Electrodeposition of copper-lead alloys from a 7.2 per cent amine solution saturated with respect to copper and lead. Study of the production of cupric oxide to be used as solute

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ELECTRODEPOSITION OF COPPER-LEAD ALLOYS FROM A 7.2 PER CENT AMINE SOLUTION SATURATED WITH RESPECT TO COPPER AND LEAD.

STUDY OF THE PRODUCTION OF CUPRIC OXIDE TO BE USED AS SOLUTE.

by

EDMUND SIMON ROSZKOWSKI.

A

THESIS

submitted to the faculty of the

SCHOOL OF MINES AND METALLURGY OF THE UNIVERSITY OF MISSOURI

in partial fulfillment of the work required for the

Degree of

MASTER OF SCIENCE IN CHEMICAL ENGINEERING.

Rolla, Mo.

June 1941.

Approved by

[Signature]

Professor of Metallurgy.

Approved by

[Signature]

Professor of Chemical Engineering.
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INTRODUCTION.

The purpose of this work is to deposit electrolytically a copper-lead alloy from an amine solution for use specifically as a bearing metal.

Generally speaking there are four classes of bearing metals: tin base alloys or the babbitts; the cadmium base alloys or the white metals; the silver alloys; and the copper-lead alloys. Additions of other metals may be employed to produce alloys with certain desirable properties.*

Bearings are generally chosen for their characteristic properties.** The characteristics used for the evaluation of the bearing metals are:

I - Bondability and whether it is to be used as a bushing or a lining metal.

II - Resistance to pressure.

Conformability.

Embedability.

(These factors determine the load carrying ability, compressive yield strength or the creep strength.)

III - Elastic modulus.

IV - Resistance to fatigue.

* See Appendix A.

** See Appendix B.
V- Seizure resistance.
Behavior as a lap ability.
Ability to adsorb "oiliness constituents".
(These factors are the anti-friction characteristics.)

VI- Thermal expansion and clearance required.
VII- Thermal conductivity.
VIII- Resistance to corrosion.

I- Bondability.

Bearings are generally provided as bushings or as steel strips lined with the bearing metal. In the case of the bushings the problem of bondability or adhesion does not exist. In the case of the steel backs lined with the bearing metal the problem of adhesion is very important. Babbitts and the white metals generally form better bonds with the backing than do the silver and the copper-lead alloys. These latter two serve better as bushings than as linings.

II- Resistance to pressure, conformability and embedability.

These factors have a direct bearing on each other. The resistance to pressure or creep strength determines the conformability or the embedability of the alloy. If the creep strength is low and a high pressure is exerted on the bearing, the bearing metal will be squeezed out of its support. The strength of the metal must be such that
this will not happen; the metal must adjust its shape to shafting irregularities (conformability). In addition to this the metal must engulf any hard particles of dirt so that this dirt will not mar or scar the shaft (embedability). This last property of embedability is important as the presence of dirt in the bearing for any period of time will ultimately lead, if it is not embedded in the bearing, to cold welding or freezing of the shaft through the medium of the dirt and thus prevent its rotation. Since the silver and the copper-lead alloys are the softest of the four classes they are outstanding for this property, when compared on this basis. Due consideration must be given to the load carrying capacity of the metal and the application of the proper design.

III-Elastic modulus.

This property is important as it determines the characteristics and many of the general properties that will be discussed in this section. The elastic modulus of the above listed four classes of alloys given in millions of pounds per square inch are as follows: silver $10^{12}$, white metals 9, babbits $7^{12}$, and the 70-30 copper-lead. (1)

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IV-Resistance to fatigue.

This property is generally dependent on the strength of the materials involved. Some metals may fail under repeated stress and thus their use would prove of little advantage. No further general statement can be made regarding this property.

V-Seizure resistance, behaviour as a lap ability, and ability to adsorb "oiliness constituents".

Seizure is the property of a bearing whereby it will cold weld with the shaft preventing its rotation. This is especially true when the bare metals come in contact during starting, stopping and occasionally during the operating period. This property is also dependent on the extent to which the metal will become wetted by the oil. The wettability is dependent on the metallic constituents and the surface condition of the metal. There is no general statement that can be made about these properties as the characteristics of the oil are as important as those of the metallic constituents.

V-Thermal expansion and clearance required.

Thermal expansion has little effect on the clearance required for operating conditions although a coefficient of expansion which is too high would be undesirable. Clearance is important as it affects the lubrication of the bearing. Generally speaking the clearance required by
the copper-lead alloys is about twice that required by the other type of bearing metals. The thermal expansions of the various alloys given in degrees Centigrade is of the following order: white metals $29 \times 10^{-6}$, babbitts $23 \times 10^{-6}$, copper-lead $23 \times 10^{-6}$ and silver $20 \times 10^{-6}$ \(^{(1)}\).

**VII-Thermal conductivity.**

Thermal conductivity of a bearing is very slightly governed by the lining itself but generally by the bearing assembly only. The conductivity of the lining becomes important only if attempts are made at the prevention of local hot spots. The thermal conductivity of the various metals at 150 degrees Centigrade in kilogram calories per meter per degree Centigrade per hour is of the following order: pure silver 360 (aprox.), copper-lead 116, white metals 70 and the babbitts 40 \(^{(1)}\).

**VIII-Resistance to corrosion.**

This property is important as it is desirable to have the metals resist the corrosive action of the oxidation products of the lubricating oils which at times must withstand operation at about 250 degrees Centigrade. Corroded linings will have the detrimental effect of scoring and scratching the shaft and thus ultimately lead to freezing. Generally the lead constituent of the

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copper-lead alloys made at the present time shows susceptibility in this manner.

No attempt will be made in the evaluation of the above characteristics as much work has been done on this subject elsewhere. No attempt will be made to discuss the reasons why a particular metal or alloy has any particular property. Speaking generally the silver and the copper-lead alloys, when made correctly, physically outclass the other types of bearing metals used, unless the other metals are desired for a particular property that they possess. The silver and the copper-lead alloys have almost identical properties. The babbitts and the white metals are harder than the silver or the copper-lead alloys so that for a given job smaller bearings are required.

Economics is another factor of importance in determining which alloy to use. The silver and the copper-lead alloys are much more expensive than the white metals or babbitts. For this reason the white metals and the babbitts have been much used in the past. Off hand the cost of the copper-lead alloy would not be comparable with the silver alloy. On closer examination the cost of production of the copper-lead alloys rather than the cost of the metals themselves becomes evident as the important economic factor. In the case of the silver alloys the reverse is true. If a copper-lead alloy could be produced at low costs it would entirely replace the
silver alloys and would be a very good competitor with the babbitts and the white metals. In spite of the economics involved the copper-lead alloys are still preferred for heavy duty work as is indicated by its use in railway journals, bearings, etc..*

*See Appendix C.
REVIEW.

With a few exceptions alloys of the copper-lead system have been prepared thermally. Much work has been done in the study of the equilibrium of the copper-lead system (2-12).

It has been found that the copper-lead system is a completely soluble system in the liquid state, but in the solid state it is completely insoluble.

The cooling of an alloy of copper-lead from the liquid point to the solid point will lead to the crystallization of the copper previous to the solidification of the matrix (mostly lead) thus giving a segregated structure which is entirely undesirable (13-15). Thus any commercial process for the production of this alloy must consider and avoid this problem of segregation (16-18).

(14) Claus, W., Segregation phenomena in lead bronzes," Cuivre et Laiton, 10(86): 13, 15, 17 (1937).
Since the segregation is begun in the liquid state there will be a tendency to a different degree of segregation depending on the extent of the action of gravity, e.g., due to the difference of the densities of the segregated materials the lighter copper crystals will tend to rise so that a greater degree of segregation will appear at the top (19). Endeavours have been made to eliminate this by centrifugal casting.

Two methods of casting prevail (17). In one the bearing support is of such a nature that when immersed in the metal bath and taken out, the centrifugal action is such that some of the molten alloy is taken out also. The rapid rotation of this assembly in air cools it and at the same time distributes the metal over the bearing backing. In the other method some powdered copper and lead is introduced into a properly designed bearing holder where it is alloyed by the action of an induction furnace on the metals involved.

The most recent effort for the thermomechanical


preparation of copper-lead alloys is ascribed to Frank Hodson (20). According to the patent issued to him, he is to apply the alloys by spraying the backing with a finely divided molten metal alloy. Further treatment consists in the heat treatment of the metal while still in the plastic condition. As in the other cases the alloy will tend to liquate. On the other hand the homogeneity of the alloy will be dependent on the fineness of the metallic mists that are being produced.

Efforts to eliminate this fault of segregation by means of heat treatment have been unsuccessful due to a process of liquation which will take place at the temperatures near and above the melting point of the lead (21). For a good heat treatment temperatures much above the melting point of the lead are required. Liquation is the process whereby the metal with the lower melting point will sweat out of a combination of metals where there is a great difference in the melting points of the metals involved.

Efforts aimed at the prevention of segregation take

(20) Hodson, Frank, "Composite metal bearings," U. S. Pat. 2,137,343, Jan. 16, 1940.

many forms. Not only must segregation be prevented but also good adhesion between the lining and the steel backing must be in evidence. Misch claims these effects by drastic cooling of the molten alloys (22). Edkins claims similar results by casting on a wire mesh which is embedded diagonally to the bearing strip in the bearing lining while cooling, thus preventing the localization of the contraction to one spot but extending it over a large area (23).

Continuing along this same line Hassenbruck and Rohn extended the utilization of the copper net (24). The first step in the production of the alloy is the rolling of a number of sheets of copper mesh so that the result will be a honeycomb of fine copper wire. This is then rolled onto a steel strip which is to serve as a backing for the alloy. The final step is the filling of the interstices of the copper mat with lead by immersion in a molten lead bath. Claims are put forth that

Metal Ind. (London), 48: 415-6 (1936).

(23) Edkins, B. C., "Casting thin strips of metal,"
U. S. Pat. 1,937,367, Mar. 28, 1911.

(24) Hassenbruck, W. and Rohn, W., "Copper-lead alloys,"
U. S. Pat. 2,212,473, Aug. 30, 1940.
the structure of the alloy consists substantially of lead inserted between copper particles.

Among other methods of preparing alloys, several techniques are found whereby endeavours are made to disperse the copper at a temperature below the melting point of the copper so that the fine particles of copper have no time to coalesce. In one the molten lead is treated with oxygen free hydrogen previous to the addition of other alloy constituents (25-26). This is to aid the production of a homogeneous alloy by decreasing the oxidizable extent of the lead and copper. Peterman introduces copper salts (except the chloride) into the molten lead and a molten chloride like sodium chloride which is capable of reacting with the copper salt to form copper chloride (27). Smith in order to produce an alloy free from alkali metal introduces into the lead bath a chloride of copper in amounts sufficient to give the final alloy (based on the principle that the heat of formation of the lead chloride is greater than that of the copper chloride) (28).

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Willard on the other hand introduces the copper into the lead bath as an organic compound which will not form oxides of copper, i.e., acetate (29).

The melting of these alloys under fluxes has also been considered. Butcher not only uses the flux as a slag but also uses it as a means of getting the copper into the lead bath which is under the flux (30). The flux is a lead halide and floats over the molten lead. The copper is added as the oxide and under the conditions of operation has a smaller affinity for the oxygen than does the lead. Thus the copper enters the lead bath leaving the lead oxide which can be separated just before casting. Pike on the other hand uses a silicious or borax flux (31). The oxide of copper containing lead is melted at a temperature above that of the melting point of the copper. Excess copper oxide is added to make up for that entering the slag. After thickening with silica most of

(30) Butcher, W. T., "Alloying lead with metals such as copper," U. S. Pat. 2,138,729, Nov. 29, 1938.
the slag is removed. The alloy is then poured from beneath the remaining slag. Frölich, on the other hand, claims that the flux suppresses the lead segregation to a moderate extent by its mere presence (32).

Not only has the bearing metal entering the lining received attention, but also the treatment of the steel backing has been given consideration so that excellent bondability and adhesion are maintained. Among methods that have been described for the bonding of the lining to the backing, some are outstanding. Semmler claims good bondability by the treatment of the steel back with molten borax at 1050-1085 degrees Fahrenheit previous to the casting of the lining and the final cooling of the cast assembly by water (33). Another method developed by the Leadizing Company consists of treating the backing with a 50-75 per cent aqueous zinc chloride solution and the immersion in molten solder at 340-370 degrees Centigrade previous to casting at not less than 280 degrees Centigrade (34). Another consists of a thermal deposition

of an alloy on the backing previous to casting of the lining metal (35). Alloys which are to serve this purpose are 66.7 per cent copper and 33.3 per cent lead or 70 per cent copper and 30 per cent thallium.

From among all thermal processes only two have been applied commercially. One consisted of casting the molten alloy metal on a previously prepared steel strip that was travelling horizontally through a channel (36). Before the combination of steel and lining left the machine it was properly cooled so that it had the desirable crystalline structure. This type of machine has been used extensively for babbitt metals, although it has not been applied to copper-lead alloys. A process used by Ford consisted of moving a steel strip vertically through a molten bath of the alloy (37). The moving strip entered a graphite die at the bottom of the kettle in which the molten metal and the upper part of the die were at 2100

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degrees Fahrenheit. As the steel strip moved through the die it dragged along some of the molten bearing metal; the amount of metal that passed through depended on the construction of the graphite die. The lower end of the die was water cooled so that the metal leaving the die was frozen with a desirable structure. The bath was protected against oxidation by a curtain of hydrogen over its top. This hydrogen curtain also served to deoxidize the steel strip which passed through it before it entered the metal bath.

This process developed by Ford had not been in operation long before the plant had to shut down due to operational difficulties. Claus claims that the lack of mutual solubility is the basis of all troubles encountered in the thermal production of the copper-lead alloys (38). Arend has even gone to the point of using an induction furnace to keep his lead emulsified in order to get a homogeneous alloy (39).

Additions of third elements have been made and their

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effects on segregation studied (40). Claims have been put forth as to the benefits of impurities in the copper-lead system (41). In addition to the study of nickel (42), zinc and tin additions other metals have been considered. Alkali and alkaline earths (43), lithium (44), iron and manganese (45), sulfur (42, 46), tellurium and selenium (47).


and beryllium (48) have been added with the idea of decreasing the segregation tendencies. In the case of nickel it has been definitely found that its presence decreases the mutual immiscibility of the copper and lead in the solid state thus ultimately decreasing the tendency to segregate.

To do away with the segregation tendencies of copper-lead system other methods of production have been developed which do not require casting. Some of these come from the realms of powder metallurgy. Koering has developed one whereby powdered copper is briquetted into the desired shape and sintered in an nonoxidizing atmosphere thus forming a porous network not unlike a sponge (49). This copper sponge is brought in contact with lead vapors from a lead bath at a temperature above the melting point of the lead and below the melting point of the copper-lead briquet so that the capillaries of the copper briquet can absorb the lead vapors thus forming a fairly homogeneous alloy. Cooper claims to make his alloy by hydrogen reduction of a mixture of the oxides of copper and lead below the vaporization temperature of the lead and the subsequent

(48) Kormann, F. A., "Copper-lead bearing metals,"
U. S. Pat. 1,912,716, June 6, 1933.

(49) Koehring, R. P., "Copper-lead bearing metals,"
compression and sintering of the product at 500 degrees Fahrenheit (50).

