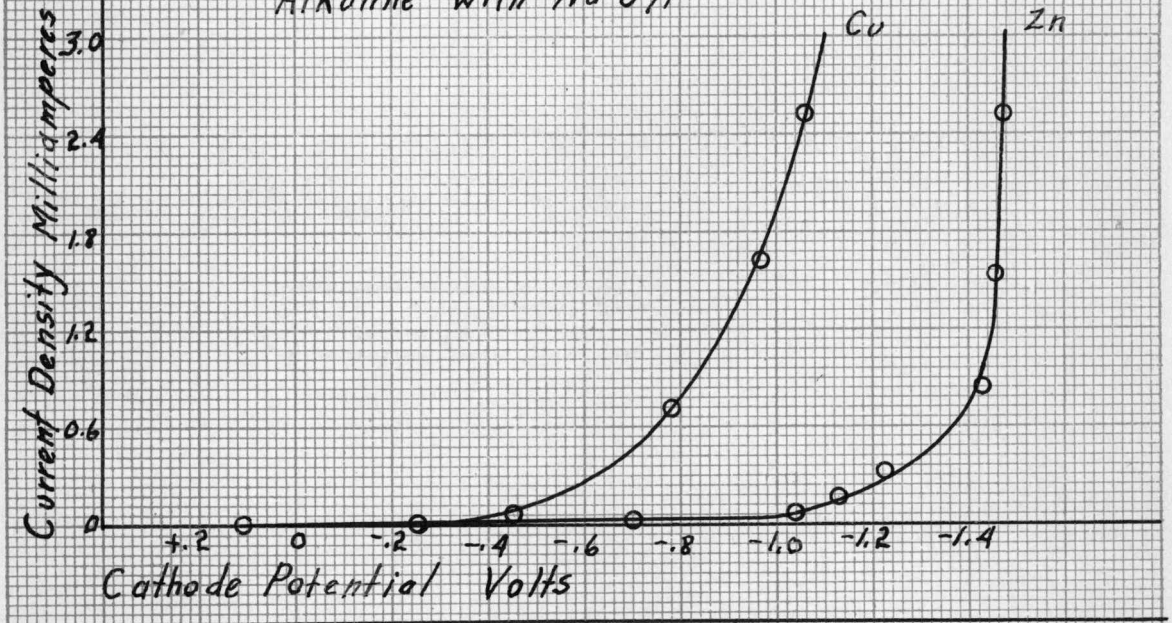
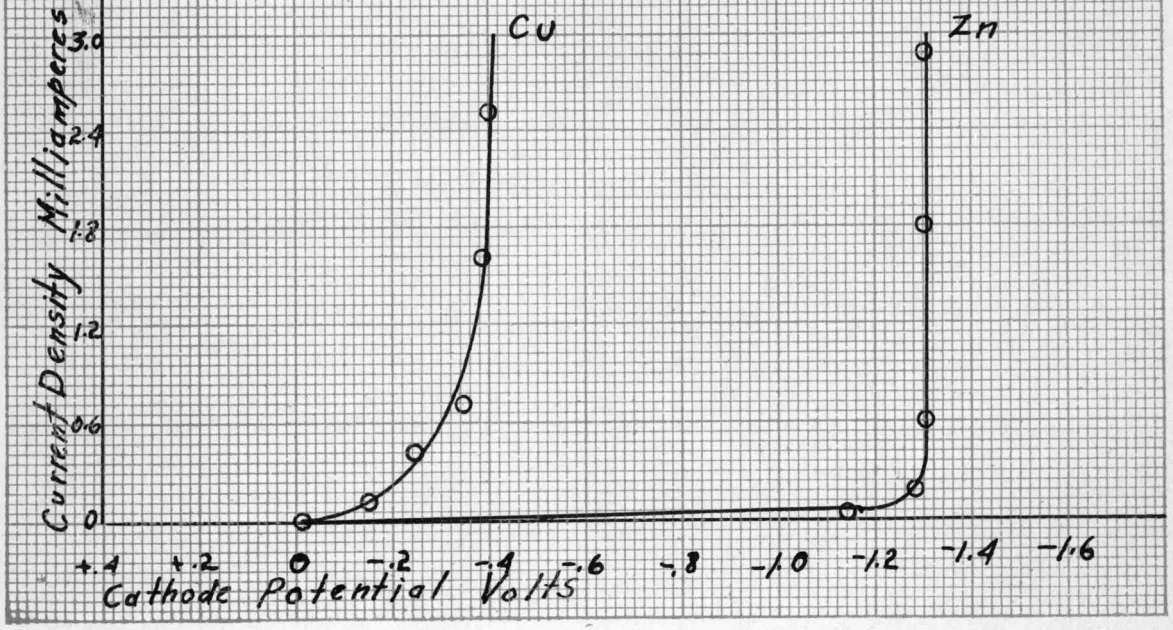


