

[54] **ELECTROLYTIC COPPER-PLATING SOLUTIONS**

[75] Inventor: Michel Tixier, Billancourt, France

[73] Assignees: Regie Nationale Des Usines Renault, Billancourt; Automobiles Peugeot, Paris, both of France

[22] Filed: Mar. 16, 1971

[21] Appl. No.: 124,950

[30] **Foreign Application Priority Data**

Apr. 1, 1970 France 7011656

[52] U.S. Cl. 204/52 R, 204/DIG. 2

[51] Int. Cl. C23b 5/20

[58] Field of Search 204/52 R, DIG. 2

[56] **References Cited**

UNITED STATES PATENTS

3,101,305 8/1963 Roth et al. 204/52 R

Primary Examiner—F. C. Edmundson

Attorney—Stevens, Davis, Miller & Mosher

[57]

ABSTRACT

Acid aqueous electrolytic copper-plating solution containing one or a plurality of copper salts, a surface-active agent and organic additives adapted to promote the deposit of bright and levelled metal, characterized in that the organic additives are both derived from a resin issuing from the condensation of two moles of formaldehyde over one mole of thiourea, the resulting product being etherified or thioetherified by one molecule having the general formula HA—R, wherein A designates a sulfur or oxygen molecule and R an aliphatic or aromatic radical.

8 Claims, No Drawings

ELECTROLYTIC COPPER-PLATING SOLUTIONS

The present invention relates in general to electrolytic acid solutions intended for depositing plain and bright copper films and has specific reference to the improvement in the electrolytic deposition from acid aqueous solutions of copper salts.

It is already old to add small amounts of certain organic substances to electrolytic copper acids containing mostly sulfuric acid with a view to form bright copper deposits in lieu of crystalline and mat coatings. Thus, for instance, the use of organic thio-derivatives such as thiourea, thiohydantoin, thiocarbamic esters or thio-phosphoric esters, has already been proposed. However, these substances are objectionable owing to their numerous inconveniences accounting for their replacement by other methods in modern bright copper plating baths; in fact, with these known solution:

the copper coating ductility is strongly reduced, the regularity or uniformity of the thickness distribution of the copper films is far from satisfactory, stria or relief portions are observed on the layer of metal thus deposited; the field of optimum use of these substances is rather limited, and the presence of a slight excess leads to the formation of nodules.

Another proposition consisted in adding brightening-levelling compounds to the acid copper plating solutions, these compounds resulting from the condensation of formaldehyde and thiourea.

However, these substances are also objectionable on account of the serious inconvenience consisting in their poor solubility in water and under certain operating conditions, whereby costly processing arrangement must be resorted to.

Finally, organic addition compounds are known which meet the desired levelling and brightening requirements; these are:

thiophosphoric acid compounds;
heterocyclic sulfur compounds;
thiourea substitution compounds;
mercuric salts of triaryl-methanes;
dyes of the methylene blue group.

Unfortunately, the high cost of these products leads to an increment of about 30 percent in the cost of the electrolytic copper plating.

It is the primary object of the present invention to provide a range of electrolytic copper plating solutions comprising surface levelling and brightening additives having an efficiency sufficient to eliminate any subsequent mechanical processing while involving an increment in the final cost of the copper plating by only about one-tenth of the cost resulting from the use of the above-mentioned additives.

Basically, the acid copper-plating solution according to this invention is characterized in that the surface brightening and levelling organic additives incorporated therein are both derived from a resin resulting from the condensation of two formaldehyde moles over one thiourea mole, the product thus obtained being subsequently modified by a molecule having the general formula HA-R wherein:

A is a sulfur or oxygen atom

R is an aliphatic, aromatic or cyclic radical.

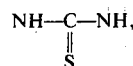
The difference between the brightening additive and the levelling additive lies chiefly in their degree of con-

densation, which is of the order of 300 to 600 for the former and of the order of 1,500 to 2,000 for the latter.

The additives to be incorporated in the solution according to this invention are therefore derived from thiourea-formaldehyde resin by modifying same with the assistance of organic products having at least one —OH and/or —SH function which, by etherification or thioetherification of one —OH function of the thio-urea-formaldehyde resin, create an O or S bridging attended by the elimination of one mole of water.

The HA-R agents utilized for modifying the thiourea-formaldehyde resin are selected from the groups comprising:

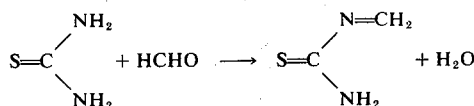
1. Heavy aliphatic alcohols: butanol, pentanol, hexanol, etc. . . ;
2. aromatic or cyclic alcohols: phenol, benzylalcohol, cyclohexanol, etc. . . ;
3. glycol esters: glycol phthalate, etc. . . ;
4. Aliphatic and aromatic thio-alcohols: thiobutanol, thiophenol, etc. . . ;
5. Compounds incorporating in their formula the characteristic linkage:



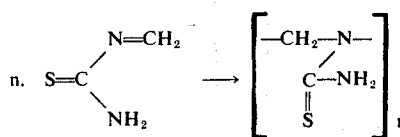
such as diethanol thiourea, having a direct relationship with the brightening and levelling effects contemplated for the purpose of this invention.