Fetz gives a review of the study of the production of copper-lead alloys by sintering methods (51). He says that mixtures of copper and lead compressed with pressures of 5-50 tons per square inch showed no sintering below the melting point of the lead, but if heated above the melting point segregation became evident. Copper coated or plated lead powder when mixed with copper showed good cohesive properties.

Two methods have been used for the coating of lead by copper. One was the use of a metallic spray where the dispersing medium was 16.5 grams of vynilite per liter of acetone. Results were not good, as the coat had a tendency to crack and peel at elevated temperatures. A method which served best was coating lead powder by immersion in a solution containing 20 per cent copper acetate and 1 per cent acetic acid at 32 degrees Centigrade. The lead powder was -100 mesh.

Good adhesion of these sintered materials with the


steel back was not obtainable. Adhesion was obtained by the bonding of these sintered alloys onto some copper which could then be bonded to the steel. Another method would be the plating of the steel strip with copper which is to serve as backing to which the sintered alloy could be bonded.

Copper-lead alloys have also been prepared electrolytically. These methods will be discussed in the order of their appearance in the literature. First mention is made of solutions of copper and lead in a benzene disulphonate bath (52, 53). Theory of alloy plating calls for the equalization of the single electrode potentials of the metals which are to enter into the alloy. Not much material is given relative to this bath outside of the mention of some of the effects produced by changing the variables of the bath. The authors claim that an increase in the current density, decrease in temperature and the addition of colloidal agents increases the difference in the

potential between the two metals. Current densities of 1 to 4 amperes per square decimeter were used and alloys of a composition between 5 and 90 per cent lead have been obtained. The solution used contained a sum total of lead and copper of 1 normal. Effects of agitation are mentioned with evidence as to the decrease of the lead in the alloy with an increase in agitation.

Next mention is made of plates obtainable from baths consisting of tartrates, paratartrates or oxalates in aqueous ammonia (54). No data has been seen as to the effects of the variables or as to the compositions of plates that are obtainable.

Next mention is made of the study of the effects of sodium plumbite on solutions of copper cyanide (55). The solution used contained the following: sodium cyanide 35 grams per liter, copper cyanide 25 grams per liter, sodium carbonate 5 grams per liter and sodium hydroxide 15 grams per liter. The lead was added in

Metal Ind. (London), 50: 539 (1937).
various amounts and the effects on the plates were observed.

Lead to the extent of 1 gram per liter in the form of sodium plumbite gave a deposit containing 45 per cent copper. It also was found that the first mil of the deposit had a higher lead concentration than the rest of the plate. The structure of the deposit was badly treed and the deposit could be easily removed by washing.

Lead to the extent of 0.1 gram per liter gave an alloy containing 5.1 per cent lead in the first half mil of deposit. The plate was bright, brittle and nodular. Periodic banding or striations were in evidence in its structure.

Lead to the extent of 0.01 gram per liter gave an alloy containing 0.54 per cent lead. The deposit was dense, compact and visually bright and usable. It was more brittle than copper with a slight banding effect evidenced in its structure.

Lead to the extent of 0.001 gram per liter showed no evidence of banding and had the structure of pure copper. This made it evident that lead below a concentration of 0.002 gram per liter was of no effect.

Baths that yield the high lead alloy also yield an alloy which is highly treed and commercially unusable.
This evidently is due to the fact that the copper that is electrolytically deposited will deposit lead galvanically.

Next mention is made of fluosilicate baths (56). The same work also claims the deposition of the alloys by alternate deposition of the individual layers from the respective baths of the individual metals. The thinner the intermittent layers of the individual metals, the closer will the product approach an alloy character.

Composition of two solutions are given that could be used for the simultaneous deposition of the metals and are given below. Temperature of operation is 88-125 degrees Fahrenheit. Current densities to be used are between 10 and 15 amperes per square foot. The fluosilicate can entirely or in part replace the hydrofluoric acid. Effects of variables on the plates produced from these baths are not given:

Compositions of fluosilicate baths is grams per liter.

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<td>Boric acid</td>
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<tr>
<td>Hydrofluoric acid</td>
<td>240</td>
<td>240</td>
</tr>
<tr>
<td>Basic lead carbonate</td>
<td>70</td>
<td>105</td>
</tr>
<tr>
<td>Copper carbonate</td>
<td>50</td>
<td>35</td>
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<td>Glue</td>
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</tr>
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<td>Potassium chloride</td>
<td>-</td>
<td>2</td>
</tr>
</tbody>
</table>
Another type of a bath which can be used for the deposition of copper-lead alloys has been developed by Prof. H. R. Hanley and R. G. Courtney (57). The purpose of this thesis is the study of this particular bath beyond the point to which it has been developed. The bath is a 7.2 per cent aqueous solution of ethylene diamine which is saturated with respect to the copper and lead.

The above work indicated that the 7.2 per cent solution is the most practical from the standpoint of economics and mechanics of the reaction. The presence of any anions in the bath was detrimental to the plate. All indications have led to the necessity of utilization of cupric oxide and lead hydroxide. Temperatures of electrolysis must be rather low, i.e., about 10 degrees Centigrade, otherwise the deposit tends to be spongy. The cathode (in order to prevent a spongy deposit) must be moved through the solution at a high rate. This necessitates an assembly with a rotating cathode. Since soluble anodes of lead or copper or copper-lead were not sufficiently soluble to keep the bath in a state of balance, insoluble anodes were used.


EXPERIMENTAL.

The basis for the design of the cell and the cathode was the work previously done (p. 25) (57).

The Cell (Fig. 1).

The physical characteristics of the cell can be noted on the diagram. The electrolyte is placed in the middle compartment. The outer annular compartment about the electrolyte compartment contains the thermostatic bath. It was found that at normal room temperature a bath of ice and water in the thermostat compartment kept the temperature of the electrolyte at 9 degrees Centigrade. This temperature was chosen as the temperature for the operation of the cell. The level of the cooling mixture in the outer compartment was even with the outlet tube. The level of the electrolyte was maintained by means of a rubber tube placed over the outlet tube of the inner compartment. Thus a longer rubber tubing on the outlet tube of the inner compartment served to maintain a greater depth of electrolyte.

The Anode (Fig. 1).

The anode is a stationary steel cylinder whose dimensions are noted in the figure. The base of the anode is drilled and tapped to fit a 3/16 inch iron rod which serves

(57) Hanley, H. R., Courtney, R. G., loc. cit..
FIG. 1 - ELECTROLYTIC CELL (construction - steel, all parts welded).
as a lead to the electrical circuit. To prevent anodic action on the wire rod which is submerged in the electrolyte a cover of rubber tubing from the anode to a point 6 inches out of the electrolyte serves as an insulator. Thus the steel cylinder is the only part of the apparatus which will act anodically. Due to the oxygen liberation and the oxidizing conditions at the anode surface there is a tendency of the anode towards the oxidation of the lead that is in solution which results in the precipitation of this lead as an oxide. If this precipitate is allowed to disperse through the electrolyte it will be occluded in the cathodic deposit causing bad plates. To prevent this or to localize the precipitation of the lead oxides a vinyon cloth sleeve is placed around the anode and separated from it about 1/8 of an inch. The precipitate will thus be kept on the anode side of the cloth. This cloth will also tend to decrease the circulation of the electrolyte about the anode resulting in a decrease in the overall effect of the anodic oxygen on the solution. In other words the amount of solution that undergoes anodic oxidation would be at a minimum.

The cathode assembly consists of two parts: the cathode holder and the cathode itself.

The Cathode Holder (Fig. 2). The cathode holder which is made of steel has been
FIG. 2 - CATHODE HOLDER (all joints welded).
provided in two sizes. The size used in each test will be noted with the experimental data. The cathode holder must be insulated from the solution as it is undesirable to have it act as a cathode. A portion of the cathode holder 1 inch from the bottom and on the inside must remain uninsulated so that contact will be made with the cathode itself. The insulation used on the cathode holder consists of a fairly heavy coat of "chlorinated rubber". The shape of the plate holder had been determined by the shape and size of the steel backing that was to be used to deposit the bearing lining.

The Cathode.

Until enough experimental data have been gathered so as to produce a good bearing lining on a commercial steel backing the cathode will be of zinc rolled sheet iron after proper treatment and of dimensions similar to the commercial backing. The strip will be one inch wide and of sufficient length to fit snugly against the uninsulated part of the cathode holder. Due to the high polish of the specimens it was necessary first to strip the zinc and then to etch the specimen sufficiently to reveal its crystalline structure.

Before stripping, the specimen was cleaned to remove all grease and oil. If the dirt has not been removed the strips will not etch evenly nor will the zinc be stripped off evenly. Two methods of cleaning have been tried. One
consisted of making the cathode a cathode in a bath containing 50 grams of sodium hydroxide and 50 grams of sodium cyanide in one liter of water. Another consisted of a simple wash in a hot solution of the above noted composition. A specimen was considered to be clean when it showed no water marks when placed under running water. It was found that best results were obtained when the specimens soaked in the hot solution for about 15 minutes.

The zinc was then stripped off in a 10 per cent solution of hydrochloric acid. The specimens were next placed in an etching solution whose composition was 50cc. of concentrated hydrochloric acid and 50 cc. of concentrated hydrofluoric acid in one liter of water. The specimens then were made anodic and a current density of about 200 amperes per square foot was applied. Since the strip was a cylindrical piece and the cathode was a thin rod in the middle of this strip the current tended to flow through the inner face. Thus the current densities in this case and all future cases will be given in terms based on the inner face of the strip. The material was etched for a sufficient time to show its crystalline form. The time required was about 15 minutes.

Care was taken in all these operations to touch the inner face as little as possible. After the specimen had been sufficiently etched it was placed in the cathode holder and then cleaned cathodically in the previously
mentioned cyanide-caustic cleaner so that a clean surface is obtained in case any dirt had a chance to settle on it. The cathode inside the cathode holder is then placed in the electrolytic bath.

**Cell Assembly.**

The cathode holder is then connected by means of a collar to a steel shaft as shown in Figures 3 and 4. The shaft is long enough so that when the stem of the cathode holder is in contact with the bottom end of the shaft the top of the plate is 5/32 of an inch below the top of the anode.

**Rotation.**

The cathode is rotated by means of the shaft that supports it. Two views of the shaft, pulleys and motor are shown in Figures 3 and 4. The diameter of the shaft and the stem of the cathode holder is the same so that a good connection is obtained by means of the collar connecting the two. The speed of the cathode rotation is governed by the speed of the motor and the size of the pulleys on the motor and cathode shafts.

**Agitation.**

Agitation is maintained by means of the cathode holder itself. As noted in Figure 2 holes are cut at an angle in the top of the cathode holder so that they will cause agitation. Due to the angle of slant of the holes the
Figure 3  Front view of cell set-up.

Figure 4  Side view of cell set-up.
Direction of the rotation of the cathode is important. Looking down on the cell a counterclockwise rotation moved the electrolyte upward inside of the cathode holder. On the other hand a clockwise rotation moved the electrolyte downward. Since the natural tendency for the gas formed during electrolysis is to rise upward, a downward motion of the liquid inside the cathode holder will hinder to some extent the liberation of the gases evolved, unless the rotation of the cathode is such that the rate of flow of the liquid in the downward direction is so high that it will carry the gases out with it at the bottom of the holder. An upward motion of the liquid will aid the escape of the gases.

Among other factors that would affect the rate of agitation would be the centrifugal effects that the cathode in rotation would have on the liquid. Eccentricities of the holder would also have an effect on the degree of agitation.

If necessary the agitation in the cell can be increased either by placing a propeller inside of the holder at the top in a position where it would not interfere with the operation of the cell, or the openings at the top of the cathode holder can be enlarged and thus affect the agitation. On the other hand a combination of the two may be used.
Temperature.

The temperature of nine degrees Centigrade is maintained by means of an ice-water mixture in the outer annular compartment of the cell. The temperature of the bath is measured by means of a thermometer immersed to its immersion mark in the electrolyte near the wall of the cell.

Circulation of the Electrolyte.

The electrolyte will be discussed in a later section. Circulation of the electrolyte as differentiated from the agitation which has been previously discussed is the introduction of electrolyte into the cell and its removal during operation. In all cases the electrolyte is maintained at the level indicated in Figure 1. This level corresponds to the top of the rubber tubing which is placed over the outlet tube in the electrolyte compartment.

A decrease of five per cent of the metal concentration was arbitrarily defined as the maximum allowable variation in the concentration during any particular run. This value was chosen due to the inconvenience of the continual fortification of the solution with respect to the metals involved. If in any particular run the change in the metal content would be less than five percent no electrolyte would be added. If the change in the metal content was five per cent or above, solution was to be fed to the cell and the excess was allowed to drain out by gravity through
the outlet tube. A reservoir of the electrolyte was placed above the level of the cell and the solution was allowed to drain into the cell. The rate of inflow was controlled by a stopcock placed in the line leading to the cell. Where circulation of the electrolyte was employed the rate of circulation will be given together with the data obtained.

The Electric Circuit.

The electric circuit is essentially as shown in the circuit diagram (Figure 5). The current and the voltage is measured by means of a standard ammeter and voltmeter. The anode is connected directly to the electrical circuit. The cathode is connected to the electrical circuit indirectly. The means of transmitting the current from the cathode is as follows:

cathode to cathode holder,
cathode holder to shaft,
shaft to bushing (shown in Figure 3), bushing to graphite block, graphite block to spring

and from the spring steel strip to the rest of the electrical circuit. In Figure 3 the bushing is shown in contact with the graphite block. The rest of the assembly above mentioned can be seen in the same figure. The spring steel strip not only serves to keep the graphite contact
in place but also exerts sufficient pressure so that a
good contact is made. A direct current generator-set is
used to supply the power.

In addition to the cell voltage there were measured
a so called "cathode" and "anode voltage". The cathode
voltage was measured between the spring steel strip and
the electrolyte outside of the cathode holder. The anode
voltage was measured between the electrolyte outside of
the cathode holder and a point on the anode lead rod
outside of the solution. The cell voltage was the volt-
age between the above point on the anode rod and the
spring steel strip. The contact in the electrolyte for
voltage measurements of the anode and cathode voltages
was a copper rod immersed in the solution outside of
the cathode holder. Due to the high resistance of the
voltmeter there was a negligible electrode effect on
this rod due to the very small amount of current that
flowed through its circuit. Thus the measurement of the
anode voltage would be the voltage due to the sum of the
resistance of the anode rod from the point of contact to
the liquid film at the anode, and the resistance of the
electrolyte film at the anode, and the resistance of the
electrolyte from the liquid film at the anode to the
liquid film at the immersed copper rod, and the resistance
of the electrolyte film at the copper rod and the resis-
tance of the copper rod. Since the effects on the film
on the copper rod are negligible as has been previously
mentioned and since the resistance of the remaining factors except that of the anode film is constant, the measurement of the anode voltage will be an indication of the anode effects or polarization. Since the voltage measurements will be made from the same points at all times the various voltage measurements can be compared even though the actual measurements are not made regarding the anode film. Thus the effects of the various variables on anode polarization, etc., can be followed indirectly.

The effects of alternating current, when superimposed on direct current, on cell operation can be studied by means of the three circuits whose diagrams are shown in Figures 6 to 8. The circuit used together with the values of the critical components will be mentioned whenever used.