Fig. 4

Cathode Potentials for Electrolysis of Solutions of $\frac{1}{2}$N $ZnSO_4$ and $\frac{1}{2}$N $CuSO_4$ in N $Na_2C_4H_4O_6$ with NH_4OH



tartrate, and made alkaline to phenolphthalein with sodium hydroxide. it appears that there may be a possibility of the curves' converging at a higher current density; hence a possibility of the simultaneous deposition of the two metals from such a solution. Solutions less basic with sodium hydroxide were also tried, but the curves did not approach so closely to each other as in Fig. 3. This indicates that the sodium hydroxide has a greater effect on the cathode decomposition potential of copper than it has on zinc.

Fig. 4 shows cathode potentials plotted against current density for solutions of the same concentration as in Fig. 3, but with the difference that, in Fig. 4, the solutions were made alkaline with ammonium hydroxide instead of with sodium hydroxide. In this case there appears to be little convergence of the curves; therefore, brass deposition from such a solution is less likely than from the sodium hydroxide solution. Various concentrations of ammonium hydroxide were tried, and the change in cathode potentials with change in alkalinity for a given current density was less marked than the difference in various concentrations of sodium hydroxide.

A number of combinations of the tartrate bath were investigated. From a solution, containing 33.7 grams $Zn\ SO_4 \cdot 6\ H_2O$, 31.22 grams of $Cu\ SO_4 \cdot 5\ H_2O$, 215 grams of $Na_2\ C_4\ H_4\ O_6 \cdot 2\ H_2O$, and 20 grams of Na OH per liter, which was electrolyzed with brass anodes and a steel cathode at a current density of 21.6 milliamperes per sq. in. or 3.35 milliamperes per sq. cm., a thin, sort of brown translucent metal deposit was obtained. The adherence of this

deposit seemed fairly good. A current density of 6.7 milliamperer per sq. cm. gave a rather rough black deposit.

A solution consisting of 33.7 grams of zinc sulfate, 31.22 grams of copper sulfate, 115 grams of sodium tartrate, and just enough sodium hydroxide to dissolve the precipitate which formed when the base was first added to the solution gave, on a stainless steel cathode which was operated at a current density of 9 milliamperes per sq. cm., a brittle deposit having somewhat of a brass-like appearance. At a current density of 13.4 milliamperes per sq. cm. a flaky black deposit was formed.

The sodium tartrate concentration was decreased still further. A solution containing 33.7 grams of zinc sulfate, 31.22 grams of copper sulfate, 57.5 grams of sodium tartrate, and enough sodium hydroxide to clear the solution was next used. The solution turned to a deep purple color and was free from precipitate when the sodium hydroxide was first added. After the solution stood for a while, however, a white precipitate, which was soluble only upon the addition of considerable amounts of sodium hydroxide, separated out.

This phenomenon was observed in the case of all the tartrate solutions used when they were made basic with sodium hydroxide. Furthermore, wherever these solutions came in contact with glass, there was a hard, white, crystalline deposit formed. This deposit attached itself tenaciously to the glass. This material was easily soluble in acid but seemed quite insoluble in water.

When this solution was electrolyzed with a stainless steel cathode and brass anodes at current densities of 13.4 to 24.5 milliamperes per sq. cm., pinkish-gray deposits were obtained. These, in many respects, had a very brass like appearance. The adherence of these deposits to the cathode, however, was poor. Excepting in the case of extremely thin deposits, they were brittle and readily flaked off.