In order to afford a clearer understanding of the above disclosure, the formulations of the different intermediate steps leading to the additives constituting the subject-matter of this invention will now be described in detail.

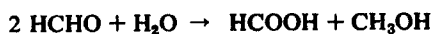
Firstly, the action of formaldehyde on thiourea leads to the formation of methylene-thiourea as follows:



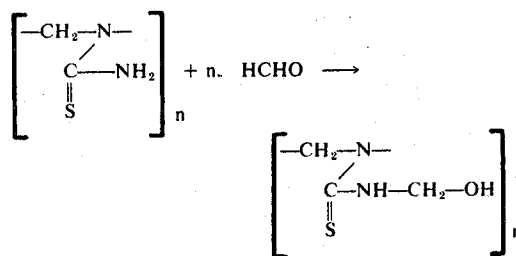
Thus, the thiourea methylene polymerizes as follows:



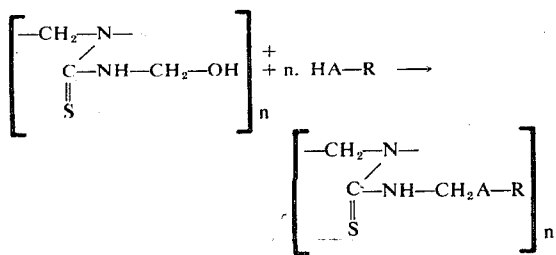
This reaction is facilitated by the development of the secondary reaction according to Cannizzaro causing the pH value of the initially basic reaction medium to evolve towards a more favorable acid pH value, due to the action of the formic acid created as a consequence of the effect of one mole of water on two moles of formaldehyde according to the formula:



and reacting with an excess of formaldehyde:

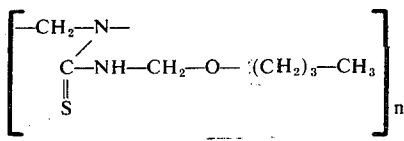


It is clear that the alcohol function of the present resin, acting as a reagent, will tend itself to the etherification or thioetherification with the above-defined HA—R mole :

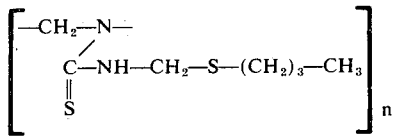


By way of illustration, the following modified products resulting from the preceding reaction are obtained in case the modifying agent is in succession :

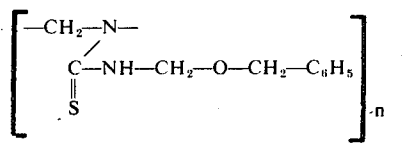
a. Butanol :



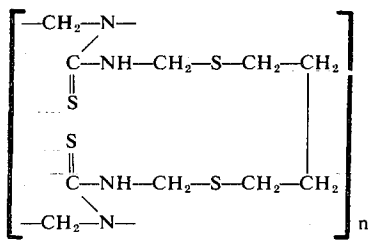
b. Thiobutanol :



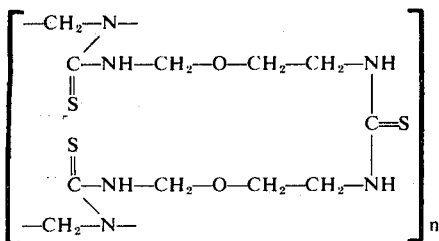
c. Benzyl alcohol :



d. Dithioglycol :



e. Diethanol thiourea :



Preferably the operating conditions of these syntheses are as follows :

The ingredients listed hereinafter are mixed in an autoclave equipped with an agitator and refrigerating means, in the order given :

- 5 Modifying agent type HA—R . . . 5.00 litres
- Toluene . . . 0.3 litre
- 30% formaldehyde solution . . . 0.5 litre
- Phthalic anhydride . . . 0.03 kilograms
- 10 Initial pH value, about . . . 8

The temperature is gradually brought to 35°C. Then a solution consisting of 1.5 kg of thiourea in 4.5 litres of 30 percent formaldehyde is poured slowly into the autoclave.

- 15 The temperature is kept at 95°C ; the water distillates off slowly by azeotropy ; the condensation of organic compound molecules takes place and continues during a period of 1 to 3 hours respectively, according as it is desired to obtain a brightening agent (lower degree of condensation n , of the order of 500) or a levelling agent (higher degree of condensation n , of the order of 1,500).

As already mentioned in the foregoing and as a consequence of the Cannizaro reaction the pH value measured at the end of the reaction will be about 3.

- 25 The resulting resin acting as a levelling or brightening agent is dissolved in 30 percent (by volume) sulfuric acid solution, in order to subsequently add same to the electrolytic acid copper plating solution containing furthermore one or a plurality of copper salts (such as sulfate), a small amount of Cl^- ions in the form of hydrochloric acid and a surface-active agent.