Data.

Using a 7.2 per cent solution of ethylene diamine in water saturated with respect to copper oxide and lead hydroxide, the composition of alloys that were deposited will be presented graphically as a function of the current density and the speed of rotation of the cathode. The temperature of the electrolyte was 9 degrees Centigrade. Changes in the speed of rotation were obtained by changing the diameter of the pulleys on the motor, cathode shafts or both. The variation in the current was obtained by means of the variable resistance which is connected as
Circuits for Superimposition of Alternating Current on Direct Current.
shown in the circuit represented in Figure 5.

After obtaining this graphical correlation a suitable choice of factors was made in order to obtain an alloy of a desirable composition. Attempts were then made to deposit an alloy 0.015 of an inch thick which is commercially usable providing it has the proper adhesion and ductility.

Control.

Chemical analysis of both the solution and the alloys was necessary. The alloy was invariably of copper and lead. Parts of the plate were mechanically stripped from the base and after weighing were analyzed for the copper and lead. The solution of the metal was performed with nitric acid. After the solution of the metals was complete, sulfuric acid was added and this mixture was heated until fumes of sulfur trioxide were liberated. This resulted in both the lead and the copper being present as sulfates.

The electrolyte on the other hand offered a different problem. The organic material was first destroyed by the action of a mixture of potassium chlorate and nitric acid on a measured sample (5 cc.). After the destruction of the organic material was complete sulfuric acid was added and the resulting mixture was heated to fumes of sulfur trioxide. This also put the copper and lead into the form of sulfates.

From this point on the procedure was the same no matter
what the origin of the sample was. Due to the subsequent analytical procedure it was desirable to standardize this procedure. The amounts of reagents added at all times were the same so that the same amounts of materials were present in all cases in the final solution. Thus all titrations were performed under conditions as alike as it was possible to make them.

The solutions after being brought to the fuming point with sulphuric acid, no matter what the origin of the samples, were allowed to cool. They were then diluted with water and heated on a hot plate to boiling to dissolve the crystalized copper sulphate salt. When the solution began to boil it was set aside to cool. During the cooling the insoluble lead sulphate was allowed to settle and condition itself into a form readily filterable. After a sufficient time had elapsed it was filtered. The filtrate was then made ammoniacal with ammonium hydroxide, allowed to cool to room temperature and then it was titrated with standard potassium cyanide solution according to method given by Scott(58). The lead on the other hand that was filtered was digested on a hot plate with an acid solution of ammonium acetate made by mixing 400 cc. of glacial acetic, 400 grams of ammonium acetate and 600 cc. of water.

After digestion for 15 minutes, the material was diluted and titrated by the molybdate method given by Scott (59). The volumes of solutions that were titrated here were also standardized to constant volume.

The molybdate and cyanide solutions were standardized by finding the equivalent of the solution in terms of grams per cc. of chemically pure lead or copper respectively. The standardization was carried out under the same conditions which the samples for control work were analyzed.

Heat Treatment.

Heat treatment of the alloys was carried out in a standard electric muffle. Temperatures were measured by a calibrated thermocouple. To prevent the oxidation of the copper and lead, helium gas was used for the atmosphere of the muffle. This result was obtained by blowing helium through the muffle during the process of heat treatment.

Solubility Tests.

The solubility tests of copper oxide and of lead hydroxide were made in an agitator (Figures 9 and 10) on samples of a given weight mixed with 70 cc. of the solvent in a 100 cc. Erlenmeyer flask. The agitator was

rotated at 24 R.P.M. for a period of two hours. All tests were made under the same conditions. The Erlenmeyer was stoppered with a rubber stopper to prevent spillage. The flask was wrapped in a cloth so that when placed into the compartment of the agitator it would be in the center of the compartment of the agitator and at the same time it would prevent breakage. The flasks were placed into the compartments so that the stoppered ends were pointing in the direction of rotation. The drive of the agitator consisted of the power being transmitted by a motor clutch arrangement from the motor to a pulley which was connected by a belt to a pulley on the agitator shaft.
Roasting.

The cupric oxide used for the preparation of the solution was made by roasting a salt or a particular compound of copper. Roasts on small samples were conducted in an electric muffle. Air could be blown through the muffle so as to get a condition of forced draft. The air was supplied from the laboratory air line and was fed at such a rate as to produce a minimum of dusting.

Roasts on greater quantities were conducted in a "Glo-Bar" furnace as shown in Figure 11. Air lines were built into the furnace to give a forced air draft. In both cases the temperatures were read by means of thermocouples.
Figure 10 Photograph of agitator.

Figure 11 Photograph of "Glo-Bar" furnace.
MANUFACTURE OF ELECTROLYTE.

The electrolyte consists of a 7.2 per cent amine solution which is first saturated with copper oxide and then saturated with lead hydroxide.

The solvent.

The solvent consists of a 7.2 per cent ethylene diamine solution in water. It was supplied commercially by the manufacturer as a solution containing 60 per cent ethylene diamine. The introduction of 120 cc. of this commercial solution per liter of final solution will result in the 7.2 per cent ethylene diamine solution.

The solute.

The solute consisting of two separate materials was cupric oxide and plumbous hydroxide.

Cupric oxide. Cupric oxide serves as one part of the solute. Cupric hydroxide can be used as well as cupric oxide. The hydroxide can be precipitated by sodium hydroxide from a solution of a cupric salt. The precipitate should be allowed to settle, the supernatant liquid decanted off and fresh water added. In this manner the salt impurities that are present can be washed out. After the final washing and decantation the precipitate can be dissolved in the amine solution if due allowance is made for the water present in the precipitate. This water content is the disadvantage for the use of the
cupric hydroxide since repeated addition of wet hydroxide to a given solution causes the dilution of the electrolyte. In preparing fresh solution this disadvantage is not serious. On the other hand fortification of the spent electrolyte is required as it is too expensive to replace it with fresh electrolyte. The use of the hydroxide in fortification would then lead to an introduction of excessive amounts of water. The precipitate can be filtered but at best this is unsatisfactory. Therefore the use of another source of copper that is water free is advisable even though it is necessary to prepare the oxide from the copper salts by roasting.

So far cupric oxide has been found to be the best material for the introduction of copper into the electrolyte. A study was conducted of the different types of salts and the conditions of roasting necessary to produce an oxide that is about 100 per cent soluble. Materials available were metallic copper, cuprous and cupric oxides, and the cuprous and cupric salts. It was found that the cuprous oxide and salts did not form amine complexes and thus had to be oxidized to the higher state of oxidation. The oxidation of metallic copper and the cuprous salts with the apparatus available was at best only a surface phenomenon which excluded them from use. In spite of this some tests were run on the oxidation of cuprous oxide. The method of oxidation spoken of here was by means of a
roast in air or oxygen. This narrowed down the source of the cupric oxide to the cupric salts of copper and to cupric oxide itself.

It was found that commercial cuprous oxide (Test I-A)* was insoluble (Table I A). A properly prepared cupric oxide on the other hand was soluble to the extent of 30 grams of copper per liter of solution. A sample of the cuprous oxide was roasted at 600 degrees Centigrade in a muffle with oxygen under forced draft for a period of one hour. The solubility of the product (Test I-B) is recorded in Table I A where it can be compared with the solubilities of other products of roasting. An assay showed 83 per cent copper as compared with the theoretical 79.9 per cent for the cupric oxide and 37.6 per cent for the cuprous oxide. Results indicate first the incomplete conversion and then slight solubility of the product. Apparently the surface of the cuprous oxide particles was oxidized only, with the resulting effects on the solubility being due to the nuclear cuprous oxide.

A commercial sample of cupric oxide (Test I-A) was found to have a slight solubility (Table I A). It was believed that during the thermal production of the oxide temperatures may have been sufficiently high so that the surface of the cupric oxide particles may have been fused

* Number of sample of the particular test.
Table I A.
Solubility of cupric oxide produced, in grams per liter and the per cent solubility (in parenthesis) based on the assays of the roast for copper.

<table>
<thead>
<tr>
<th>Material for roast</th>
<th>Weight of sample in grams per 70 cc. of testing solution.</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>2</td>
</tr>
<tr>
<td>Cuprous oxide I-A.</td>
<td>nil</td>
</tr>
<tr>
<td>Cuprous oxide I-B.</td>
<td></td>
</tr>
<tr>
<td>Cupric oxide I-A.</td>
<td></td>
</tr>
<tr>
<td>Cupric oxide I-B</td>
<td>nil</td>
</tr>
<tr>
<td>Bluestone Lot 6</td>
<td>17.1</td>
</tr>
<tr>
<td></td>
<td>(74.5)</td>
</tr>
<tr>
<td>Bluestone Lot 5 A.</td>
<td>8.6</td>
</tr>
<tr>
<td></td>
<td>(30.0)</td>
</tr>
<tr>
<td>Bluestone Lot 5 B.</td>
<td>nil</td>
</tr>
<tr>
<td>Bluestone Lot 4.</td>
<td>53% maximum solubility noted.</td>
</tr>
<tr>
<td>Bluestone Lot 3.</td>
<td>nil</td>
</tr>
<tr>
<td>Bluestone Lot 2.</td>
<td>49.4% maximum solubility noted.</td>
</tr>
<tr>
<td>Bluestone Lot 1.</td>
<td>nil</td>
</tr>
<tr>
<td>Cupric acetate I-A.</td>
<td>15.7</td>
</tr>
<tr>
<td></td>
<td>(61.1)</td>
</tr>
<tr>
<td>Cupric acetate I-B.</td>
<td>23.5</td>
</tr>
<tr>
<td></td>
<td>(91.4)</td>
</tr>
<tr>
<td>Cupric acetate II-A.</td>
<td>18.9</td>
</tr>
<tr>
<td></td>
<td>(78.7)</td>
</tr>
<tr>
<td>Cupric acetate II-B.</td>
<td>26.5</td>
</tr>
<tr>
<td></td>
<td>(77.2)</td>
</tr>
<tr>
<td>Cupric nitrate I.</td>
<td>25.8</td>
</tr>
<tr>
<td></td>
<td>(75.2)</td>
</tr>
<tr>
<td>Cupric nitrate II.</td>
<td>fused-rejected</td>
</tr>
<tr>
<td>Basic cupric carbonate</td>
<td>24.0</td>
</tr>
<tr>
<td></td>
<td>(100.0)</td>
</tr>
</tbody>
</table>

* See Table I B.
Table I B.

Explanation of the first column of Table I A.

Cuprous oxide I A. A commercial grade of cuprous oxide.

Cuprous oxide I B. A roast of a commercial grade of oxide for 1 hour at 600°C, with a forced draft.

Cupric oxide I A. A commercial grade of cupric oxide.

Cupric oxide I B. A commercial grade of cupric oxide roasted in a rotary kiln for 1 hour at 600°C, in oxygen.

Bluestone Lot 6. Blue vitriol roast in "Glo-Bar" furnace till converted to copper oxide at 750°C, with a forced air draft.

Bluestone Lot 5 A. Blue vitriol roast in "Glo-Bar" furnace till converted to cupric oxide at 750°C, with a natural air draft.

Bluestone Lot 5 B. Due to low solubility of Lot 5 A it was reroasted. Accidentally lead was introduced into the roast.

Bluestone Lot 4. Roast under the same conditions of Lot 5 A.

Bluestone Lot 3. Roast under the same conditions of Lot 5 A. Original bluestone had 1.22 per cent lead.

Bluestone Lot 2. Roast under the same conditions of Lot 5 A.

Bluestone Lot 1. Roast under the same conditions of Lot 5 A except that the temperature is much higher.

Cupric acetate I A. Sample heated on hot plate for 2 hrs.

Cupric acetate I B. Sample I A heated in a muffle with a forced air draft at 400°C, for 20 minutes.

(cont. next page)
Table I B (cont. from preceding page).

Cupric acetate II A. Sample heated in a muffle at 350°C. for 30 minutes with a forced air draft.

Cupric acetate II B. Sample II A heated in a muffle at 600°C. with a forced draft for an additional half an hour.

Cupric nitrate I. Sample heated on hot plate for 2 hours. This sample then heated in muffle at 450°C. with a forced air draft for 20 minutes.

Cupric nitrate II. Sample heated in muffle at 350°C. with a forced air draft. Sample rejected as it fused.

Basic cupric carbonate. Sample heated in muffle at 500°C. for 1 hour.
or dissociated into the cuprous oxide. The material was then reoxidized (Test I-B) in a rotary kiln with an oxygen atmosphere at 600 degrees Centigrade for a period of one hour. The solubility (Table I A) instead of increasing decreased to nothing. The kiln had previously been used for the reduction of ores with hydrogen at elevated temperatures. Before the introduction of the copper oxide the kiln was cleaned but apparently was not cleaned enough. The roasted material was tested for the presence of metallic copper by means of amalgamation with mercury. This test showed the absence of metallic copper. The insolubility was due either to a greater degree of surface fusion or to the presence of a film of cuprous oxide on the surface as an assay showed the material to be cupric oxide. This condition probably was formed by the higher temperatures existing on the surface of the particles or by the reaction of a reducing material above mentioned which was present on the surface of the kiln. The results of the above roasting process indicate that an insoluble material may cause a soluble material to become practically insoluble.

Cupric salts have been investigated. The first salt used was blue vitriol. It was ground to -20 mesh and roasted in a "Glo-Bar" furnace as previous work indicated this was a favorable method (57). A total of 3600 grams was roasted. The weight of the cupric oxide pro-
duced was 585 grams. There was a loss in the furnace of 50.2 per cent of the copper. An assay of the roast showed the composition of cupric oxide. The copper sulphate roast was carried out at 750°C, with a forced air draft of such a velocity that the air entering the furnace was just on the point of dusting. This may explain the losses in the copper shown above. The time required for a roast was 8 to 9 hours. The solubility of the product is given under blue stone Lot 6.

Copper sulphate has been previously used at five different times (57). The results of these tests are shown in Table I A. Lots 4 and 2 show solubilities of the order of Lot 6, with a smaller solubilities indicated for the former two. The only difference in the three roasts was that in the case of Lot 6 a forced air draft was used. This would indicate that with a natural air draft a solubility of about 50 per cent should be expected whereas with a forced air draft a solubility of about 65 per cent should be expected. The explanation for the differences of the solubilities of Lot 6 and the other two may be in the greater tendency to form the surface films previously mentioned in the case of the natural air draft. The solubilities reported for the bottom four

lots of bluestone (Table I A) are not given definitely as the solubility tests were performed under different conditions. In all cases the greatest solubility would be an indication of the total solubility of the product. This is true because the smallest sample used would have entirely dissolved in the solvent still producing an unsaturated solution.

The effect of the lead on the solubility of cupric oxide can be seen from the solubility data of Lots 3, 5 A and 5 B. Lot 3 was an impure salt that contained 1.22 per cent lead. The roasting of this material gave an insoluble product. Lot 5 A was a roast similar to that of Lot 6 but with a natural draft instead of a forced draft. The maximum solubility of this material was about 30 per cent. It was decided to rareost this material. Lead was accidentally introduced during the rareosting of the material. The product of this roast was totally insoluble. The explanation for this may be the formation of a coating of the insoluble lead or lead oxide in a similar manner to that in which the previously mentioned film forms the coating. The process may be one of liqutation.