In order to determine whether this non-adherence was not perhaps due to the nature of the steel cathode, a number of other cathodes were tried. The following results from the last mentioned solution with current densities corresponding to those used with the stainless steel cathode were observed.

On carefully cleaned, ordinary sheet stove-iron a closely adhering deposit was formed. This deposit would stand considerable rubbing without being broken away from the iron. The color of the deposit was distinctly brassy although much grayer than the ordinary sheet brass.

On a small platinum electrode a very brass-like appearing deposit was obtained. When this was burnished it resembled closely a brass deposit obtained from an alkali cyanide bath. The adherence between the electrode and the deposit was good.

The deposit from this solution on a copper electrode was one of the best looking brass deposits obtained in the investigation. It had good adherence and was smooth.

A sample for analysis was deposited upon a stainless steel

cathode at a current density of 24.5 milliamperes per sq. cm. and analyzed by the method already discussed. The results showed a composition of 44.7% zinc and 55.3% copper. Although the adherence of the deposit was not so good on the steel, it was used because it was the only available electrode suitable for the quantitative work. The deposits on the other metals were assumed to be of similar composition. They were quite gray in appearance, which is in accord with the composition found by analysis. An attempt to improve the appearance of the deposits by varying the concentrations of the various substances and also by adding a small amount of gelatin did not meet with success. Another point which should be observed here is the fact that in all of these tartrate solutions the anode corrosion was very poor. At all these current densities and compositions of the bath there was a dense brown to black closely adhering coating formed on the anodes. It would not be possible for the anodes to dissolve properly with this deposit on them.

Special notice should be made in these last experiments of the dependence of the condition and characteristics of the cathode deposits on the nature of the cathode material. Good deposits are obtainable on some metals while other matals are not suitable at all for this purpose.

A series of experiments using ammonium hydroxide as the base were made. A bath composed of 16.85 grams of zinc sulfate, 31.22 grams of copper sulfate, and 115 grams of sodium tartrate per liter was made

alkaline to litmus, but not to phenolphthalein, with ammonium hydroxide. The precipitate first formed was completely dissolved. At current densities of 6.7 and 11 milliamperes per sq. cm. and 26° C temperature good smooth deposits of copper were obtained. A current density of 3.35 milliamperes per sq. cm. at 38° C gave a good copper deposit.

The ammonium hydroxide concentration was increased slightly and a good copper deposit was obtained at 34° C with a current density of 6.7 milliamperes per sq. cm.

The ammonium hydroxide concentration was increased until the solution was alkaline to phenolphthalein and then a slight excess was added. At 32° C with a current density of 30 milliamperes per sq. cm. a good deposit of copper was obtained. The deposit was somewhat darker, having a more or less muddy appearance, at a current density of 9 milliamperes per sq. cm.

An amount of zinc sulfate, equivalent to 16.85 grams per liter, was added. The copper deposited at 9 milliamperes per sq. cm. current density at 30° C from this solution was much whiter in appearance.

This solution electrolyzed for about one minute at a current density of 31.5 milliamperes per sq. cm. gave a deposit which was somewhat green when removed. When polished, this had a brassy appearance. It was, however, very thin. The deposits over longer intervals of time at this high current density were uneven quite black, brittle, and non-adhering. At lower current densities the deposits had decid-

edly the appearance of copper.

Iron, copper, and platinum electrodes were likewise tried with this solution. In general the deposits could not be said to resemble brass. They were more or less of a muddy copper color and looked much as if they were nothing but burned copper. In all of these ammoniacal solutions there was a tendency toward the formation of bluish- green salt crystals on the brass anodes. This was especially true at the higher current densities. Prolonged electrolysis of one of these ammoniacal solutions at moderately high current density would form a heavy coating of these crystals all over the surface of the anodes. A cubic centimeter of concentrated sodium hydroxide added to a hundred cubic centimeters of the above solution hindered the formation of these crystals and gave very bright anodes, although no satisfactory cathode deposits were obtained from this solution.

Additions of hydrazine sulfate, sodium arsenite, and gelatin were ineffective in improving the deposits from the ammoniacal tartrate bath.

No mention of the use of citrates was found in the literature, and so a few experiments were carried out to see if there were any possibility of their use in brass plating baths.