Two examples of these electrolytic copper-plating solutions are given hereinafter by way of illustration :

- 35 Example No. 1 :
 $\text{CuSO}_4 \cdot 8\text{H}_2\text{O}$. . . 180 to 220 g/l
 H_2SO_4 , 66° B. . . 40 to 60 g/l
 Cl^- (in HCl form) . . . 40 to 80 mg/l
 Surface-tension agent . . . 10 to 20 mg/l
- 40 Brightening agent :
 Thiourea-formaldehyde butanol modified resin solution
 (n 500) . . . 0.5 to 1 cc/l

Levelling agent :

- 45 Benzol-modified thiourea formaldehyde resin solution
 (n 1,500) . . . 0.1 to 0.5 cc/l
 temperature . . . 20° to 29°C
 Current density . . . 2 to 5 Amp./sq.dm.

Examples No 2

- 50 $\text{CuSO}_4 \cdot 8\text{H}_2\text{O}$. . . 180 to 220 g/l
 H_2SO_4 , 66° B. . . 40 to 60 g/l
 Cl^- (in HCl form) . . . 40 to 80 mg/l
 Surface tension agent 10 to 20 mg/l

Brightening agent :

- 55 Solution of modified thiourea-formaldehyde resin or diethanol-thiourea : 0.1 to 0.5 cc/l (n 500)

Levelling agent :

- 60 Solution of thiourea-formaldehyde modified resin or cyclohexanol : 0.1 to 0.5 cc/l (n 1,500)
 Temperature . . . 20° to 29°C
 Current density . . . 2 to 5 Amp./sq.dm.

The deposit obtained from the above-described copper-plating solutions are extremely bright with current densities ranging from 0.1 to 20 Amp./sq.dm and are levelled with current densities ranging from 0.3 to 20 Amp./sq.dm.

These deposits are ductile ; samples thus copper-

plated were bent to an angle of about 90° without displaying any breaking of the coating layers.

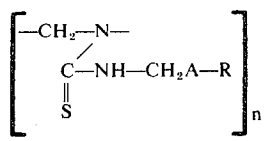
They are insensitive to current cut-offs during the electrolysis and resume by themselves the process without any impairment.

They can be nickel-plated directly without requiring any preliminary depassivation step.

Moreover, it is well to emphasize that the efficiency of the electrolytic solutions according to this invention depend essentially on the modification of the thiourea molecule as a consequence of the action exerted by the compounds described hereinabove and denoted by the symbol AH—R, which impart to the brightening agents and levelling agents deriving therefrom a high capacity of solubilization in water through an extended range of condensation degrees, in contrast to what is observed in the case of non-modified thiourea-formaldehyde resin.

What is claimed as new is :

1. Aqueous acid electrolytic copper-plating solution containing at least one copper salt, a surface-active agent and organic additives adapted to promote a bright and levelled metal deposit, said organic additives having the formula:



and being derived by the condensation of two moles of formaldehyde and one mole of thiourea by the initial condensation and polymerization of one mole of formaldehyde and one mole of thiourea to form a methylene-thiourea polymerizate with subsequent condensation of the second mole of formaldehyde on each mole of thiourea, with the resulting product being etherified or thio-etherified by using a molecule according to the general formula HA—R, wherein

A designates a sulfur or oxygen atom, and

R designates an aliphatic radical having up to about 6 carbon atoms, cyclohexyl, phenyl, benzyl, diethylenethiourea and dimethylene phthalate, producing:

5 a brightening agent wherein the organic additive has a condensation degree of about 300 to 600, or a levelling agent wherein the organic additive has a condensation degree of about 1,500 to 2,000.

2. Acid electrolytic copper-plating solution according to claim 1, characterized in that the HA— function of compound HA—R partakes in the creation of an ether or thioether linkage by becoming fixed to an —OH function of the thiourea-formaldehyde molecule, with the elimination of one water molecule.

3. Acid electrolytic copper-plating solution according to claim 2, characterized in that the compound modifying the thiourea-formaldehyde resulting product is an aliphatic alcohol having up to about 6 carbon atoms.

4. Acid electrolytic copper-plating solution according to claim 2, characterized in that the compound modifying the thiourea-formaldehyde resulting product is phenol or benzyl alcohol.

5. Acid electrolytic copper-plating solution according to claim 2, characterized in that the compound modifying the thiourea-formaldehyde resulting product is diglycol phthalate.

6. Acid electrolytic copper-plating solution according to claim 2, characterized in that the compound modifying the thiourea-formaldehyde resulting product is an aliphatic thio-alcohol having up to 6 carbon atoms.

7. Acid electrolytic copper-plating solution according to claim 2, characterized in that the compound modifying the thiourea-formaldehyde resulting product is thiophenol or thiobenzyl alcohol.

8. Acid electrolytic copper-plating solution according to claim 2, characterized in that the compound modifying the thiourea-formaldehyde resin is diethanol thiourea.

* * * * *

45

50

55

60

65