Lot I was roasted similarly to the manner in which the other roasts were made except that the temperature of roasting was much higher. The air draft was a natural one. The product formed was very slightly soluble. This may be due to the formation of the fused surface on the
particles because of the higher temperatures or due to the formation of the cuprous oxide coating on the particles through dissociation in quantities small enough to escape recognition in an assay yet present in such a finely distributed state that the material assumes the properties of the cuprous oxide. The choice of a roasting temperature of 750°C. was based on this test.

Other salts of copper were tried. The tests were conducted in a muffle with a forced air draft of sufficient strength to give a draft just on the point of causing dusting. Cupric nitrate and cupric acetate were chosen for these tests. Samples of both materials were first heated on a hot plate. The products were then put into a muffle for 20 minutes at a temperature of 400°C. The solubility of the cupric acetate as it came off the hot plate (Test I A) and the solubilities of the nitrate (Test I) and the acetate (Test I B) as they came from the muffle were tested. Results are recorded in Table I A.

The results were favorable so that it was decided to roast the materials directly in a muffle. Thus another sample of the acetate (Test II A) and the nitrate (Test II) was heated in the muffle at 350°C. for a period of 30 minutes. The copper nitrate sample fused and for this reason was unsatisfactory. A sample of the acetate was taken for the solubility tests and the remainder was rereosted in the muffle but at this time at 600°C.
for another 30 minute period. The solubilities of this re-roast (Test II B) are recorded in Table I A.

Results of this roast were among the best obtained. During the roast of the acetate points of incandescence were observed in the mass that was roasting. These were due to the oxidation of the carbon that had been formed during the decomposition of the organic material. This gave a reducing atmosphere and a product which was about 78.9 per cent soluble. The assay of the product indicated a 79 per cent copper content. Thus a greater solubility is evident possibly due to the decrease in the tendency to form the surface films. During this run it was observed that a material which decrepitated during roasting gave a product of a very good solubility.

These conclusions led to the use of basic cupric carbonate for the roast. This material showed the property of decrepitation and produced a non-reducing atmosphere. Roasting was carried on for a period of one hour at 500°C. as no change in the weight was noticed after this time. The solubilities of this product are also recorded in Table I A.

A roast of greater magnitude was undertaken. A lot of 2000 grams of the basic carbonate was roasted at 500°C. for a period of two hours when tests indicated complete decomposition of the basic carbonate. A comparison of
the operational data for this and the bluestone roasts is made in Table II.

Table II.

Production data for preparation of cupric oxide.

<table>
<thead>
<tr>
<th>Material roasted</th>
<th>blue vitriol</th>
<th>basic carbonate</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature</td>
<td>750°C</td>
<td>500°C</td>
</tr>
<tr>
<td>Solubility</td>
<td>74.5%</td>
<td>100%</td>
</tr>
<tr>
<td>Roasting time</td>
<td>8-9 hours</td>
<td>2 hours</td>
</tr>
<tr>
<td>Weight of product</td>
<td>585 grams</td>
<td>1250 grams</td>
</tr>
<tr>
<td>Weight of charge</td>
<td>3600 grams</td>
<td>2000 grams</td>
</tr>
<tr>
<td>Copper recovered in product</td>
<td>49.8%</td>
<td>86.6%</td>
</tr>
</tbody>
</table>

The advantages of preparing the cupric oxide from the basic carbonate are clearly evident from the table. Since the time required for roasting the carbonate is shorter than that required for roasting the sulphate, this will increase the capacity of a given furnace. Since the temperature of roasting is lower for the carbonate, this point is important both economically and physically. The cost of the energy required for a given time of operation of the furnace will be smaller. The lower temperature will provide less opportunity for the formation of the insoluble surface films. From the weight quantities involved it is seen that the recovery of the copper that was put into the furnace was greater in the case of the carbonate than in the case of the sulphate.
which also is a very important economic factor. The most important point is that the basic carbonate is 100 per cent soluble while the sulphate is 74.5 per cent soluble.

Plumbous hydroxide. The only form of lead that was found to be soluble was plumbous hydroxide. Even in this case it was found soluble in the amine solution in the presence of copper and when the solution was unsaturated with respect to lead. The solubility of the lead hydroxide in a solution containing 7.2 per cent amine in water and which was saturated with respect to cupric oxide was 8.5 grams of lead per liter. The mechanics of solubility will be discussed later. The hydroxide of lead is prepared from a commercial grade of litharge. The litharge is dissolved in a dilute solution of nitric acid which is present in slight excess over that required to react with the litharge to form the nitrate. The hydroxide is then precipitated with ammonium hydroxide which is added in slight excess over that required to precipitate the hydroxide completely. The precipitate is allowed to settle, the supernatant liquid is drained off and fresh water is added. In this manner the precipitate is freed from its impurities. The presence of a slight excess of ammonium hydroxide at all times is found to help as it favored settling of the precipitate. After the liquid is drained off after the final washing, the remainder of the water is filtered off. The filter cake consists of slightly moist plumbous hydroxide. The cake is put into a container that is air tight so that
the moisture of the cake is retained. An assay of the moist material for the lead content will give a certain lead equivalent which is used in adding the material to the solution. It was found that if the precipitate is allowed to dry it became insoluble.

Preparing the Electrolyte.

As already mentioned the lead hydroxide is insoluble in the amine solution unless copper is present. Thus in preparing or fortifying the electrolyte the copper must be dissolved first. The solution is prepared in a stone jar using a wooden paddle agitator. Sufficient copper oxide is added to the solution so that it is present in excess of that required for saturating the solution. A period of one hour is a sufficient length of time for the process of dissolution. The solution is filtered and then returned to the jar. The lead hydroxide is then added in a sufficient amount so that an excess will be present over that required to saturate the solution with respect to the lead. The solution is filtered and then is in a condition to be used for the electrolytic work.

There are a few unusual features in the leaching process. The excess copper oxide which has not dissolved in the amine solution is still soluble but the degree of solubility in a given period of time for a given type of agitation has decreased. This would be indicated from the theories of leaching. The material in the first case
presents a greater area and thus can form a more saturated solution in a given period of time than could be formed from the material in the second case providing other variables are constant.

The presence of undissolved lead hydroxide interferes with the dissolution of the copper oxide. If the lead hydroxide is dissolved it has no effect. Qualitative tests have shown that the presence of a sufficient quantity of solid lead hydroxide mixed with copper oxide, the copper oxide can be rendered completely insoluble even in the presence of a fresh amine solution, i.e., one containing no copper. The presence of undissolved copper oxide also has an effect on the solubility of the lead hydroxide. The presence of a sufficient quantity of cupric oxide will completely insolubilize the lead hydroxide even in a lead free amine solution that is saturated with respect to copper. It is believed that there is a point of equivalence for the possible reduction of the cupric oxide to cuprous compound and the accompanying oxidation of the lead from plumbous hydroxide to plumbic compounds thus forming insoluble materials. The presence of either one of the materials above this point of equivalence will give a dissolution of the excess material only in the respective solution in which it is soluble. This has also been indicated qualitatively where copper oxide was added to material which had an excess of lead hydroxide till a point was
reached where the cupric oxide began to dissolve. This type of insolubility due to lead is differentiated from the insolubility due to lead in the roast. The insolubility in this latter case may be due to the possible oxidation-reduction reactions taking place in the furnace, and may also be due to the presence of an insoluble coat of lead or lead oxide on the copper oxide particles.

It was also found that the solubility of cupric oxide in amine solution containing no lead in terms of metallic copper was 30-31 grams per liter. The presence or addition of lead to the solution reduced the solubility to about 28 grams per liter under the same conditions of solution. This effect was observed in all tests. As will be shown in the section discussing the electrolyte, copper increases the basicity of the amine. The addition of the lead increases the basicity still further. The decrease in the concentration of the copper may be due to the possible oxidation-reduction reactions taking place in the solution at the concentrations involved forming insoluble products. This condition may be favored by the increased basicity.

In addition to these irregularities it was found that the solubilities of the copper and lead in the preparation of the electrolyte on a large scale were slightly smaller than the solubility tests have indicated. Outside of a difference in the type of agitation the only change that
accompanied the process of solution was the magnification of the process and the presence of air in the magnified process. At the time it was thought that the carbon dioxide of the air may have had an effect. Thus the solubility tests were conducted with air being blown through the solution during the process of dissolution. It was found there was very little if any effect on the solubility. Thus the slight variation of the solubility between the magnified process and the solubility tests was solely due to the magnification of the process and to the type of agitation used. In the solubility tests the agitation was of a tumbler effect whereas the agitation in the magnified process was that of a rotational type which has reached the turbulent stage.
THE ELECTROLYTE.

The Solvent.

The solvent consists of a 7.2 per cent ethylene diamine solution in water. The resultant solution is a basic solution with a pH of 11.72 as given by a Beckman and a pH of 11.9 as given by a Coleman pH meter. Because of the absence of sodium ions in the solution the results are fairly accurate. Variations of these from the true values possibly may be due to the calibration of the instruments as no indications were evident of factors being present which would affect the accuracy.

The structural formula of the amine compound is
\[
\text{NH}_2 \text{NH}_2 \quad \text{CH}_2-\text{CH}_2
\]
which in combination with water may add an a hydrogen or two hydrogens to its general makeup so as to give the cation \(\text{NH}_3^+\text{NH}_3^+\) in the latter case. The remaining ions in solution from the decomposition of water would give a basic reaction as the cations are apparently of a very weak acidity. Such a cation may be called ethylene diaminium ion in a manner which is similar to that of the naming of the ammonium ion.

Titration of the alkalinity of the solution with standard acid using methyl orange as an indicator indicates an alkalinity equivalent to 109 grams of sodium hydroxide per liter which is equivalent to a 2.7 molar sodium hydroxide solution. Since the solution contains 7.2 per
cent of ethylene diamine there are 72 grams of the amine per liter of solution (density of 0.9903). The molar concentration of the amine is thus 1.2, since its molecular weight is 60. Since the alkalinity is approximately double the molar concentration of the amine, the amine apparently adds on a hydrogen ion to both of the amine groups to give the dibasic cation. The degree of ionization apparently is equivalent to 45 per cent.

The Solute.

Cupric oxide. The copper dissolves in the solvent by forming a complex ion in a manner similar to the way in which the cupriammonium ion forms. The solubility of the copper in the 7.2 per cent amine solution amounts to about 30 grams per liter. The mole ratio of amine (1.2 moles) to copper (0.47 moles) is 2.55. Assuming that the combination between the copper and the amine takes place according to whole numbers and there is only one form of aggregation, either the copper molecule combines with two molecules of amine with 20 per cent of the amine approximately uncombined or there is a combination of the copper molecule and three molecules of the amine with approximately 21 per cent of the copper being uncombined existing simply in solution the cupric hydroxide. The formulas in the two respective cases would be $\text{Cu(en)}_2(\text{OH})_2$ in the first case and $\text{Cu(en)}_3(\text{OH})_2$ in the second case where "en" represents
a molecule of the amine.

In the past not much work has been done on the study of the copper amines. Beilstein (60) mentions work that has been done. He reports the presence of either two or three molecules of amine with a molecule of copper forming the compounds above represented supporting the two assumptions made above. The presence of cupric hydroxide in solution uncombined is inconceivable since it is insoluble. Thus the formation of the complex with the two molecules of amine will be here considered.

Attempts at the crystallization of the amine complex from solution in a manner similar to that in which the ammoniacal complex is crystallized have failed. This specifically refers to the crystallization of the amine complex by the introduction of alcohol into the solution which according to our belief would decrease the solubility of the complex. Attempts at crystallization of the complex by evaporation of the solvent, i.e., water, formed a product which looked like a mixture of the amine complex and the cupric oxide. This fact may support the assumption made above that part of the copper is dissolved as the simple cupric hydroxide or the cupric oxide

may have been formed by the decomposition of the complex with the two amine groups. The presence of two amine groups per molecule of copper in the complex may be indicated by the concept of the coordinate valence of copper. In other words the copper ions add 4 ammonia groups which in this case are equivalent to 4 amine groups. The structure of the complex on this basis may contain two diamine molecules or it may add one amine group from each of four different diamine molecules or a condition may exist between these two extremes. On this latter basis it is conceivable that a diamine molecule may give both of its amine groups, one to each of two individual copper ions.

During the operation a crystalline crust developed on the cell walls where the liquid came in contact with the air. This crust was formed by the constant evaporation of the solvent at a very slow rate leading ultimately to the crystallization of this material. Observation indicated that the material was a homogeneous substance. Analysis of this crust for the copper content of a given sample showed that the material is entirely a copper complex of the amine with very little lead present. Analysis indicated that the crust may have had the formula Cu(en)$_3$(OH)$_2$ but due to the possible hydration (a molecule of water per molecule of complex) of the crust the complex would be Cu(en)$_2$(OH)$_2$·H$_2$O. The ratio of copper to lead
in the crust was 15 to 1 whereas the ratio of copper to lead in the electrolyte was 3.4 to 1. This showed that the presence of the lead in the crust was simply a matter of occlusion during the time that the crust was crystallizing. The order of the two values shows that there is no combination between the lead and the amine complexes. If there were any definite combination the ratio of copper to the lead in the crust would be much closer to the ratio of copper to the lead in the bath.

The pH of the copper amine solution that is free of lead is 12.23 (Beckman). This indicates that an increase in basicity was caused by the introduction of the copper. In addition to this, titration of a sample with a standard acid with methyl orange as an indicator indicates an alkalinity equivalent to 144 grams of sodium hydroxide per liter. This gives a molarity equivalent to 3.6 moles of sodium hydroxide. The introduction of 0.471 moles of copper which is dibasic explains the difference of alkalinity between 2.7 molar for the copper free amine and the 3.6 molar for the amine saturated with cupric oxide. The results also indicate that all of the above constituents can act in a basic manner. Furthermore if two molecules of amine are combined with a molecule of copper there is probably enough of uncombined amine present to give a basicity equivalent to that which has been observed on the pH meters. The amount of copper ions present in
solution is slight enough so that the copper is not deposited by replacement on the steel walls of the cell.

Titration of a solution of the copper amine with a solution of potassium cyanide will discharge the color of the amine solution. This indicates the presence of some copper ions and also the presence of an equilibrium in the solution which is dependent on all of the materials that are dissolved in the water. Thus the equilibrium between the ethylene diaminium hydroxide, cupric oxide and the amine complex of copper determines the pH of the solution.

During electrolysis the copper amine complex is attracted to the cathode where the copper is discharged. It has been found that at times the entire amine complex discharged giving a subsequent occlusion of the organic matter in the plate (61).

Attempts were made at a definite establishment of the electrovalency of the copper in order to permit calculations of efficiencies of the cell. A saturated solution of copper, and another of copper-lead were connected in series with a copper coulometer and operated at room temperatures with stationary electrodes at a current density of 3.12 amperes per square foot for a period of 2 hours and 15

minutes. A current density of 15.58 amperes per square foot indicated no concentration polarization so that it was believed safe to operate at the lower current density.