Fig. 5 gives the cathode decomposition potential curves for half normal solutions of copper and zinc sulfates and normal with respect to sodium citrate. To this solution enough sodium hydroxide was added to indicate basic to phenolphthalein. The curves are a

Fig. 5

Cathode Potentials for Electrolysis of Solutions of $\frac{1}{2}$ N $CuSO_4$ and $\frac{1}{2}$ N $ZnSO_4$ in N $Na_3C_6H_5O_7$ with NaOH

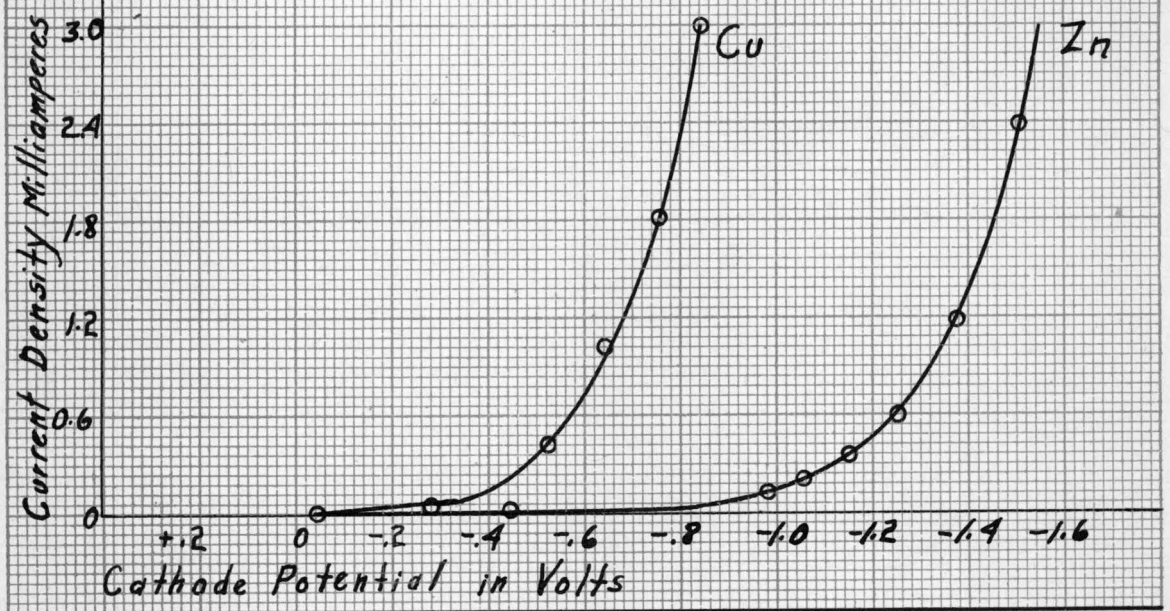
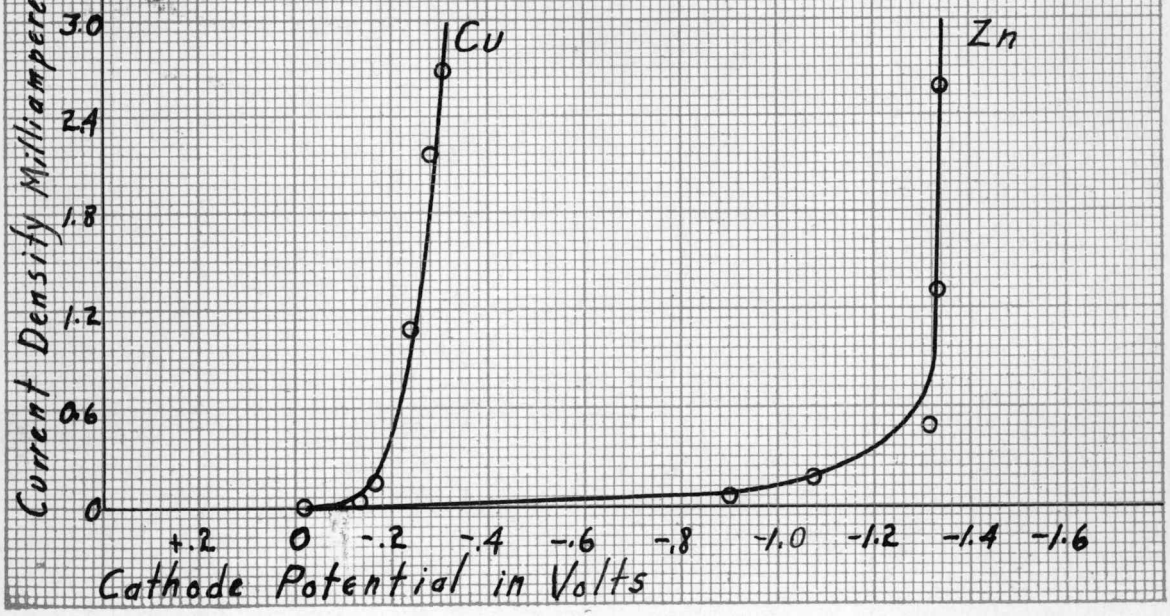


