This invention relates to the electro-deposition of copper from an acid plating bath, and more particularly to electroplating baths or solutions which are adapted to produce semi-bright and bright, smooth deposits suitable for bright nickel plating without the necessity of buffing, polishing or otherwise pre-treating the copper deposit preparatory to nickel plating.

An important object of this invention is to provide a process for producing semi-bright to bright deposits of copper which are resistant to corrosion and yet ductile, being easily buffed when it is desired to increase the coverage of imperfections in the base metal.

A further object of the invention is to produce a fine grained ductile metal deposit which is especially suitable in the electroforming trade.

A further object of the invention is to provide an electroplating solution having a relatively wide bright or lustrous plating range capacity and one which is operable employing high current densities and such as cannot be used ordinarily because of the difficulties encountered with burning and treeing of the deposits. A current density range of between 20 and 200 amperes/sq. ft. is made possible, and very fine grain deposits obtained.

A further object of the invention is to provide an improved plating bath containing a primary brightener agent and a filter or auxiliary brightening and grain refining agent which produces copper deposits which are bright and ductile.

A still further object or advancement in this art is the discovery of a new use for polycrylamides, and which as found by tests to function, when added to electroplating acid baths, as an agent which prevents metal grains from agglomerating during plating whereby a finer grain deposit results than otherwise is obtained.

These and other objects and advantages will become apparent to those skilled in the art from the following description.

In accordance with the invention, it has been unexpectedly discovered, after experimenting with a large number of different substances, that by adding a small quantity of polycrylamide with a primary brightener to the acid copper plating solution the brightness of the deposit is markedly increased over the same plating solution containing no polycrylamide or polycrylamide alone. Moreover, a bright metal deposit is produced using lower concentrations of primary brighteners, and without decreasing the ductility of the plating deposit. Polycrylamide, such as prepared by polymerizing acryl acid and an amide comprises a resinous or horn-like mass which is sparingly soluble in the acid plating solution or electrolyte.

The presence of even very small amounts of polycrylamide along with primary brighteners, e.g., thiourea or water-soluble heterocyclic nitrogen compound, e.g. pyridine, functions synergistically to refine the grain of the metal deposited and brighten the coating deposit. The electroplate is closely packed, uniform size metal grains as may be seen with the aid of a microscope. It is believed, though not confirmed by conclusive tests, that polycrylamide modifies the electrical charge on the metal grains during deposition whereby the tendency to agglomerate, unite or to build up one on another is inhibited or at least greatly lessened.

Polycrylamide may be used effectively in the acid plating bath in concentrations from 0.005 to 0.50 gram/liter of solution. A preferred concentration to use, however, is between about 0.02 to 0.04 gram/liter of plating solution. The primary brighteners present may comprise, for example, thiourea, acetyl thiourea, allyl thiourea, guanylthiourea, 2-thiohydantoin, 1-acetyl-2-thiohydantoin, and derivatives thereof. Use of these water-soluble thioure compounds in combination with polycrylamide is essential since the combination of these addition agents, as aforementioned, produce a synergistic grain refining effect resulting in improving the luster or brightness of the plate, which use of the addition agents alone or separately do not accomplish.

It is believed, and test results so indicate, that the polycrylamide addition agent functions to enhance the effectiveness and efficiency of the primary brightener.

The presence of even small amounts of the polycrylamide together with primary brighteners increases the effectiveness of the primary brighteners, and they function for a longer period of time and show less tendency to decompose under like temperatures and plating conditions than when no addition of polycrylamide is made.

Polycrylamide has the structural formula

$$[\text{H}_n]$$

where $n$ is 2 or more, and which may vary over a wide range.

Polycrylamide acid has the structural formula

$$\text{COOH}$$

wherein $n$ is 2 or more to form a long chain of high molecular weight. For example, where $n$ is 20 the product is a viscous, colorless oil which dissolves in benzene and has a molecular weight of 2000. A polycrylamide suitable for use may be produced by reacting an ester, anhydride or acid halide of polycrylamide acid with ammonia.