Deposits obtained weighed 1.0834 grams (assay 54.1 percent lead) from the copper-lead amine cell, 0.6790 grams from the copper amine cell and 0.4834 grams from the coulometer. The efficiency of the copper amine cell based on dibasic copper gives a current efficiency of 140.7 percent for the copper deposition. This unusual efficiency may be explained first by the occlusion of organic matter in the plate and secondly by the unusual reducing ability of the amine. The first phenomenon has been mentioned on page 68 and has been observed by Greenspan (61). The reducing tendency of the amine which would act similarly to cupriammoniacal baths is suggested by Purman's mention of the tendency to reduction of the copper by ammonia in cupriammoniacal baths (62). Reports of efficiencies of electrolytes similar to the one used have been given by other workers. C. L. Brockman reports an efficiency of 122 per cent in one article (63) and an efficiency of

(61) Greenspan, L., loc. cit.
191 per cent in another article (64). Apparently these unusual efficiencies are to be expected with baths of this type, with no definite explanation of the phenomenon as yet.

The efficiency of the copper-lead cell based on bivalent copper and bivalent lead (which will be shown later) gives a value of 152.6 per cent. This seems to be consistent in a general sense with the results obtained by Brockman. A colorimetric test has indicated that the lead has little if any effect on the association of the copper amine complexes.

An attempt at further clarification of the above data by the use of an ammoniacal copper cell has resulted in an efficiency of 152.6 per cent. This serves to bring into view the unusual character of the amine derivative baths. Apparently the low current densities used had an increased tendency to bring out the unusual characteristics since current densities much higher had the effect of causing the current density to decrease to below 100 per cent. Higher current densities on the other hand would lead to erroneous results due to concentration polarization which would give lower theoretical efficiencies. All this

work reported and performed in the past serves to empha-
size the unusual character of the bath but does not give
a clear picture of the mechanism of the electrodeposition
of the copper.

Plumbous hydroxide. During the process of solution and
precipitation the lead is kept in the bivalent state.
The lead as plumbous hydroxide is soluble in an amine
solution containing copper but is not soluble in an amine
solution containing no copper. So far no data have been
found that would substantiate a belief in the formation
of lead amines under conditions under which the amine is
dissolved in the electrolyte. The solubility of the lead
in the amine takes a form other than would be expected.

The pH of the solutions in their various stages of
manufacture is as follows: amine 11.72, amine saturated
with respect to copper 12.23 and a solution saturated
with respect to both copper and lead 12.5. These values
have been measured by a Beckman pH meter. This indicates
a basicity of the solution of the order of a normal
sodium hydroxide solution. This serves to show the
mechanism by which the lead dissolves. Lead is an amphi-
teric substance and in solutions of this basicity dissolves
to form the plumbite ions as represented by its solubility
in sodium hydroxide. The electrolyte when it reaches this
stage of the manufacture has a basicity great enough to
dissolve the lead thus forming the plumbite ions.
The insolubility of the lead in an amine solution that contains no copper must be explained. The basicity of the solution with copper is slightly greater than that without copper. The solubility of the lead in ethylene diaminium hydroxide is zero. There are certain materials present in the copper amine which are absent in the straight amine, i.e., the copper amine complex and the excess diamine which has not combined with the copper. In case of the straight amine the first is absent and only the diamine is present. The lead diaminium complex if formed may have practically no stability; the stability of the copper complex plumbite or even the copper plumbite may be such as to permit the dissolution of the lead. The formulas for the last two compounds in their respective order and following the past conventions could be \( \text{Cu(en)}_2\text{PbO}_2 \) and \( \text{CuPbO}_2 \). These materials may be hydrated but at the present time the extent of their hydration is unimportant as the structure of the above compounds is based on supposition.

This compound would ionize to give plumbite ions. The presence of the plumbite ion is indicated by the reaction that takes place at the anode. During electrolysis there is precipitated at the anode a red compound which is one of the lead oxides. A possible reaction taking place at the anode can be represented by the equation \( \text{PbO}_2^{2-} - 2e = \text{PbO}_2 \). Lead alloys are obtained
at the cathode so that some explanation must be given for the deposition of the lead from the plumbite ion. The plumbite anion should migrate to the anode and no lead should be precipitated at the cathode.

The mechanism for the discharge of a metal from a complex anion is still in the speculative stage. M. R. Thompson has presented a paper in which he attempts to explain the mechanism by a number of existing theories (65). He has studied the deposition of the metals from complex cyanide radicals (anions). His work is enlarged upon and the theories are presented in a form that would be applicable to the case of the plumbite ion.

One theory supports the primary discharge of the cathion and the secondary discharge of the metal from the anion by replacement by the cathion discharged in the first step. In this case both copper and hydrogen could be discharged. The nascent hydrogen would be in a more active state so that it is considered as the one entering the secondary reaction. In the cathode film there would be anions formed by the dissociation of the associated compound in solution even though the anion

would migrate from the film under the influence of the potential existing in the bath. In other words there would at all times be an equilibrium amount of the plumb-bite ion. The nascent hydrogen which had been discharged from the bath could then replace the lead from the anion in the film thus giving the metallic lead which enters the plate. These reactions can be represented by the following formulas:

\[ H^+ + e = H^0, \]
\[ 2 H^0 + PbO_2 = Pb + 2 OH^- . \]

A second theory is based on the idea of secondary ionization which takes place giving a cathion of the metal of the anion in a form which could be discharged at the cathode. This can be represented by the equations:

\[ PbO_2 + 2 H_2O = Pb^{++} + 4 OH^-, \]
\[ Pb^{++} + 2 e = Pb. \]

A third idea is based on the discharge by the cathode any anion that may be present at the cathode surface to deposit the metal concerned. The presence of the anions in the cathode film has been mentioned in a previous paragraph. The discharge of the metal of the anion can take place at the cathode according to the reaction:

\[ PbO_2 + 2 H_2O + 2 e = Pb + 4 OH^- . \]

A fourth theory is an extension of the belief in secondary ionization. The metal ion is found to be present
in very minute amounts. Secondary ionization would give metal ions which in some cases could be identified. The belief of the absence of these ions is based on the absence of the chemical properties that these ions would have or on a concentration of the metal ions that is too small to be recognized by chemical properties. The absence of the metal ions would give a condition where concentration polarization readily takes place. In order to explain the mechanism of these baths, since the concentration polarization is not too extreme, a theory has been proposed on the further association of the ions to give a cathion which would not lead to the possibility of complete concentration polarization. Since the metal would be present in large concentrations in the complex cathion form about the cathode, concentration polarization would be brought to a minimum. These possible reactions are shown by the following series of equations:

\[ \text{PbO}_2^- + 2 \text{H}_2\text{O} = \text{Pb}^{4+} + 4 \text{OH}^- , \]
\[ 2 \text{Pb}^{4+} + 2 \text{OH}^- = \text{Pb}_2(\text{OH})_2^{++} , \]
\[ \text{Pb}_2(\text{OH})_2^{++} + 2 e = \text{H}_2\text{PbO}_2 + \text{Pb} , \text{ or } \]
\[ \text{Pb}_2(\text{OH})_2^{++} + 4 e = 2 \text{Pb} + 2 \text{OH}^- . \]

As previously mentioned the mechanism of deposition is not completely understood. As shown above various theories are in existence and support can be found for each. The choice of any one of these theories to explain the possible mechanism is undesirable as it has been
shown that almost any one of these theories can be used. Thus there is no choice of a particular theory from those that have been presented.

The pH of the copper-lead amine is 12.5 indicating an increase in basicity over that of the lead free copper amine solution. Titration of an amine solution saturated with copper and lead for alkalinity with a standard acid solution with methyl orange as indicator indicated an alkalinity equivalent to 148 grams of sodium hydroxide per liter. The increase of the alkalinity over that of a lead free copper amine solution is equivalent to the addition of the dibasic lead with the slight decrease of the copper concentration to the point where the solubility is 28 grams per liter. This titration also indicates that the materials are in a state of equilibrium which could be shifted in either direction by changing the factors that possibly would affect the equilibrium.
COOPER-LEAD ALLOYS AS A FUNCTION OF CURRENT DENSITY AND
SPEED OF ROTATION.

Using the cell shown in Figure 1 alloys were deposited at nine degrees Centigrade from a 7.2 per cent amine solution saturated with respect to copper and lead. The solution assayed 27.6 grams metallic copper and 8.4 grams metallic lead per liter. A limit on the rotational speed possible was set by the centrifuging effect of the solution at the high speed of rotation where the solution was thrown out of the cell. The maximum current density was set by the polarization of both the anode and cathode. The time of operation for these tests was arbitrarily set for one hour. Since the metal depletion was lower than the arbitrarily set limit of 5 per cent the solution was not replenished during any particular run but enough solution was put into the cell for the one hour run. The volume of the electrolyte used for each run was 1.625 liters. After each run the spent electrolyte was replaced with fresh solution.

During operation, the cell, the anode and the cathode voltages were measured as described on page 37. The observed values are given in Table III A-1. The current given is in amperes per 6.76 square inches since the cathode was 2 3/16 inches in diameter and one inch in width. The polarization effects are shown in Table III A-2 which shows the variation of the cell voltage with time. This effect was
Table III A-l.

*Observed voltages versus current and R.P.M. of cathode.

Cell voltage in volts.

<table>
<thead>
<tr>
<th>Current in amperes</th>
<th>R.P.M.</th>
<th>0</th>
<th>297</th>
<th>370</th>
<th>344</th>
<th>1776</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5</td>
<td>2.0*</td>
<td>2.4</td>
<td>1.8</td>
<td>1.8</td>
<td>2.1</td>
<td></td>
</tr>
<tr>
<td>1.0</td>
<td>3.4</td>
<td>2.3</td>
<td>2.7</td>
<td>2.6</td>
<td>2.1</td>
<td></td>
</tr>
<tr>
<td>1.5</td>
<td>3.5</td>
<td>5.2</td>
<td>3.1</td>
<td>3.2</td>
<td>3.5</td>
<td></td>
</tr>
<tr>
<td>2.0</td>
<td>4.0</td>
<td>3.2</td>
<td>3.6</td>
<td>3.8</td>
<td>3.6</td>
<td></td>
</tr>
<tr>
<td>2.5</td>
<td>5.4</td>
<td>4.0</td>
<td>4.7</td>
<td>3.8</td>
<td>4.1</td>
<td></td>
</tr>
</tbody>
</table>

Anode voltage.

<table>
<thead>
<tr>
<th>Current in amperes</th>
<th>R.P.M.</th>
<th>0</th>
<th>297</th>
<th>370</th>
<th>344</th>
<th>1776</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5</td>
<td>1.2</td>
<td>1.4</td>
<td>1.0</td>
<td>1.2</td>
<td>1.2</td>
<td></td>
</tr>
<tr>
<td>1.0</td>
<td>2.5</td>
<td>2.0</td>
<td>1.7</td>
<td>1.6</td>
<td>1.8</td>
<td></td>
</tr>
<tr>
<td>1.5</td>
<td>2.4</td>
<td>4.8</td>
<td>1.8</td>
<td>2.2</td>
<td>2.4</td>
<td></td>
</tr>
<tr>
<td>2.0</td>
<td>3.0</td>
<td>1.8</td>
<td>2.4</td>
<td>2.4</td>
<td>2.2</td>
<td></td>
</tr>
<tr>
<td>2.5</td>
<td>4.2</td>
<td>2.8</td>
<td>3.4</td>
<td>2.6</td>
<td>2.9</td>
<td></td>
</tr>
</tbody>
</table>

Cathode voltage.

<table>
<thead>
<tr>
<th>Current in amperes</th>
<th>R.P.M.</th>
<th>0</th>
<th>297</th>
<th>370</th>
<th>344</th>
<th>1776</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5</td>
<td>0.3</td>
<td>0.4</td>
<td>0.3</td>
<td>0.4</td>
<td>0.3</td>
<td></td>
</tr>
<tr>
<td>1.0</td>
<td>0.4</td>
<td>0.6</td>
<td>0.6</td>
<td>0.6</td>
<td>0.6</td>
<td></td>
</tr>
<tr>
<td>1.5</td>
<td>0.6</td>
<td>0.8</td>
<td>1.0</td>
<td>0.7</td>
<td>0.6</td>
<td></td>
</tr>
<tr>
<td>2.0</td>
<td>0.6</td>
<td>0.7</td>
<td>0.8</td>
<td>0.6</td>
<td>0.8</td>
<td></td>
</tr>
<tr>
<td>2.5</td>
<td>0.8</td>
<td>1.0</td>
<td>1.0</td>
<td>1.0</td>
<td>1.0</td>
<td></td>
</tr>
</tbody>
</table>

*Area of cathode = 6.76 sq. in.  Electrolyte: 27.6 g./l.

of copper, 3.42 g./l. of lead in 7.2 % ethylene diamine.

*See Table III A-2.
Table III A-2

Observed cell voltages versus current and time at zero R.P.M.

<table>
<thead>
<tr>
<th>Time in minutes</th>
<th>Current in amps. (area = 6.78 sq. in.)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0.5</td>
</tr>
<tr>
<td>0</td>
<td>2.0</td>
</tr>
<tr>
<td>5</td>
<td></td>
</tr>
<tr>
<td>10</td>
<td></td>
</tr>
<tr>
<td>14</td>
<td></td>
</tr>
<tr>
<td>15</td>
<td></td>
</tr>
<tr>
<td>17</td>
<td></td>
</tr>
<tr>
<td>20</td>
<td></td>
</tr>
<tr>
<td>30</td>
<td>3.3</td>
</tr>
<tr>
<td>45</td>
<td>5.7</td>
</tr>
<tr>
<td>60</td>
<td>6.0</td>
</tr>
</tbody>
</table>

* Cell operation stopped as further operation at constant current density required voltages above the capacity of the generator.
especially noticeable for runs with stationary cathodes. The generator could deliver a maximum of 13 volts so that in any run where the cell voltage approached this maximum the run was discontinued. The time at which the run was discontinued is noted and is shown in Table III A-2.

The increase in cell voltage was due solely to the gas polarization at the anode. The cathode voltage was constant during this time of operation with the increase thus being due to the anode as stated. During the runs it was found that if sufficient allowance were not made for the gas removal at the anode the voltage of the cell would rise during continued operation. In the case of the rotating cathode the rotary action of the liquid would tend to drag the vinyon cloth with it thus tending to scrub the gas from the anode surface. If the cloth were securely fastened at the bottom of the sleeve so as to prevent this movement or if the sleeve were closed at the top the cell voltage would rise, since the opportunity for the gas elimination was at a minimum. In the case of the stationary cathode there was no such scrubbing action by the vinyon cloth on the anode surface which resulted in the accumulation of the gases and the subsequent increase in the voltage.

Table III A-1 shows that generally the cathode voltage is 0.6 volts. In a few cases the voltage was below this median voltage of 0.6 volts. On the other hand
the anode voltage is generally from 2 to 3 times as high as the cathode voltage thus indicating that the consumption of the greater part of the energy supplied to the cell is in the reaction occurring at the anode. In cases where the gas elimination is insufficient the anode voltage makes the cell operation impossible.

After proper cleaning and etching as described on page 30, the cathode is rinsed in water, dried and weighed. After weighing it is inserted into the cathode holder, given an electrolytic cleaning treatment in the basic-cyanide cleaner previously mentioned, rinsed in water again and inserted in the cell in position for operation. Rotation of the cathode is begun previous to the passage of current through the cell. At the end of the allotted time for the run the rotation is stopped, the cathode is removed from its holder, rinsed in water, allowed to dry and finally weighed. The difference in the two weights gives the weight of deposit for the given conditions. A sample for analysis is removed by bending the plate sufficiently so that the plate will become detached from the base. A weighed sample of this plate is analysed for the copper and lead content by the method described on page 40.

