Patented Aug. 7, 1951 2,563,360

UNITED STATES PATENT OFFICE

2,563,360

ELECTRODEPOSITION OF COPPER

William M. Phillips, Birmingham, and Frank L. Clifton, Detroit, Mich., assignors to General Motors Corporation, Detroit, Mich., a corporation of Delaware

No Drawing. Application December 19, 1946, Serial No. 717,333

12 Claims. (Cl. 204—52)

1

This application is a continuation-in-part 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 and 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 unnecessary 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 if 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 cadminum, zinc, cobalt and nickel have somewhat similar effects. They may be added in the form of salts, for example, sulphates. Cadminum 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 with the copper in small 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.

2

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" and
"Tergitol 08"

From the standpoint of cost, results and complete compatability 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—

$$Ar(OC_2H_4)_nOC_2H_4SO_3M—$$

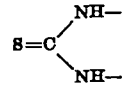
wherein Ar is a hydrocarbon substituted aromatic nucleus, M is a metal of the group consisting of sodium, potassium, calcium and magnesium, or is an ammonia or amine group, n is any whole number from three to six and the hydrocarbon substituent of the aryl group has carbon atoms within the range of four 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 essentially the sulfate ester of secondary higher alcohols. The "neomerpin" compounds are alkyl naphthalene sulphonic acids and sodium salts thereof.

Other organic sulphonates that have been satisfactorily used along with thiourea in the acid coopper 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. Other wetting agents well known in the commercial field such as, for example, Duponol, may be used. Duponol is essentially sodium lauryl

sulfate. 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.

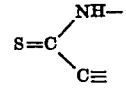
Further additions may be made of agents that have the function of increasing the bright-plating range. For example, ammonium sulphate in amounts of 1–100 grams per liter has been found effective.

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 together with one or more nitrogen atoms also directly connected to the carbon atom. It is understood, of course, that in this group of compounds the double bond may in some cases exist or alternate between the sulphur or nitrogen atom and the carbon atom. The thioureas having the nucleus

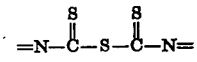


and the iso-thiocyanates having the grouping S=C=N— are considered representative types. Thiosinamine (allyl thiourea) and thiosemicarbazide may be mentioned as additional examples of the thioureas.

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 B-dithioglycoll and thiosalicylic acid have also a brightening effect.

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. It is essential, of course, that materials should not be added to the bath which would precipitate or destroy the brightening effect of the brightening agent. As an illustration of this it is pointed out that the presence of chloride ions to be avoided as much as possible since they tend to precipitate thiourea with consequent loss of brightness.

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)

250 grams technical copper sulphate
35 grams cadmium sulphate
10 grams sulphuric acid
10 grams di-chloro-benzene sulphonic acid
0.1 gram thiourea
Water to make up one liter

(2)

250 grams copper sulphate
35 grams nickel phosphate ($Ni_3(PO_4)_2.7H_2O$)
10 grams sulphuric acid
10 grams phosphoric acid
10 grams naphthylamine disulphonic acid
0.1 gram thiourea
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)

250 grams copper sulphate
10 grams sulphuric acid
1 cc. "Triton 720"
0.01 gram thiourea
Water to make up one liter

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

(4)

250 grams copper sulphate
10 grams sulphuric acid
.01 gram thiourea
Water to make up one liter

(5)

250 grams copper sulphate
10 grams sulphuric acid
.03 gram thiosemicarbazide
Water to make up one liter

(6)

250 grams copper sulphate
10 grams sulphuric acid
.02 gram thiosinamine
Water to make up one liter

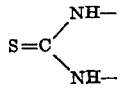
The primary addition agent is slowly depleted during the plating operation and is to be replenished as required. The control or range increasing and wetting agents however, other than the metallic type, are apparently not depleted by plating and need replenishing only as the composition of the bath changes 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 case of buffing to brilliance as compared with copper deposits from the ordinary acid copper baths. The invention is therefore of special 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. An electrolyte for electrodepositing bright or semi-bright copper consisting essentially of an aqueous acid solution of copper sulphate and free sulphuric acid and having dissolved therein a compound having the nucleus



said compound having a concentration in said solution within the range of 0.002–5 grams per liter.

2. The method of cathodically depositing copper in a form having a substantial degree of brightness comprising passing current through a bath consisting essentially of an aqueous solution of copper sulphate, free sulphuric acid and a thiourea in amount between 0.002 and 5 grams per liter of solution.

