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ELECTRODEPOSITION OF COPPER

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4 Claims. (Cl. 204—52)

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This application is a division of our copending application Serial No. 395,004, filed May 24, 1941.

The invention relates to the electrodeposition of copper from acid baths and has for its object the formation of deposits which have a greater degree of smoothness or brilliance than is ordinarily obtained as well as deposits which are characterized by remarkable "buffability" or capability of being buffed or "colored" by the usual buffing instrumentalities, when necessary.

The invention is based upon the use of certain addition agents in novel relationship and the determination of the factors affecting the action of these agents to produce most satisfactory results.

In accordance with the present invention it is proposed to employ copper plating baths of the usual sulphuric acid type in which the copper is present in the form of copper sulphate. To such bath is added as a "primary" addition agent a very small proportion of an organic brightening and structure-controlling agent which may be characterized by the presence of "active" sulphur, a thiourea being a typical example. In a standard acid copper bath containing, for example, 250 grams of copper sulphate,

$$CuSO_4.5H_2O$$

and 10 grams more or less of sulphuric acid per liter, the addition of as little as 0.002 gram per liter of thiourea will bring about a noticeable improvement in brightness and structure. Much larger additions up to above five grams per liter of thiourea have been successfully employed, but the larger amounts are necessary for best results and therefore it is generally preferred to use in the neighborhood of 0.01 to 0.1 gram per liter.

Further improvement in the uniformity of distribution of the effect of the primary or active-sulphur containing addition agents and in the range of plating conditions, such as current density, as well as the characteristics of the deposit may be obtained by the use of further additions of what we may term "control" agents. These may be of either or both, metallic and organic non-metallic character. Of the metallic type, the metals cadmium, zinc, cobalt and nickel have somewhat similar effects. They may be added in the form of salts, for example, sulphates. Cadmium sulphate, in amounts up to about 75 grams per liter of bath, seems to enhance the brightening effect in combination with thiourea. It also improves the deposit as to softness and texture. When thus present in the bath the metals are deposited along the copper in small

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proportions. With cadmium sulphate, for example, we have found up to five hundredths of one percent of cadmium in the deposit.

Other salts than the sulphates may be employed if compatible with the bath and, in the case of some of the metals named, may be preferable to the sulphates. With nickel, for example, very satisfactory results have been obtained by the use of nickel phosphate in amounts, for example, of about 35 grams per liter, a small amount of phosphoric acid being added also.

Of the non-metallic control agents we have found the most effective to be organic compounds of the class generally known as surface tension reducing or "wetting" agents. Many of the wetting agents found suitable are aromatic sulphonates and a considerable number are on the market under various trade names. Among those that are useful in the acid copper sulphate bath in combination with the primary addition agents, the following have been found especially beneficial:

"Triton 720"
"Neomerpin"
"Tergitol 08"

From the standpoint of cost, results and complete compatibility with the acid copper bath the "Triton 720" has proven highly satisfactory. It is a sulphonated ether containing a branch chain and an aromatic nucleus. More specifically it is one or more compounds of the formula

$$Ar(OC_2H_4)_nOC_2H_4SO_3M$$

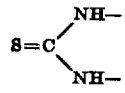
wherein Ar is a hydrocarbon substituted aromatic nucleus, M is a metal of the group consisting of sodium, potassium, calcium and magnesium, or is an ammonia or amine group, n is any whole number from three to six and the hydrocarbon substituent of the aryl group has carbon atoms within the range of four to twelve. Attention is also directed to U. S. Patent 2,115,192 which discloses this known wetting agent. It is sold generally in the form of an aqueous paste capable of being poured or measured by volume and, since the amounts to be used are not critical, the paste may be added by volume, one c. c. corresponding to approximately one gram of other like agents. "Tergitol 08" is described in literature and issued patents as being a sodium secondary alcohol sulphate. The "neomerpin" compounds are understood to be alkyl naphthalene sulphonic acids and sodium salts thereof.

Other organic sulphonates that have been satisfactorily used along with thiourea in the acid copper bath, particularly in combination with the

metallic additions, are di-chloro-benzene sulphonic acid, nickel benzene disulphonate, toluene sulphonic acid, naphthylamine disulphonic acid and sodium tri-isopropyl naphthalene sulphonate. These are representative of a considerable variety of aromatic sulphonates that possess similar properties and may be effectively employed. Where the wetting agent is added by weight, amounts of 0.01 to 5 grams per liter may be used, larger amounts being generally associated with higher content of the primary addition agent.

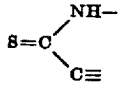
Further additions may be made of agents that have the function of increasing the bright-plating range. For example, ammonium sulphate in amounts of 1–100 grams per liter has been found effective.