The composition of the alloy in terms of lead content in per cent is given in Table III B as a function of the current and the speed of rotation. The weight of alloy
in grams plated out is also given as a function of the current and speed of rotation in Table III C. A graph of the per cent composition versus the speed of rotation at constant current densities is given in Figure 12. The per cent composition versus current density at a constant speed of rotation is shown graphically in Figure 13. Observed values in the latter figure are shown in solid lines. Apparently there is no definite simple mathematical relation that can be applied to the curves of Figures 12 and 13. In Figure 13 there are humps in the curves of the observed values which theoretically may not exist and may be due to some variation which was not observable during the cell operation. On this assumption that the curves are regular the humps have been eliminated and the corrections as estimated are shown in a dotted line on Figure 13.

The above mentioned humps may actually exist making the observed curves the true ones. These humps may be due to the action of the more noble metal which in this case is copper. This statement later will be proved mathematically. The more noble copper can be galvanically deposited by the lead which probably goes through an especially active stage before deposition. This will tend to give spongy plates and spongy plates have at times been obtained from this solution. The plates obtained during these test runs have been rather too solid to be
Table III B.
Composition of deposit versus current and R.P.M. given as per cent lead. (area = 6.78 sq. in.)

<table>
<thead>
<tr>
<th>Current in amperes</th>
<th>R.P.M.</th>
<th>0</th>
<th>297</th>
<th>570</th>
<th>844</th>
<th>1176</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5</td>
<td></td>
<td>5.47</td>
<td>10.4</td>
<td>31.2</td>
<td>17.5</td>
<td>15.57</td>
</tr>
<tr>
<td>1.0</td>
<td></td>
<td>1.2</td>
<td>20.2</td>
<td>29.3</td>
<td>25.0</td>
<td>16.98</td>
</tr>
<tr>
<td>1.5</td>
<td></td>
<td>9.5</td>
<td>20.76</td>
<td>26.9</td>
<td>25.5</td>
<td>23.2</td>
</tr>
<tr>
<td>2.0</td>
<td></td>
<td>5.1</td>
<td>24.4</td>
<td>24.2</td>
<td>21.8</td>
<td>23.5</td>
</tr>
<tr>
<td>2.5</td>
<td></td>
<td>0.0</td>
<td>24.9</td>
<td>21.1</td>
<td>22.8</td>
<td>24.1</td>
</tr>
</tbody>
</table>

Table III C.
Weight of deposit in grams for one hours run versus current and speed of rotation in R.P.M. (area = 6.78 sq. in.)

<table>
<thead>
<tr>
<th>Current in amperes</th>
<th>R.P.M.</th>
<th>0</th>
<th>297</th>
<th>570</th>
<th>844</th>
<th>1176</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5</td>
<td></td>
<td>0.486</td>
<td>0.300</td>
<td>0.431</td>
<td>0.406</td>
<td>0.272</td>
</tr>
<tr>
<td>1.0</td>
<td></td>
<td>0.549*</td>
<td>0.984*</td>
<td>0.900</td>
<td>0.825</td>
<td>0.578</td>
</tr>
<tr>
<td>1.5</td>
<td></td>
<td>0.539**</td>
<td>1.288</td>
<td>1.343</td>
<td>1.287</td>
<td>1.102</td>
</tr>
<tr>
<td>2.0</td>
<td></td>
<td>0.399**</td>
<td>2.055</td>
<td>1.842</td>
<td>1.663</td>
<td>1.738</td>
</tr>
<tr>
<td>2.5</td>
<td></td>
<td>0.347***</td>
<td>1.660</td>
<td>2.592</td>
<td>1.890</td>
<td>2.411</td>
</tr>
</tbody>
</table>

* Time is 45 minutes.
* Time is 1 hour and 4 minutes.
** Time is 30 minutes.
*** Time is 17 minutes.
**** Time is 14 minutes.
FIG. 12 - Per Cent Lead Versus Speed of Rotation at Constant Current Density.
Observed data in solid line. Straightened curves in dotted line (theoretical).

FIG. 13 - Per Cent Lead Versus Current Density at Constant Speed of Rotation.
called spongy so that this would tend to favor the estimated curves of Figure 13.

The estimated curves of Figure 13 aroused enough interest so that they were redrawn in a form similar to that of Figure 12, i.e., the composition of the alloy versus speed of rotation at constant current density. Results are shown in Figure 14. A group of unusual curves results which appear to intersect in common points. The curves have been drawn directly from the values from the estimated curves of Figure 13 and are the true curves of the estimated values. The order of these curves between the points of intersection is more than a coincidence and points to the probability that these curves are the true representation of the actual conditions of cell operation.

The points of coincidence show four phases of electrolysis which may possibly be explained by the four stages of ionic equilibrium which occur at the different conditions of operation and which exist between the bath and the cathode. Copper is the more noble of the metals and this fact explains its predominance in the deposit. The concentration of the lead ions in the bath is very low so that polarization of the cathode with respect to the lead is easily accomplished.

Thus for the very low speeds of rotation existing
FIG. 14 - Estimated Per Cent Lead Versus Speed of Rotation at Constant Current Density.
between the vertical axis and the first point of coincidence, the nobility of the copper and the polarization of the film at the cathode with respect to the copper and lead controls the composition of the plate. Increase of current densities in this region will serve to increase the polarization of the film with regard to the copper and thus forcibly bring in the lead tending to give plates of a higher lead content. On the other hand increases in the degree of agitation affects the renewal of lead and copper in the film which would favor the slight deposition of the lead into the plate. This explains the increase of the lead content in the plate with an increase in agitation.

For speeds of rotation that exist between the first and second point of coincidence the same above mentioned conditions apply. The cathode film is being renewed at such a rate that the lead will find its way into the plate in greater amounts due to the concentration polarization of the copper. The rate of renewal of the lead takes such a form that the lead content of the plate is dependent on the current used. An increase in agitation on the other hand not only serves to renew the lead but the renewal is such that the lead increase is rather great compared to the increase in the rate of agitation. As the second point of coincidence is approached the effect begins to reach a maximum so that the lead content in the plate
approaches a maximum value at a slower rate.

Agitation as existing between the second and third point of coincidence shows a decreasing effect on the plate as the lead in the film has received the maximum effect possible. Any further effect will be felt by the copper so that actually the lead content begins to decrease once it has reached its point of maxima. The current density increases on the other hand would serve to favor the greater rate of deposition of copper as the lead is already entering the plate at a maximum rate. These points are shown both by the slope of the curves and the order of the curves for the respective current densities.

Conditions beyond the third point of coincidence have little additional effect on the concentration polarization of both metals. From this point out the nobility of the metal will be the deciding factor for the plate composition. The order of the curves here can be seen from the fact that with increasing current densities the rate of lead deposition will increase so that efficiencies are kept at a maximum since the copper will still tend to polarize to a greater extent.

As previously mentioned material taken for the analysis to obtain the plate compositions was weighed. The assay weights did not check with the weighed samples although
the assays done in duplicate checked each other. The deviation is shown in Table III F in terms of the weighed sample over the weight indicated by the assay. This tends to show apparently the occlusion of material in the plate as had been observed by Greenspan (61) in his plates obtained from an amine solution. The negative variation in one or two cases may be due to some unavoidable experimental error.

Part of the following tables were developed making allowance for this deviation in weight. Table III D shows the conversion of the weights of deposit for given periods of time (Table III C) into terms of grams of deposit per ampere hour making no allowance for the deviation of the weighed sample from the assayed weight of the sample. Efficiencies of the process operating under the different values of the variables were calculated on the basis of bivalent copper and bivalent lead and are shown in Table III E. The values thus obtained show a tendency to decrease with increasing agitation and an increase with an increasing current density. This generalization is exactly in the opposite direction from what would theoretically be expected if the deposition of the alloy were the main reaction in the cell.

The values in grams deposited per ampere hour (Table III D) if corrected for the deviation of the

(61) Greenspan, L., loc. cit.
Table III D.

Data of Table III C converted into terms of grams deposited per ampere hour.

<table>
<thead>
<tr>
<th>Current in amperes</th>
<th>R.P.M.</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0</td>
</tr>
<tr>
<td>0.5</td>
<td>0.972</td>
</tr>
<tr>
<td>1.0</td>
<td>0.730</td>
</tr>
<tr>
<td>1.5</td>
<td>0.716</td>
</tr>
<tr>
<td>2.0</td>
<td>0.706</td>
</tr>
<tr>
<td>2.5</td>
<td>0.745</td>
</tr>
</tbody>
</table>

Table III E.

Current efficiencies in per cent from data of runs presented in Table III B and Table III D assuming divalent copper and divalent lead.

<table>
<thead>
<tr>
<th>Current in amperes</th>
<th>R.P.M.</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0</td>
</tr>
<tr>
<td>0.5</td>
<td>40.0</td>
</tr>
<tr>
<td>1.0</td>
<td>30.3</td>
</tr>
<tr>
<td>1.5</td>
<td>29.0</td>
</tr>
<tr>
<td>2.0</td>
<td>29.0</td>
</tr>
<tr>
<td>2.5</td>
<td>31.3</td>
</tr>
</tbody>
</table>
Table III F.
Weight of sample of plate taken for assay over weight of sample as reported by assay.

<table>
<thead>
<tr>
<th>Current in amperes</th>
<th>R.P.M. 0</th>
<th>R.P.M. 297</th>
<th>R.P.M. 570</th>
<th>R.P.M. 844</th>
<th>R.P.M. 1176</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5</td>
<td>1.076</td>
<td>1.057</td>
<td>0.918</td>
<td>1.192</td>
<td>1.091</td>
</tr>
<tr>
<td>1.0</td>
<td>1.148</td>
<td>1.000</td>
<td>1.259</td>
<td>1.194</td>
<td>1.124</td>
</tr>
<tr>
<td>1.5</td>
<td>1.004</td>
<td>0.878</td>
<td>1.092</td>
<td>1.112</td>
<td>0.864</td>
</tr>
<tr>
<td>2.0</td>
<td>1.021</td>
<td>0.960</td>
<td>1.063</td>
<td>1.109</td>
<td>1.209</td>
</tr>
<tr>
<td>2.5</td>
<td>0.998</td>
<td>1.232</td>
<td>1.073</td>
<td>1.114</td>
<td>1.018</td>
</tr>
</tbody>
</table>

Table III G.
Weight of deposit per ampere hour as corrected for the deviations shown in Table III F using the data of Table III F and Table III C.

<table>
<thead>
<tr>
<th>Current in amperes</th>
<th>R.P.M. 0</th>
<th>R.P.M. 297</th>
<th>R.P.M. 570</th>
<th>R.P.M. 844</th>
<th>R.P.M. 1176</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5</td>
<td>0.903</td>
<td>0.568</td>
<td>1.048</td>
<td>0.661</td>
<td>0.493</td>
</tr>
<tr>
<td>1.0</td>
<td>0.699</td>
<td>0.923</td>
<td>0.715</td>
<td>0.714</td>
<td>0.514</td>
</tr>
<tr>
<td>1.5</td>
<td>0.712</td>
<td>0.969</td>
<td>0.819</td>
<td>0.772</td>
<td>0.843</td>
</tr>
<tr>
<td>2.0</td>
<td>0.692</td>
<td>1.069</td>
<td>0.867</td>
<td>0.751</td>
<td>0.718</td>
</tr>
<tr>
<td>2.5</td>
<td>0.746</td>
<td>0.596</td>
<td>0.964</td>
<td>0.678</td>
<td>0.947</td>
</tr>
</tbody>
</table>
weighed sample from the assayed weight (Table III F) shows values as recorded in Table III G. The computed current efficiencies on the basis of the corrected rate of metal deposition, bivalent lead and bivalent copper appear in Table III H. The tendencies of the variation of the current efficiency is as noted above although more markedly so, i.e., decrease of efficiency with an increase in rotational speed and the increase of efficiency with an increased current density. Offhand this would lead one to suppose that the deposition of the alloy is not the main reaction taking place.

Table III H.

Corrected current efficiencies using the data of Table III G.

<table>
<thead>
<tr>
<th>current in amperes</th>
<th>R.P.M.</th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0</td>
<td>297</td>
<td>570</td>
<td>844</td>
</tr>
<tr>
<td>0.5</td>
<td>37.2</td>
<td>22.9</td>
<td>38.9</td>
<td>26.7</td>
</tr>
<tr>
<td>1.0</td>
<td>29.3</td>
<td>35.8</td>
<td>26.6</td>
<td>28.7</td>
</tr>
<tr>
<td>1.5</td>
<td>28.8</td>
<td>37.4</td>
<td>30.9</td>
<td>29.6</td>
</tr>
<tr>
<td>2.0</td>
<td>23.5</td>
<td>42.2</td>
<td>33.0</td>
<td>28.9</td>
</tr>
<tr>
<td>2.5</td>
<td>31.4</td>
<td>19.3</td>
<td>37.0</td>
<td>24.2</td>
</tr>
</tbody>
</table>

As mentioned above the probability of the deposition of the copper-lead alloy being of a secondary nature is very great. The probability of any reaction taking place in the cell can be judged from the calculated values of the reaction potentials of the possible reactions that
could take place in the cell. The reactions that may occur in the cell are: (1) the discharge of the copper ions, (2) the discharge of the lead ions, (3) the discharge of hydrogen from the solution and (4) the reduction of the amine forming ammonia and ethane.

The potential for any one of the above reactions taking place can be computed from the free energy changes involved in the reaction. The discharge of the copper can be represented by the equation:

\[ 2 \text{Z}^- + \text{CuO} (\text{s}) + \text{H}_2\text{O} (\text{L}) = \text{Cu} (\text{s}) + 2 \text{OH}^- \]

Essentially the reaction that takes place is from copper ions in solution but it has been found by extended calculations that the value obtained from the above equation is about the same as that obtained by the extended calculations. For simplicity the above equation is used. The reaction potential is computed from the free energy change of the above reaction. The free energies of the materials involved here and those involved in the next three calculations are taken from Lange's Handbook of Chemistry (66). The free energies of the materials involved are as follows:

- \( \text{CuO} (\text{s}) = -30,300 \text{ cals. per mole} \)
- \( \text{H}_2\text{O} (\text{L}) = -56,560 \text{ cals. per mole} \)
- \( \text{OH}^- = -37,455 \text{ cals. per mole} \)

Substituting in the above reaction the free energy change is found to be 11,950 cal. per mole. The molar reaction potential \( E^0 \) is found from the relation that

\[ nE^0F = -\Delta F \]

where \( n \) is the number of Faradays of electricity required for the reaction, \( F \) is the value of the Faraday in coulombs and \( \Delta F \) is the free energy change of the reaction in joules.