Suitable polycrylamide for use as a brightener may be produced by reacting a polycrylamide ester with ammonia as follows—

**Example A**

Polyethylacrylate (M. wt. 2000) is reacted with aqueous ammonia using mol equivalent weights at a temperature of 0-5°C. to form a polymerized ethyl acrylamide.

Other polycrylamides amides may be made using substituted ammonia compounds reacted with polycrylamide derivatives to form useful polycrylamide brighteners or grain refining agents in acce copper plating solutions in accordance with applicant's invention.

An example illustrating another suitable polycrylamide is as follows:

**Example B**

A 1:1 mol equivalent of methyl acrylate (M. wt. 4000) is reacted with ammonia as in Example A at 0-5°C. to produce polycrylamide which separates from the solution as an insoluble mass.

A modified polycrylamido addition agent may be prepared by heating a mixture of polycrylamide chloride with aniline, the reaction being carried out at 100°C. until a horny insoluble mass is formed.

Further electroplating tests carried out using a 300 milliliter Hull cell with air agitation at temperatures of 30 to 40°C. showed that the presence of a small quantity
of polyacrylamide with thiourea or water-soluble derivatives thereof in the acid copper bath produced bright, uniform metal deposits and improved the results as compared with the use of like electrolytes wherein polyacrylamide was absent. It was also observed that with polyacrylamide present in the acid copper solution, lower concentrations of primary brighteners could be used with equally good results being obtained as compared with higher concentrations where polyacrylamide was omitted.

The use of high concentrations of primary brighteners is to be avoided because this increases the impurities as the result of breakdown of the brighteners during operation of the bath. High concentrations of primary brighteners also causes "skipping" of the deposit in low current density area.

It was found that the addition of one pound of polyacrylamide to 4000 gallons of acid copper electrolyte of the conventional bright plating type and containing a primary brightener, while plating was in progress immediately permitted approximately a 10% increase in current density without encountering the usual burning or treecing effects at the edges of the workpiece. The overall bright plating range was increased and the deposit of copper was of a more even, uniform luster than when using the conventional acid copper plating electrolyte. It was further observed that the finished chrome plated product, e.g., plated twenty minutes in an acid copper bath and twelve minutes in nickel sulfate bath and then chromium plated, was far superior in color and appearance than obtained using the same process cycle without the use of polyacrylamide addition agent.

The following examples are illustrative but not limitative of the invention—

Example I

An aqueous electroplating electrolyte of the following composition was prepared—

<table>
<thead>
<tr>
<th>Compound</th>
<th>Ounces/gal.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Copper sulfate crystals (CuSO₄·5H₂O)</td>
<td>26.0</td>
</tr>
<tr>
<td>Sulfuric acid 98% (H₂SO₄)</td>
<td>6.5</td>
</tr>
<tr>
<td>Dextrin</td>
<td>0.008</td>
</tr>
<tr>
<td>Thiourea</td>
<td>0.002</td>
</tr>
<tr>
<td>Polyacrylamide (Example A)</td>
<td>0.005</td>
</tr>
</tbody>
</table>

The bath was used to plate copper on clean steel panels (3 x 5 inches) and the bath operated with air agitation over a wide temperature range with excellent results. Copper was plated from the bath using direct current and air agitation at current densities of from 30 to 100 amperes/sq. ft. and bath temperature of 25 to 40° C. In each case the copper plate deposit was quite bright, ductile and suitable for bright nickel plating without buffing. The results obtained from Example I were far superior to the results obtained from the same bath without the use of polyacrylamide.