The primary addition agent above referred to as "active-sulphur containing" and represented typically by thiourea is not limited to thiourea alone. The class is characterized generally as containing a bivalent sulphur atom both bonds of which are directly connected to a carbon atom. The thioureas having the nucleus

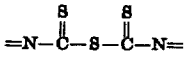


and the isothiocyanates having the grouping S=C=N— are considered representative types.

Compounds containing the nucleus



characteristic of thioacetamide, and the nucleus



for example tetra methyl thiuram monosulphide, are also effective brighteners.

The water soluble mercaptans, for example β-dithioglycoll and thiosalicylic acid, and even some nitrogen-containing compounds not containing sulphur, as a cyanamide and particularly dicyandiamide, have also a brightening effect. The concentrations of the cyanamide and dicyandiamide are the same as for the thiourea.

It will be understood that the compound employed should be soluble in the acid bath and should be compatible with the other constituents. Cost and commercial availability will, of course, be factors in determining the product to be used and since thiourea, per se, $CS(NH_2)_2$, is suitable from all standpoints, it is at present preferred for plant use.

The constitution of the bath exclusive of the novel addition agents is of standard character. For example, aqueous solutions containing 125 to 250 grams per liter of the technical copper sulphate ordinarily supplied for plating and 5 to 100 grams of sulphuric acid are well known and thiourea is effective over the entire range with suitable adjustment as to plating conditions. However, the composition of the bath with reference to the content of copper sulphate and sulphuric acid is not critical within operating limits.

The temperature of the bath for best results may vary from relatively low limits, for example, 40° F., up to near 120° F. For maximum brilliance the recommended temperature is 70–80° F.

A suitable current density is 18–48 amperes per square foot of cathode area without agitation. This can be greatly increased and the brilliance improved by agitation, as by movement of the cathodes. With rates of movement of 10–25 feet per minute, the upper limit of current density may be readily raised to 72 amperes per square foot. Even higher current densities up to about 96 amperes per square foot have been successfully used.

The following may be given, as examples merely, of baths from which satisfactory results have been obtained:

(1)

	Grams
Technical copper sulphate	250
Cadmium sulphate	35
Sulphur acid	10
Di-chloro-benzene sulphonic acid	10
Thiourea	0.1
Water to make up one liter	

(2)

	Grams
Copper sulphate	250
Nickel phosphate ($Ni_3(PO_4)_2.7H_2O$)	35
Sulphuric acid	10
Phosphoric acid	10
Naphthylamine disulphonic acid	10
Thiourea	0.1
Water to make up one liter	

(The amounts of the metallic addition agents above are given only by way of examples as the quantities are not at all critical. For best results we recommend, for example, 10–75 grams per liter, which addition may consist of salts of one or more of the metals named.)

(3)

Copper sulphate	grams	250
Sulphuric acid	do	10
"Triton 720"	c. c.	1
Thiourea	grams	0.01
Water to make up one liter		

(This produces a semi-bright deposit which is soft and easily buffed.)

The primary addition agent is slowly depleted during the plating operation and is to be replenished as required. The control or range increasign and wetting agents, however, other than the metallic type, are apparently not depleted by plating and need replenishing only as the composition of the bath changes due to dragout or addition of fresh bath constituents.

The baths described enable plated deposits of copper, or chiefly of copper, to be obtained which, within a certain medium range of conditions, are truly brilliant. However, even if the conditions are not so accurately maintained as to produce an entirely brilliant deposit or uniform brightness over the entire area, still the deposits are characterized by extreme fineness of crystal structure and remarkable ease of buffing to brilliance as compared with copper deposits from the ordinary acid copper baths. The invention is therefore of especial utility in the plating of objects of irregular contour on which a bright surface is required, as where bright deposits of nickel or chromium are to be later applied. Furthermore, by reason of the reduction in the amount and severity of the buffing operation where such may be necessary, the requirements of labor, equipment, and buffing materials are greatly reduced and the danger of buffing through the coating is substantially eliminated.

We claim:

1. A bath for electrodepositing copper comprising an aqueous acid copper solution comprising essentially copper sulfate and sulfuric acid

and having dissolved therein a compound selected from the group consisting of cyanamide and dicyandiamide, said compound having a concentration in said solution of about 0.1 gram per liter.

2. A bath for electrodepositing copper comprising an aqueous acid copper solution comprising essentially copper sulfate and sulfuric acid and having dissolved therein a compound selected from the group consisting of cyanamide and dicyandiamide, said compound having a concentration in said solution within the range 0.002 to 5 grams per liter.

3. A bath for electrodepositing copper comprising essentially copper sulphate and sulphuric acid and having dissolved therein cyanamide in a concentration within the range of 0.002 to 5 grams per liter.

4. A bath for electrodepositing copper comprising essentially copper sulphate and sulphuric acid and having dissolved therein dicyandiamide in a concentration within the range of 0.002 to 5 grams per liter.

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REFERENCES CITED

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