3. An electrolyte for the electrodeposition of copper in bright or semi-bright form consisting essentially of an aqueous solution of copper sulphate, sulphuric acid, thiourea and cadmium sluphate in substantially the following proportions, per liter:

	Grams
Copper sulphate	125–250
Sulphuric acid	10–50
Thiourea	0.002–5
Cadmium sulphate	10–75

4. An electrolyte for electrodepositing copper consisting essentially of an aqueous acid solution of copper sulphate and sulphuric acid and having dissolved therein a thiourea, said thiourea having a concentration in said solution of 0.002–5 grams per liter.

5. An electrolyte for electrodepositing copper consisting essentially of an aqueous acid solution of copper sulphate and sulphuric acid and having dissolved therein a thiourea and an organic sulphonate wetting agent, said thiourea having a concentration in said solution of 0.002–5 grams per liter, and the wetting agent a concentration of 0.01–5 grams per liter.

6. An electrolyte for electrodeposition of copper in bright or semi-bright form which consists essentially of an aqueous solution of copper sulphate and sulphuric acid to which has been added, per liter of solution, 0.002–5 grams of thiourea.

7. An electrolyte for electrodeposition of copper in bright or semi-bright form which consists essentially of copper sulphate and sulphuric acid to which has been added, per liter of solution, 0.002–5 grams of thiourea and 0.01–5 grams of a sulphonated ether having a branch chain and an aromatic nucleus.

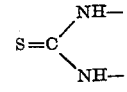
8. An electrolyte for electrodeposition of copper in bright or semi-bright form which consists essentially of an aqueous solution of copper sulphate and sulphuric acid to which has been added, per liter of solution, 0.002–5 grams of thiourea and 10–75 grams of a salt of a metal of the class consisting of cadmium, zinc, nickel and cobalt.

9. An electrolyte for electrodeposition of copper in bright or semi-bright form which consists essentially of an aqueous copper sulphate solution containing free sulphuric acid and to which has been added 0.01–0.1 gram of thiourea per liter of solution.

10. An electrolyte for the electrodeposition of copper consisting essentially of an aqueous acid solution of copper sulfate, sulfuric acid, and thiourea, the copper sulfate being present in an amount within the range of 125 to 250 grams per liter, the sulfuric acid within the range of 10 to 50 grams per liter and the thiourea within the range of 0.002 to 5 grams per liter.

11. An electrolyte for the electrodeposition of copper consisting essentially of an aqueous acid solution of copper sulfate, sulfuric acid and thiourea, the copper sulfate being present in an amount within the range of approximately 125 to 250 grams per liter, the sulfuric acid within the range of approximately 10 to 50 grams per liter and thiourea within the range of 0.01 to 0.1 gram per liter.

12. An electrolyte for the electrodeposition of copper consisting essentially of an aqueous acid solution of copper sulphate and free sulphuric acid to which has been added a compound having the nucleus



the copper sulphate being present within the range of approximately 125 to 250 grams per liter, the sulphuric acid within the range of approximately 10 to 50 grams per liter and the compound having said nucleus being present within the range of approximately 0.002 to 5 grams per liter.

WILLIAM M. PHILLIPS.
FRANK L. CLIFTON.

REFERENCES CITED

The following references are of record in the file of this patent:

UNITED STATES PATENTS

Number	Name	Date
103,947	Walenn	Dec. 24, 1863
1,328,666	Greenwalt	Jan. 26, 1920
1,903,860	Gockel	Apr. 18, 1933
2,112,818	Waite	Mar. 29, 1938

OTHER REFERENCES

Alien Property Custodian Publication 351,241, published May 18, 1943, filed August 3, 1940. Ser. No. 351,241 (A.P.C.), published May 18, 1943.

Certificate of Correction

Patent No. 2,563,360 August 7, 1951

WILLIAM M. PHILLIPS ET AL.

It is hereby certified that error appears in the printed specification of the above numbered patent requiring correction as follows:

Column 1, line 14, for "affecting and" read *affecting the*; column 2, line 50, for "coopper" read *copper*; column 3, line 70, for "ions to" read *ions is to*; column 5, line 8, for "case" read *ease*;

and that the said Letters Patent should be read as corrected above, so that the same may conform to the record of the case in the Patent Office.

Signed and sealed this 23rd day of October, A. D. 1951.

[SEAL]

THOMAS F. MURPHY,
Assistant Commissioner of Patents.