Fig. 6

Cathode Potentials for Electrolysis of Solutions of $\frac{1}{2}$ N $CuSO_4$ and $\frac{1}{2}$ N $ZnSO_4$ in N $Na_3C_6H_5O_7$ with NH_4OH



considerable distance apart, showing little tendency toward convergence.

Fig. 6 gives the curves for solutions half normal with respect to sodium citrate, made very slightly alkaline to phenolphthalein with NH_4OH. The curves of Fig. 6 are further apart than those in Fig. 5 and show less tendency toward convergence. The citrate solutions did not seem to be too promising because of the fact that with a slight addition of base there was a precipitate formed which was not soluble in excess of the base.

A number of these solutions were, however, electrolyzed and a few typical examples are given. An electrolyte was made up equivalent to half normal zinc sulfate, half normal copper sulfate, normal to sodium citrate, and sodium hydroxide was added until it was nearly alkaline to litmus. All depositions were carried out at 26° C.

At given current densities in milliamperes per sq. cm. the following deposits were obtained:

Current Density	Nature of Deposit
3.35	poorly adhering Cu deposit
6.70	Cu deposit of somewhat lighter color
10.05	deposit with appearance of copper, but rather white
16.85	rough and rather light colored deposit
23.00	very brittle flaky deposit resembling copper.

The addition of a small amount more sodium hydroxide did not improve

the deposits.

From another solution which was equivalent to one fourth normal zinc sulfate, one forth normal copper sulfate, half normal sodium citrate, and made strongly alkaline with sodium hydroxide there was considerable white precipitate which was held in suspension by the mechanical stirrer. The best deposit from this electrolyte was obtained on an ordinary iron cathode. The deposit was decidedly gray with a somewhat reddish hue. It was not a good looking brass deposit but resembled somewhat the brasses obtained from the tartrate solutions. The deposits on platinum and stainless steel were not too good. They had the appearance of burned copper.

The precipitate formed by the addition of sodium hydroxide could be dissolved by a large excess of concentrated ammonium hydroxide. No worthwhile deposits were obtained from these strongly basic solutions.

A solution less basic, pH about 8, containing sodium hydroxide and ammonium hydroxide and the equivalent of one fourth normal zinc sulfate, one fourth normal copper sulfate, and one third normal sodium citrate gave no brass. The deposits had a burned copper appearance.

Copper Plating from Ammoniacal Tartrate Solutions

As already described on page 27, some very good copper deposits were obtained from the ammoniacal tartrate solutions used in attempting to find a brass plating bath. A number of experiments were car-

ried out using copper sulfate, sodium tartrate, and ammonium hydroxide in the electrolyte. A cathode made from commercial sheet iron and an anode of electrolytic sheet copper were used as electrodes.

A solution half normal with respect to copper sulfate, normal with respect to sodium tartrate, and alkaline to litmus, but not to phenolphthalein, was electrolyzed for an hour at a cathode current density of 49.4 milliamperes per sq. in. and an anode current density of 49 milliamperes per sq. in. The deposit was very fine grained, evenly distributed, and a rather dark copper color. 0.0268 grams were deposited and 0.0325 grams were dissolved from the anode. A coulombmeter was not used, but, on the basis of the time and ammeter reading, this corresponds to a cathode current efficiency of 75.5% and an anode current efficiency of 91% Too much reliance cannot be placed upon these efficiencies because of the fact that a coulombmeter was not used. They do indicate, however, that the cathode efficiency is much lower than the anode efficiency. The deposit was calculated to have a thickness of 0.0007663 cm.