Thus \( E^0 = \frac{-\Delta F}{nF} = \frac{-11,950(4.18)}{2(96,500)} = -0.256 \text{ volts} \). In making a correction for the variation of the materials from standard states and assuming unit activity for the solids and water the following equation results:

\[ E = E^0 - \frac{NRT}{nF} \ln (\text{OH}^-)^2. \]

The symbols used mean the same as above and \( N \) is the number of moles undergoing reaction and \( R \) and \( T \) represent the perfect gas constant and the absolute temperature (298 degrees Kelvins) respectively. Since the pH of the bath is 12.8 the hydroxyl ion concentration is \( 10^{-1.2} \) moles per liter. Substituting in the equation above the reaction potential (\( E \)) becomes

\[ E = E^0 - \frac{NRT}{nF} \ln (\text{OH}^-)^2 = -0.256 - \frac{0.05915}{2} \log (10^{-1.2})^2 = -0.256 - 0.071 = -0.327 \text{ volts}. \]

The discharge of the lead ion can be given by the following simplified equation:

\[ 2 \text{E}^- + \text{PbO (s)} + \text{H}_2\text{O (L)} = \text{Pb}^2+ (s) + 2\text{OH}^- . \]
The free energies given in Lange's Handbook (66) for the materials involved are:

\[
\begin{align*}
PbO (s) &= -41,000 \text{ cals. per mole}, \\
H_2O (L) &= -56,560 \text{ cals. per mole and} \\
OH^- &= -37,455 \text{ cals. per mole.}
\end{align*}
\]

Proceeding in the same manner as above the standard molal electrode potential \((E^0)\) is \(-0.487\) volts which if corrected for the variation from the standard state yields a reaction potential \((E)\) of \(-0.416\).

The discharge of the hydrogen ion takes the form represented by the reaction:

\[
2 E^- + 2 H^+ = H_2 (g).
\]

Continuing in a manner similar to the above the standard molal potential is zero volts since the free energy change of the above reaction is zero. Making allowance for the variation of the actual potential from the standard electrode potential and keeping in mind that the pH of the solution is 12.8, the electrode potential becomes \(-0.757\).

The reduction of the amine can be represented as taking place according to the equation:

\[
en (L) + 4 H_2O (L) + 4 E^- = C_2H_6 (g) + 2 NH_3 (g) + 4 OH^-.
\]

The free energies of the materials involved are as follows:

\[
\begin{align*}
C_2H_6 (g) &= -10,700 \text{ cals. per mole,} \\
NH_3 (g) &= -3,900 \text{ cals. per mole,}
\end{align*}
\]

(66) Lange, N. A., loc. cit.
$\text{OH}^- = -37,455 \text{ cals. per mole,}$

$\text{H}_2\text{O} \ (\text{L}) = -56,560 \text{ cals. per mole and}$

$\text{en} \ (\text{L})$ must be estimated.

The free energy of gaseous \( \text{C}_2\text{H}_6 \) is given as -10,700 cals. per mole. The substitution of \( \text{NH}_2 \) for a hydrogen in a compound produces a free energy change of 6000 cals. per mole of substitution as given in Getman and Daniels\(^{(67)}\). The combination of these two factors will give a free energy content of gaseous en of 1,300 cals. per mole. Since in the equation the free energy of liquid en is required rather than the gas, estimations must be made of the free energy change produced in converting the gas to the liquid. Assuming a mole of en is equivalent to two moles of ammonia and since the free energy change of $\text{NH}_3 \ (g) = \text{NH}_3 \ (L)$ is given in Lewis and Randall\(^{(68)}\) as 1,230 cals. per mole the free energy change of $\text{en} \ (g) = \text{en} \ (L)$ will be -2,580 cals. per mole. Thus the free energy of liquid en will be 3,370 cals. per mole. Having this value


and the others of the free energies of the reacting materials the free energy of the reduction of the amine can be calculated. The standard molal electrode potential for the reduction can be calculated as has been done previously. The standard molal potential of reduction is \(-0.578\) which if corrected for the variations from the standard states becomes \(-0.491\) volts.

The results of the calculations of the reaction potentials of the possible reactions is given in Table IV. The

<table>
<thead>
<tr>
<th>reaction</th>
<th>potential</th>
</tr>
</thead>
<tbody>
<tr>
<td>discharge of copper</td>
<td>(-0.185)</td>
</tr>
<tr>
<td>discharge of lead</td>
<td>(-0.410)</td>
</tr>
<tr>
<td>discharge of hydrogen</td>
<td>(-0.757)</td>
</tr>
<tr>
<td>reduction of amine</td>
<td>(-0.578)</td>
</tr>
</tbody>
</table>

table indicates that the probable order of the reactions that take place is the discharge of the copper first, the discharge of the lead second, the reduction of the amine third and the discharge of the hydrogen last. The order does not necessarily take place as stated but to a certain extent depends on the current density and the speed of rotation used. It has been found that for very low current densities there is no reduction of amine and the reaction consists solely of the deposition of the copper and lead since the efficiencies are of the order of a
hundred per cent or more. On the other hand the high
current densities yield current efficiencies of the order
of 25-35 per cent. Since the cathode voltage is 0.6 volts
(p. 78) the discharge of the hydrogen is inconceivable.
Thus the reaction that does take place must be the reduc-
tion of amine since Faraday's laws must hold in all cases.
The polarization of the cathode film with respect to
copper and lead would greatly favor the reduction of the
amine. Not only would this reduction be favored by the
polarization but the increase in basicity of the cathode
film would require higher potentials for the discharge
of the metals and hydrogen and thus in its way tend to
favor the reduction of the amine since these higher
potentials will be necessary.

As mentioned by Greenspan (61), with efficiencies of
above 100 per cent, occlusions of organic matter were found
to exist in his plates. The difference between this and
his work is the great difference existing between the
order of efficiencies in both cases. Occlusions in the
plate were found first by the discrepancy of the weights
as has been mentioned (Table III F) and in the second
case by the discoloration of the plate on standing.
Greenspan has observed the same effect of discoloration in
his plates. Since no inflammable material, either hydrogen

(61) Greenspan, L., loc. cit.
or methane, was detected at the cathode by a flame test, it can be assumed that the ethane formed could have been occluded in the plate in addition to the organic occlusions possible from the complex.

The brittleness of the plate together with the previously mentioned facts may show that the occlusions in the plate are of organic material. A properly cleaned steel backing gave a plate of good adherent quality. The brittleness of this plate such as were deposited is not serious as the fine crystals of the plate adhere to the base. However, plates to be used commercially must be at least of 15 thousands of an inch thick. In plates of this thickness the physical property of adherence may be of a secondary nature and the property of ductility may become the deciding factor. The thick plate if brittle will on breaking up into small crystals lose its adherence if it were bent or distorted to any extent. The fine crystals will tend to force each other off of the backing thus showing apparent lack of adherence.
COPPER-LEAD ALLOYS.

The deposition of the copper-lead alloys at 570 R.P.M. and a current density of 30 amperes was chosen for this work. Alloys of 27.5 per cent lead should be obtainable if the electrolyte is saturated with respect to copper and lead. As previously mentioned, plates of one hours time of deposition have good adhesive properties, if the base has been properly treated. Ductility is of a secondary importance. Calculations based on the values chosen for operation show that there must be at least 8 hours of deposition before the thickness of 15 thousandths of an inch is reached. A run of 7 hours and 10 minutes under the above conditions resulted in a plate of a substantially solid nature. On the other hand the brittleness was such that the slightest flexion caused the plate to entirely disintegrate and to fall away from the base with the apparent absence of adhesion. At first it was believed that adhesion was bad. Further work based on plating of the alloy on steel strips coated with nickel or tin showed that the adhesion to the clean steel base was the best. It was therefore decided to use the plain steel base. The work here and the following work was of a qualitative nature so that control of the solution and control of the plate composition was not attempted.

The plate obtained from the solution was evidently
not of a form to be utilized commercially because of its brittleness. The brittleness may have been due to the physical nature of the alloy itself or to the occlusion of material in the plate. If the brittleness were due to the physical characteristics of the metals themselves, improvement of the properties could be obtained by proper heat treatment. On the other hand if the brittleness of the alloy were due to the property of the bath itself, conditions in the bath would have to be changed as to prevent disadvantageous cell actions. Possible changes for the conditions of the bath were: superimposition of alternating current on direct current, tilting the cathode so that during operation the plate would come in contact with the air which would remove gases that might have been occluded on the cathode, and finally the introduction into the bath of additional organic or inorganic materials.

Heat treatment is a promising means of making the alloy ductile since the fineness and manner of dispersion of the lead might be the factor affecting the brittleness. During heat treatment the lead would have a tendency to coagulate forming glebules, thus giving a ductile plate if the brittleness is due to the lead dispersion. On the other hand if the brittleness were due to occlusions of material in the plate the heat treatments should allow these materials to escape if
they can be gasified at the temperatures used.

For heat treatment an electric muffle as mentioned on page 42 is used. An inert helium atmosphere is used in the furnace because of the oxidizable nature of the metals involved. A "two to three hour plate" was tested in these runs. Two heat treating procedures were used. The muffle was brought to the temperature required, helium was allowed to flow through the air tight muffle during the warming operation, the plate was introduced into the muffle where it was kept at the operating temperature for the proper time after which the furnace was allowed to cool.

Temperatures as measured by a thermocouple designated the operating temperature of the furnace. Temperatures below the melting point of the lead (327.5°C.) were ineffective in altering the properties of the alloy. Heat treatments above the melting point of the lead (450°C. and 550°C.) caused a slight improvement in the ductility. On the other hand the plate turned black and looked as if it were oxidized. The oxidation may have been due to the incomplete removal of the oxygen from the muffle or the introduction of oxygen into the muffle when the plate was being introduced. In addition to this effect of the oxidation, the plate had lost all of its adhesion to the base. The plate flaked away from the base and was attached to it only at one or two points.
Another method of heat treatment was undertaken. In this method the plate was put into the cool muffle. Helium was allowed to flow through the furnace to remove the air. Heating was begun after the helium had been flowing through the furnace for 5 minutes. A run made at 550 degrees Centigrade gave a plate that had not lost any of its physical appearance or characteristics. On the other hand it had not gained any desirable properties. The ductility of the plate had not been affected enough to be observed. The furnace required an hour and a quarter to heat up to 550 degrees Centigrade, the heat treatment continued for 1 hour at this temperature after which time the furnace was allowed to cool completely before the plate was removed. During this entire operation helium was blown through the furnace.

Heat treatment was then undertaken at 800 degrees Centigrade. The specimen went through the same procedure recorded above for 550 degrees Centigrade. To heat the muffle to 800 degrees Centigrade required one and three quarters hours. Heat treatment was continued for two hours at this temperature of 800 degrees Centigrade after which time the muffle was allowed to cool to room temperature.

There was no apparent change in ductility. The adhesion was slightly decreased with a corresponding darkening of the color. Photomicrographs of the plate
were made before and after heat treatment. The plate was produced at a current density of 31.9 amps. per sq. ft., 570 R.P.M., 9 degrees Centigrade and from a solution which assayed 22 grams per liter of copper and 4.5 grams per liter of lead. The electrolyte was circulated through the cell at the rate of 1.5 liters per hour. The plate assayed 21 per cent lead. The microstructure of other plates produced under different conditions of current density and speeds of rotation is similar to that of the above plate which is shown in Figure 15. Apparently a homogeneous phase exists in a matrix which binds the grains. The matrix is lead whereas the homogeneous phase is a mixture of copper and lead. Heat treatment of this alloy at 800 degrees Centigrade resulted in a microstructure shown in Figure 16. The conclusions to be drawn as to the effect of heat treatment on the microstructure of this alloy are that heat treatment will:

(1) decrease grain size,

(2) increase the lead present in the grain boundaries and

(3) precipitate lead inside the grains themselves.

From the above if the precipitation of the lead is desired to make alloy ductile, heat treatment is the
Microstructure of copper-lead alloy containing 21 per cent lead before and after heat treatment at 800°C.

Figure 15 No heat treatment. 500 Dia.

Figure 16 Heat treatment at 800°C for 2 hrs. 500 Dia.
answer to the problem. On the other hand if the lead must be removed from the grain boundaries, heat treatment will not serve but some other means must be depended upon to make the alloy ductile.

It is known that superimposition of an alternating current upon a direct current during electrolysis has some effect on decreasing the operating voltage and on decreasing the brittleness of copper which is produced electrolytically. Very little work on this type of deposition is reported, therefore it was necessary to design suitable electrical circuits. Three possible circuits that could be used are shown on page 39. The circuit in Figure 6 was used and the superimposition of the alternating current upon the direct current was checked by a cathode ray oscillograph. Apparently there were no effects on the properties of the alloy by the slight superimposition.

The circuit in Figure 8 was next used. Two condensers were connected in parallel with a total capacity of 57 microfarads. A choke coil was also used in the circuit as shown in the circuit diagram and consisted of the secondary winding of a transformer. The impedance of the choke coil to alternating current was 7500 ohms and the resistance to direct current was 0.5 ohms. The circuit shown in the diagram is a binary circuit. The right hand branch of the circuit is a direct current circuit whereas
the left had branch is an alternating current circuit. The branch containing the cell is a part of both the alternating and the direct current circuits. In this manner both the alternating current and the direct current will pass through the cell. To prevent the alternating current from entering the direct current circuit the above choke coil is provided. This choke coil serves as a safeguard in protecting the electrical apparatus that may be in the direct current circuit, i.e., generator, etc. To prevent the direct current from entering the alternating circuit the above used condensers are provided. This is to force all of the direct current through the cell branch of the circuit.

Direct currents of any amounts could be used with the assurance that all of it will go through the cell. Alternating currents of 2.5 amperes were obtainable with the above circuit and higher amperages were possible. Since the alternating current has equal effects on the electrode reactions considering the instantaneous direction of the current flow, its utilization will have no resultant effect so that calculations based on Faraday's laws and only on direct current will be true representations of the operating conditions, i.e., current density, current efficiency, etc.

The utilization of a smaller cathode holder for plating required a current of 1.435 amperes which is equivalent to
a current density of 31.9 amperes per sq. ft. Alternating currents that were superimposed on the direct current were 2.5, 1.5 and 1.2 amperes. Superimposed alternating current of 1.2 amperes caused the fluctuation of the instantaneous current between a maximum and a minimum value depending on the frequency of the alternating current used. At all times the current was flowing in the same direction so that the cathode was cathodic in nature. The superimposition of an alternating current of 1.5 amperes caused a similar fluctuation. Since the alternating current was of a greater value than the direct current, during a part of the cycle the cathode was anodic due to the reversal of the current at points in the cycle where the instantaneous value of the alternating current was greater than the direct current and when it was flowing in the opposite direction to the direct current. The superimposition of an alternating current of 2.5 amperes gave similar results to the ones that had been obtained with alternating currents of 1.5 amperes. The difference between the effects for these two currents was due to the anodic effect being greater at times for the greater current and also being experienced for a greater period of time during any cycle for the case of the greater current. It can thus be said that a smaller reducing tendency was produced in the cathode film when a comparatively smaller alternating current was superimposed.
Results of these runs with various amounts of alternating currents show no apparent increase in ductility. Cathode voltages that were measured at the time appeared to have a tendency to drop with the higher current (Table V). The conditions of operation were 570 R.P.M., 31.9 amps. per sq. ft. and 9 degrees Centigrade. The tendency for the voltage to decrease was due to the lowered reducing conditions existing at the cathode surface in the cathode film created by the greater anodic effects produced on the cathode by the larger alternating currents. The decrease in cathode voltage with the increased alternating current would lead one to suspect that if some of the brittleness and the low efficiency were due to the reduction of the amine, the use of still higher alternating currents would correct these faults.

Table V.

Effects of alternating current on the cathode voltages at 570 R.P.M., 31.9 amps. per sq. ft. and 90°C.