Example II

A procedure was carried out that was the same as that described in Example I, except that the following concentrations of ingredients were used.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Ounces/gal.</th>
</tr>
</thead>
<tbody>
<tr>
<td>CuSO₄·5H₂O</td>
<td>32.0</td>
</tr>
<tr>
<td>H₂SO₄</td>
<td>8.0</td>
</tr>
<tr>
<td>Thiourea</td>
<td>0.002</td>
</tr>
<tr>
<td>Polyacrylamide (Example B)</td>
<td>0.004</td>
</tr>
</tbody>
</table>

The results were equally as good as in Example I and much better than results obtained from Example II without the use of polyacrylamide.

Example III

<table>
<thead>
<tr>
<th>Compound</th>
<th>Ounces/gal.</th>
</tr>
</thead>
<tbody>
<tr>
<td>CuSO₄·5H₂O</td>
<td>32.0</td>
</tr>
<tr>
<td>Sulfuric acid</td>
<td>8.0</td>
</tr>
<tr>
<td>Pyridine</td>
<td>0.002</td>
</tr>
<tr>
<td>Polyacrylamide (Example A)</td>
<td>0.004</td>
</tr>
</tbody>
</table>

While not quite as bright as Examples I and II, the copper deposit from this bath was fine grained and ductile.

Example IV

Example IV was the same as Example I without the use of dextrin. Similar results were obtained as in Example I.

Example V

Example II was repeated using allylthiourea in place of thiourea and wherein a bright copper deposit was obtained.

Example VI

Example II was repeated with the substitution of guanithiourea for thiourea. A bright lustrous copper deposit was obtained.

Example VII

Example II was repeated with the substitution of 2-thiobenzothiazol for thiourea. A bright copper deposit was obtained.

Example VIII

Example II copper plating bath was repeated wherein 1-allyl-2-thiobenzothiazol is substituted for thiourea as the primary brightener. A bright copper deposit resulted using this combination of brighteners.

Polyacrylamide as may be made by vinyl polymerization of acrylamide, and which is readily carried out in aqueous solution to produce polymers of varying water solubility depending on reaction conditions. Acrylamide polymers of relatively low molecular weight which are water-soluble when produced in the polymerization is effected in organic solvents.

Polyacrylamide also may be formed using a raw polymerization of acrylamide, and which is readily carried out in aqueous solution to produce polymers of varying water solubility depending on reaction conditions. Acrylamide polymers of relatively low molecular weight which are water-soluble when produced in the polymerization is effected in organic solvents.

Allylthiourea CH₆—CHCONH₂ may thus be polymerized to form N,N'-methylenebisacrylamide which is useful in electroplating baths as a grain refiner agent in accordance with this invention. Modified polyacrylamides also may be utilized, for example polyacrylamide modified by hydrolysis, imidization, methylation, and halogenation. Acrylamide copolymerized with other vinyl monomers which impart hydrophilic properties may also be used as addition agents to electroplating baths to improve the luster of the plating deposits.

The copper deposited layer produced employing acid copper electrolyte containing polyacrylamide as an addition agent to conventional brighteners was bright and ductile. After twenty to thirty minutes plating operation a soft lustrous layer of copper is deposited on the substrate.

The present application is a continuation-in-part of my parent application Ser. No. 624,737, filed November 28, 1956, and now abandoned.

While the invention has been described and specific examples given as exemplary of the improved electroplating baths and conditions for obtaining the improved plating results aforementioned, it will be understood that changes and substitutions may be made by those skilled in the art without actually departing from the invention.

The appended claims are thus intended to cover all such equivalents and uses as come within the true spirit and scope of the foregoing disclosure.

What is claimed is:

1. An aqueous electroplating electrolyte comprising essentially copper sulfate, sulfuric acid, a primary brightener in proportions of 5 to 50 mg./l. of solution, said primary brightener being selected from the group consisting of pyridine, thiourea, allylthiourea and acetythiourea, and wherein there is additionally incorporated polyacrylamide as a filler and brightener, said polyacrylamide being present in the amount of 0.005 to 0.5 g./l.