The same solution run at 96 milliamperes per sq. in. current density gave a lighter colored, but coarser, deposit. In this solution, especially at the higher current density, there was a tendency toward salt formation at the anode. Then too the metal deposit would quickly darken if exposed to the atmosphere while still covered with the electrolyte. Washing the deposit immediately with water greatly hindered this darkening. Copper deposits from these solutions did

have, even when thoroughly washed, a greater tendency toward tarnishing than did copper deposits from an acid sulfate bath.

A number of iron electrodes were given a thin strike plate from an ammoniacal solution which was half normal with respect to copper sulfate and half normal with respect to sodium tartrate. This was followed by a thicker copper plate from a solution containing 200 grams of $CuSO_4 \cdot 5H_2O$ and 50 grams of sulfuric acid per liter. The deposit from the acid sulfate bath was smooth and had very good adherence.

The ammoniacal solution would flash plate copper on iron very slightly if the ammonium hydroxide concentration were too low. In all solutions used there was some tendency toward salt formation at the anode. This seemed to be inhibited by increasing the tartrate and ammonium hydroxide concentrations. Concerning the deterioration of the bath, not much can be said at this time. A solution was, however, left exposed to the atmosphere for two days, after which time it seemed to function as well as when freshly made up. Such a solution offers good possibilities for a strike plating bath. But a further investigation needs to be made before specific recommendations are given.

Discussion of Results

In this investigation no plating bath was found that would compare favorably with the cyanide baths for commercial brass plating. Deposits containing simultaneously deposited zinc and copper were obtained in the experiments, although none of them had an appearance comparable to a good grade of yellow brass. The most likely possibility for a non-cyanide brass plating bath considered from the work done in this research is the tartrate bath.

Access was not had to the paper of Sukhodski, Kheifetz, and Chapurskii, who investigated such solutions; hence it was not known what work was done by them or what their conclusions were. A few difficulties encountered in this laboratory during this investigation would have to be overcome in order to make the bath commercially feasible. First the bad anode reactions would be highly objectionable in industrial work. A second bad feature would be the formation of a precipitate in the solution which has been allowed to stand. The third difficulty is the fact that the nature of the surface to be plated is highly important--all metals cannot be used as a base. In the fourth place, since color is the important property of the brass plate, the color of the deposits obtained in these experiments would have to be changed somewhat to have any practical value. As a fifth difficulty, the durrent density's appearing to be a most important factor would indicate a poor throwing power of the bath. If

the current density must be confined to too narrow a range, there would be much tendency to plate irregular objects ununiformly.

Considered on the basis of the experiments already carried out, the other solutions investigated in this research hold little promise for industrial application.

The problem of copper plating iron from an ammoniacal copper tartrate bath was not thoroughly investigated, but some very good copper deposits were obtained from these solutions. The solutions do not flash plate copper on iron, and the electrolytically deposited copper seems to have good adherence and color. Deposits were obtained over a fairly wide range of conditions. There was some tendency toward salt formation at the anode. Elimination of this difficulty along with more detailed investigation of throwing power, current efficiency, and durability of the bath might be further investigated.

Summary

In this thesis have been presented discussions of the experiments carried out in connection with the investigation of some cyanide-free brass plating baths already reported in the chemical literature and others investigated with the object of adding to the information already available on the subject of brass plating.

The following general types of solutions containing copper and zinc have been considered in connection with the experimental part of this thesis:

1. Those consisting of the simple sulfates to which other materials, which do not form complex ions, have been added.

2. Those composed of thiocyanate salts.

3. Those containing sodium tartrate with sodium hydroxide and ammonium hydroxide.

4. Those containing sodium citrate with sodium hydroxide and ammonium hydroxide.

This thesis also presents experimental results of an investigation of ammoniacal copper tartrate solutions as possible strike plating baths for plating iron with copper.

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