<table>
<thead>
<tr>
<th>Alternating current in amperes (area= 6.37 sq. in.)</th>
<th>Cathode voltage</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.6</td>
</tr>
<tr>
<td>1.2</td>
<td>0.6</td>
</tr>
<tr>
<td>2.6</td>
<td>0.44</td>
</tr>
</tbody>
</table>

As previously mentioned the plate if allowed to come
in contact with the air would probably free itself of surface adsorbed gaseous material which ultimately would have been occluded in the plate. Allowance was made for this by tilting the entire set-up at such an angle that the plate would at times be out of the solution. In other words the cathode and assembly (cell and all) was tilted to such an angle that one side of the cathode was above the surface of the solution. This effect was obtained by tilting the cell and support 38.2 degrees from the normal position. The cathode, since it was connected to the cell support, was automatically tilted at the same angle.

The current used was corrected for the partial submersion of the cathode so that a current density of 31.9 amps. per sq. ft. was used. The resulting plate showed no change in brittleness. On the other hand the plate when measured for thickness by a micrometer showed a thinner cross-section at the top in comparison with the cross-section at the bottom. The order of the results is supported theoretically as well since the relative time of submergence of the plate at the bottom was longer than that at the top with a subsequently greater amount of energy passing through the bottom of the plate in comparison to the top.

Calculations previously made (p. 94 showed that the discharge potential of the copper and lead was
smaller than the reduction potential of the amine which in turn was smaller than the discharge potential of the hydrogen. A run was made with the cathode voltage lower than the reduction potential of the amine. Thus the current was limited by this cathode voltage. The variables that were thus fixed were 0.22 volts for the cathode voltage and 0.2 amperes which is equivalent to 4.46 amps per sq. ft.. The resulting plate showed bright copper streaks alternating with dark streaks. The plate was of no value at all.

Additions possible to alter operating conditions of the cell are numerous. The belief in the tendency for reduction of the amine led to the addition of acetone into the bath. The acetone might have a preferential tendency to reduction when compared with the amine. The reduction of the acetone can take many forms. The first step of the reduction would be the formation of isopropyl alcohol which would be a soluble product. This reaction would be preferred. On the other hand other possible products of the reaction may be:

1. ethanol and methane from isopropyl alcohol,
2. methyl alcohol and methane from the isopropyl alcohol or the products of step 1,
3. methane and water as the final step of the series resulting in steps 1 and 2,
4. propane from acetone or the products pro-
duced in the first step,

(5) production of ethane from ethanol produced in the first step,

(6) formaldehyde or acetaldehyde from the splitting off of a carbon, with whatever is on it, from the basic structure of the acetone.

The possible ways in which the amine can be reduced at the cathode is indicated above. The preferred reaction is the formation of isopropyl alcohol as above mentioned. The above reactions would occur due to the presence of the acetone which would act as a depolarizer. Not only would these reactions possibly take place but due to the oxidation that is going on at the anode other products of oxidation would possibly be formed.

A solution made by mixing 178 cc. of acetone with 822 cc. of straight amine solution saturated with respect to copper and lead was used for a run. The resulting plate formed under the usual conditions of operation used in this work gave no apparent indication of the change in brittleness. As was shown above the reduction of the acetone a greater amount than was anticipated would form the insoluble ethane or methane. The production of these gases would not alter the conditions at the cathode surface from that which existed previous to the addition of the acetone. Reduction of aldehydes and ketones generally leads to the formation of some saturated
The addition of material which would alter the reducing atmosphere in which the amine finds itself at the cathode took the form of additions of 3 per cent hydrogen peroxide solution. It was found that the compatibility of the 3 per cent peroxide and the amine was such that 10 cc. of the peroxide per liter of amine solution could be added with no evidence of any oxidation of the amine or the decomposition of the peroxide. During electrolysis peroxide was added to the liquid inside the cathode holder at the rate of 0.25 cc. per minute. The electrolysis of this solution under the usual conditions yielded a plate that was entirely unsatisfactory.

Based on Greenspan's work (61), study was made of the effect of additions of ammonium hydroxide and ammonium sulphate to the amine solutions. Using 2.35 liters of the amine solution plates were obtained on each subsequent addition of 10 cc. of ammonia. The plates were of two hours duration under the usual conditions of operation. Ductility showed slight improvement up to a maximum addition of 40 cc. of ammonia in 2.35 liters of amine solution. After this point the addition of ammonia gave an increase in the brittleness. Not only was the

(61) Greenspan, L., loc. cit.
brittleness past this point of maximum effect increased but the property of adherence appeared to drop. On standing the latter plates tended to fall away from the base material.

Using 2.5 liters of the amine solution, additions of ammonium sulphate were made to the extent of 1, 2, 3 and 6 grams. Plates obtained after each addition showed no improvement in ductility after a maximum addition of two grams of ammonium sulphate. The plates here produced from baths containing more ammonium sulphate than that required for maximum effects were badly striated.

Based on Greenspan's work the effect of addition agents was considered (61). The effect on surface tension of the detergents listed in Table VI is given in Table VII. Wetting agents of the ester type apparently are of value in lowering the surface tension. Acidic materials on the other hand have decreased the surface tension to a certain extent but the resulting precipitation of some constituent (either due to insolubility or hydrolysis) was the reason for not using these.

The effect on plate characteristics of some wetting agents together with the effect on cathode voltages is listed in Table VIII. Apparently the use of the wetting agents in concentrations of 1 per cent was of little advantage as the brittleness was not affected
Table VI.

<table>
<thead>
<tr>
<th>Wetting agent</th>
<th>Type</th>
<th>Supplied by</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dupanol 80</td>
<td>Fatty alcohol sulphate.</td>
<td>D*</td>
</tr>
<tr>
<td>Dupanol WA (special)</td>
<td>Fatty alcohol sulphate.</td>
<td>D</td>
</tr>
<tr>
<td>Alkanol WXN</td>
<td>Sodium alkyl napthalene sulphonate.</td>
<td>D</td>
</tr>
<tr>
<td>Neomierpin SAW</td>
<td>Alkyl napthalene sulphonlic acid.</td>
<td>D</td>
</tr>
<tr>
<td>M.P. 180 S</td>
<td>Sodium alkyl napthalene sulphonate.</td>
<td>D</td>
</tr>
<tr>
<td>Aerosol O.S.</td>
<td>Alkyl amyl sulphonate.</td>
<td>A*</td>
</tr>
<tr>
<td>Aerosol OT</td>
<td>Dioctyl ester of sodium sulfo succinic acid.</td>
<td>A</td>
</tr>
<tr>
<td>Aerosol MA</td>
<td>Dihexyl ester of sodium sulfo succinic acid.</td>
<td>A</td>
</tr>
<tr>
<td>Aerosol 1B</td>
<td>Dibutyl ester of sodium sulfo succinic acid.</td>
<td>A</td>
</tr>
<tr>
<td>Aerosol AY</td>
<td>Diamyyl ester of sodium sulfo succinic acid.</td>
<td>A</td>
</tr>
<tr>
<td>Daconol</td>
<td>Alkyl amyl sodium sulphonate.</td>
<td>Da*</td>
</tr>
<tr>
<td>Tergitol 4</td>
<td>Sodium salt of higher secondary alkyl sulphate.</td>
<td>U*</td>
</tr>
<tr>
<td>Tergitol 7</td>
<td>Sodium salt of higher secondary alkyl sulphate.</td>
<td>U</td>
</tr>
</tbody>
</table>
Table VI cont.

<table>
<thead>
<tr>
<th>Wetting agent</th>
<th>Type</th>
<th>Supplied by</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tergitol 08</td>
<td>Sodium salt of higher primary alkyl sulphate.</td>
<td>U</td>
</tr>
<tr>
<td>Triton NE</td>
<td>Organic poly-ether alcohol.</td>
<td>R*</td>
</tr>
<tr>
<td>Triton 720</td>
<td>Sulphonated ester.</td>
<td>R</td>
</tr>
<tr>
<td>Naconol E.P.</td>
<td>Sodium alkyl amyl sulphonate.</td>
<td>N*</td>
</tr>
<tr>
<td>Turco Acidose</td>
<td>Aryl, amyl sulphonate.</td>
<td>T*</td>
</tr>
</tbody>
</table>

*D- du Pont, E. I., de Nemours & Co.
*A- American Cyanamid and Chemical Corp.
*Da- S. A. Day Manuf. Co.
*U- Union Carbide and Carben Corp.
*R- Rohm & Hass Inc.
*N- National Aniline and Chemical Corp. Inc.
*T- Turco Products Inc.
Table VII.

Surface tensions of amine solutions with various amounts of detergents (measured by stalingrometer).

Additions in grams or cc. per 100 cc. of amine solution depending on whether material is solid or liquid.

<table>
<thead>
<tr>
<th>Detergent</th>
<th>0</th>
<th>0.001</th>
<th>0.002</th>
<th>0.004</th>
<th>0.008</th>
<th>0.01</th>
<th>0.02</th>
<th>0.05</th>
<th>0.10</th>
<th>0.20</th>
<th>0.40</th>
<th>0.50</th>
<th>1.00</th>
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</tr>
<tr>
<td>Dupanol SC (L)</td>
<td>73.0</td>
<td>48.8</td>
<td>41.8</td>
<td>31.9</td>
<td>28.8</td>
<td>26.9</td>
<td>28.8</td>
<td>26.9</td>
<td>28.8</td>
<td>26.9</td>
<td>28.8</td>
<td>26.9</td>
<td>28.8</td>
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<tr>
<td>Dupanol WA (special) (L)</td>
<td>73.0</td>
<td>50.5</td>
<td>30.3</td>
<td>30.4</td>
<td></td>
<td></td>
<td></td>
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<td></td>
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<td></td>
</tr>
<tr>
<td>Alkanol WXN (L)</td>
<td>73.0</td>
<td>31.4</td>
<td>30.8</td>
<td>30.7</td>
<td>30.7</td>
<td>30.7</td>
<td>30.7</td>
<td>30.7</td>
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<td>Neomermip SAW (L)</td>
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<td>30.7</td>
<td>30.4</td>
<td>30.4</td>
<td>30.4</td>
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<td>30.4</td>
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<tr>
<td>M.P. 189 S (L)</td>
<td>73.0</td>
<td>63.0</td>
<td>50.1</td>
<td>36.5</td>
<td>34.9</td>
<td>34.9</td>
<td>34.9</td>
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<tr>
<td>Aerosol OS (s)</td>
<td>73.0</td>
<td>40.5</td>
<td>38.5</td>
<td>37.4</td>
<td>35.5</td>
<td>30.9</td>
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<tr>
<td>Aerosol OT (s)</td>
<td>73.0</td>
<td>52.2</td>
<td>44.3</td>
<td>35.1</td>
<td>35.9</td>
<td>35.9</td>
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<td>Aerosol MA (s)</td>
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<td>46.5</td>
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<td>Aerosol 1B (s)</td>
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<td>52.1</td>
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<td>Aerosol AY (s)</td>
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<td>46.4</td>
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<tr>
<td>Nexusol (s)</td>
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<td></td>
<td>43.0</td>
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<tr>
<td>Tergitol 4 (L)</td>
<td>73.0</td>
<td>33.0</td>
<td>31.2</td>
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<tr>
<td>Tergitol 7 (L)</td>
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<td>29.5</td>
<td>29.4</td>
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<td>22.6</td>
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<td>47.1</td>
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<td>Triton 720 (L)</td>
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<td>40.5</td>
<td>37.4</td>
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<tr>
<td>Naconol EP (s)</td>
<td>73.0</td>
<td></td>
<td>44.4</td>
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<tr>
<td>Turbo Acidose (s)</td>
<td>73.0</td>
<td></td>
<td>41.6</td>
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</tr>
</tbody>
</table>

Miscibility.

- good
- insoluble solid formed
- slight precipitate formed
- precipitate formed
- insoluble oil formed
- insoluble solid formed
- max solubility 0.4%
Table VIII.

Effect of wetting agents on voltages and plates.

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<th>Wetting agent</th>
<th>voltages</th>
<th>characteristics of plate.</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>cathode</td>
<td>anode</td>
</tr>
<tr>
<td>Tergitol QS*</td>
<td>0.6</td>
<td>1.7</td>
</tr>
<tr>
<td>Dupanol 80*</td>
<td>0.5</td>
<td>1.4</td>
</tr>
<tr>
<td>Triton NE*</td>
<td>1.0</td>
<td>1.2</td>
</tr>
<tr>
<td>Triton 720**</td>
<td>0.8</td>
<td>1.0</td>
</tr>
<tr>
<td>Alkanol WXX*</td>
<td>0.7</td>
<td>1.0</td>
</tr>
</tbody>
</table>

* 1 per cent solution of detergent in amine.

** 0.4 per cent solution of detergent in amine.
except in the case of "Alkanol WXN" which showed a slight improvement.

The effect on voltages of the various detergents used in the electrolyte is shown in Table VIII. From the values there is no definite effect nor is there any pronounced effect in either direction.
SUMMARY.

1. Cupric oxide for solute purpose is best produced from roasting basic cupric carbonate.

2. Efficiency of solution from a material standpoint is best when cupric oxide is dissolved in the absence of solid plumbous hydroxide and when plumbous hydroxide is dissolved in the absence of solid cupric oxide.

3. Composition of the alloys plated out as a function of speed of rotation and current density at nine degrees Centigrade from a 7.2 per cent amine solution in water saturated with respect to copper first and then with respect to lead (27.6 grams per liter of copper and 8.42 grams per liter of lead) is shown graphically in Figures 12, 13 and 14.

4. The alloy plated out is brittle, solid, smooth and has good adhesive properties relative to a properly cleaned and etched steel back.

5. The microstructure of the alloys produced shows a single homogeneous constituent consisting of a very intimate mixture of copper and lead with a lead binder acting as a cement between the grains. Due to this fact the ductility of the alloys may be low.

6. Heat treatment of the alloys produces a
precipitation of the lead both inside of the grain and into the grain boundary together with a relative decrease in grain size.

(7) Superimposition of alternating current on direct current has no apparent effect on the ductility of the alloy. The effect produced is solely the decrease of the cathode voltage with relatively greater amounts of alternating current in comparison to the direct current.

(8) Decrease of cathode voltage by lowered current densities did not produce good plates.

(9) Exposure of the plate regularly to air during electrolysis has no observable beneficial effect on the plate. The thickness of the plate produced is greater at the bottom of the cathode than at the top if during the production of the plate the cathode and cell assembly is tilted so as to permit the plate to come in contact with the air.

(10) Additions to the bath have the following effects:
   
   (a) acetone has no effect on the ductility,
   
   (b) hydrogen peroxide produces bad plates,
   
   (c) additions of ammonium hydroxide up to a maximum of 17.02 cc. per liter of amine solution produced a maximum increase in ductility although the resulting alloy was still brittle,
   
   (d) additions of ammonium sulphate to a maximum
of 0.8 grams per liter of amine solution produced a maximum increase in ductility with the resulting plate still being brittle.

(e) wetting agents have little if no effect on the ductility of the alloy with the exception of "Alkanol W87" which had a slight beneficial effect.

(11) The surface tension of the amine solution has been lowered by the detergents from 73 to about 30-40 dynes per centimeter squared. The best detergents that could be used are of the ester type as no insoluble solids or oils are produced as is the general case with detergents of the substituted acid type.
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