2. A bath according to claim 1, wherein said primary brightener is thiourea.

3. A bath according to claim 1, wherein said primary brightener is allylthiourea.
4. A bath according to claim 1, wherein said primary brightener is acetylthiourea.

5. A bath according to claim 1, wherein said primary brightener is pyridine.

6. In the process of depositing copper on metallic surfaces by electrodeposition from a sulfuric acid-copper sulfate aqueous bath, the step of carrying out said process with said bath containing a dissolved primary brightener selected from the group consisting of pyridine, thiourea, allylthiourea, and acetylthiourea, said primary brightener being present in the amount of between 5 and 50 mg./liter of the bath, and there being additionally present polyacrylamide as a filler and auxiliary brightener, said polyacrylamide being present in the amount of 0.005 to 0.5 g./l. in said bath.

7. An aqueous electroplating electrolyte comprising essentially copper sulfate, sulfuric acid, and a brightener in proportions of 5 to 50 mg./l. of solution, said brightener being selected from the group consisting of pyridine, thiourea, allylthiourea and acetylthiourea and additionally containing polyacrylamide as a filler in said electrolyte, said polyacrylamide being present in the amount of 0.005 to 0.5 g./l. of said electrolyte.

8. In the process of depositing copper on metallic surfaces by electro-deposition from a sulfuric acid-copper sulfate aqueous bath, the step of carrying out said process with said bath containing a dissolved brightener in proportions of 5 to 50 mg./l., selected from the group consisting of pyridine, thiourea, allylthiourea, and acetylthiourea, and there being additionally present polyacrylamide as a filler in said aqueous bath, said polyacrylamide being present in the amount of 0.005 to 0.5 g./l. of said bath.

9. A bright copper plating bath containing copper sulfate, sulfuric acid and a grain refining and filling agent consisting of polyacrylamide which is present together with thiourea in sufficient amount to produce a bright copper deposit, said polyacrylamide being present in the amount of 0.005 to 0.5 g./liter of the plating bath and said thiourea being present in proportions of 5 to 50 mg./liter of said bath.

10. A bright copper plating bath containing copper sulfate, sulfuric acid and a grain refining and filling agent consisting of polyacrylamide which is present together with allylthiourea in sufficient amount to produce a bright copper deposit, said polyacrylamide being present in the amount of 0.005 to 0.5 g./liter of the plating bath and said allylthiourea being present in proportions of 5 to 50 mg./liter of said bath.

11. A bright copper plating bath containing copper sulfate, sulfuric acid and a grain refining and filling agent consisting of polyacrylamide which is present together with acetylthiourea in sufficient amount to produce a bright copper deposit, said polyacrylamide being present in the amount of 0.005 to 0.5 g./liter of the plating bath and said acetylthiourea being present in proportions of 5 to 50 mg./liter of said bath.

12. A bright copper plating bath containing copper sulfate, sulfuric acid and a grain refining and filling agent consisting of polyacrylamide which is present together with pyridine in sufficient amount to produce a bright copper deposit, said polyacrylamide being present in the amount of 0.005 to 0.5 g./liter of the plating bath and said pyridine being present in proportions of 5 to 50 mg./liter of said bath.

13. A bright copper plating bath containing copper sulfate, sulfuric acid and a grain refining and filling agent consisting of polyacrylamide and 2-thiohydantoin in sufficient amount to produce a bright copper deposit, said polyacrylamide being present in the amount of 0.005 to 0.5 g./liter of the plating bath and said 2-thiohydantoin being present in proportions of 5 to 50 mg./liter of said bath.

14. A bright copper plating bath containing copper sulfate, sulfuric acid and a grain refining and filling agent consisting of polyacrylamide and 1-acetyl-2-thiohydantoin in sufficient amount to produce a bright copper deposit, said polyacrylamide being present in the amount of 0.005 to 0.5 g./liter of the plating bath and said 1-acetyl-2-thiohydantoin being present in proportions of 5 to 50 mg./liter of said bath.

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