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ACID COPPERING BATH

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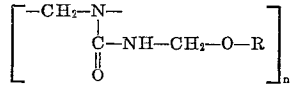
U.S. Cl. 204—52 R 2 Claims

ABSTRACT OF THE DISCLOSURE

Aqueous bright acid electrolytic coppering bath containing a copper salt, a brightener, a surface tension agent, characterized in that it further contains a levelling agent having the general formula:



wherein *n* is of the order of 500 to 1,000, resulting from the addition of two formaldehyde molecules on one urea molecule, the resultant molecule being modified by a heavy alcohol or one of its derivatives.

The present invention relates in general to the electrolytic deposit of bright copper from an acid aqueous bath, and more particularly to the use of products added to baths of this character with a view to improve the deposit obtained therefrom.

It is the essential object of the present invention to produce electrolytic copper deposits having good filling properties, i.e. deposits capable of leveling the characteristic polishing lines produced during the conventional commercial processes, or to treat pieces not subject to a glaze-polishing operation, as sometimes applied to various precision workpieces. These metal elements must further receive a complementary nickel or chromium deposit.

A number of additives giving positive results when mixed with such acid coppering baths are already known. These may consist inter alia of:

thiourea addition or substitution compounds,
mercuric salts of triarylmethanes,
certain dyestuffs of the methylene blue group, etc.

However, these products are objectionable on account of two major inconveniences:

(a) Their cost is relatively high since these products are generally not produced on a commercial scale and involve complicated synthesis operations;

(b) The degradation products resulting from their decomposition during their actual use are a cause of flaws in the surface of the deposited metal. Therefore, the electrolyte must be regenerated and this involves hold ups and additional costs.

In view of the foregoing the present invention aims at avoiding the above-disclosed inconveniences by providing a method of depositing copper by electrolysis, which consists in electrolyzing an aqueous solution containing on the one hand one or a plurality of copper salts such as copper sulfate or copper nitrate and on the other hand additives having levelling properties, which are stable and economical since their cost is only one fraction of that of other additives utilized heretofore.

To this end, the present invention provides an aqueous bright acid electrolytic coppering bath containing a copper salt, a brightener, a surface tension agent and a levelling agent resulting from the combination of two formaldehyde molecules on one urea molecule, the resultant product being firstly modified by using a heavy

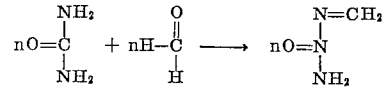
alcohol or one of its derivatives, then polymerized and possibly sulfonated.

Among the heavy alcohols suitable for carrying out this invention by modifying the basic urea-formol product obtained during a first stage, butanol is the most frequently used due on the one hand to the satisfactory results obtained therewith and on the other hand to its low cost.

However, the following linear alcohol:pentanol, hexanol, heptanol, octanol and certain cyclic alcohols of the benzyl alcohol type are also used with good results.

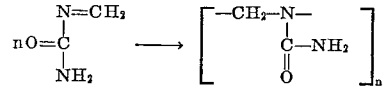
Another group of products capable of modifying the urea-formol resin is ilustrated by the glycol esters of phthalic acid, malonic acid and maleic acid.

The product eventually obtained (modified urea-formol resin) results from the following reactions: during a first stage, urea is caused to react on formol as follows:

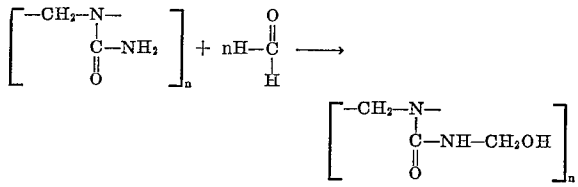


at an initial pH=8.

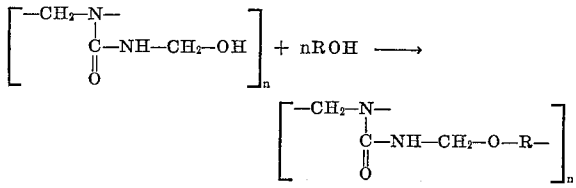
The resultant methylene-urea is then polymerized:



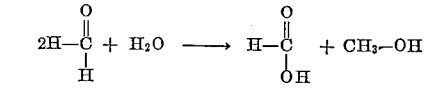
The reaction is continued in an excess of formol as follows:



of which the end product reacts with the heavy alcohol present in the reaction medium since the beginning of the operation:



However, a secondary reaction is observed which plays an important role; in fact, the conditions prevailing during the preceding reactions facilitate the development of the so-called Cannizzaro reaction with respect to one fraction of the formol available and also on the water in which it is dissolved:



the formic acid produced during the reaction tending to acidify the medium as the transformation develops, so that when the methylene-urea polymerization takes place a pH value of 3 is attained which promotes said polymerization.

Now the method will be described by way of example with reference to the production of a levelling agent of the type defined hereinabove.

The following ingredients:

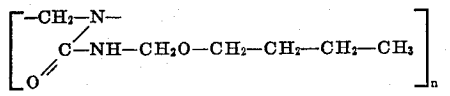
Butanol	51
Toluene	0.31
30% formol solution	0.51
Phthalic anhydride, kilogram	0.03

are mixed in the above-given order at atmospheric pressure in an autoclave equipped with stirring means and a up-and-downward flow cooler. The initial pH value is about 8. The temperature is gradually raised to 95° C.

Then, a solution consisting of 1.5 kg. urea in 4.5 liters of 30% formol is poured slowly into the mixture.

The temperature is maintained at 95° C. Then the water in the formol solution distils slowly by azeotropy and the condensation is continued during one hour. The pH value of the reaction medium is then about 3.

The resulting resin has the following formula:



wherein n has a value within the range of 500 to 1,000.

During the use of this resin, i.e. when it is introduced as a levelling agent into an aqueous bright acid electrolytic coppering bath, a sulfonation is carried out according to the known method by reason of 100 g. of resin per liter of 30% (volume) H_2SO_4 solution, with the consequence that the solubility of said resin is increased considerably in the electrolyte bath.

Experimental electrolytic copped depositing baths have thus been prepared under the following conditions:

EXAMPLE 1

The following substances are mixed in succession in the electrolytic coppering vat, with the proportions given hereinafter:

SO_4Cu, $8H_2O$ ---------- g./lit--	180–220
SO_4H_2 66° Bé ---------- g./lit--	40–60
Brightener ---------- cc./lit--	1–2
Surface tension agent ---------- mg./lit--	10–50
Chlorine ions (in the hydrochloric acid form) ---------- mg./lit--	40–80
Urea-formol resin solution modified with benzyl alcohol ---------- cc./lit--	1–2

EXAMPLE 2

SO_4Cu, $8H_2O$ ---------- g./lit--	180–220
SO_4H_2 66° Bé ---------- g./lit--	40–60
Brightener ---------- cc./lit--	1–2
Surface tension agent ---------- mg./lit--	10–50
Chlorine ions ---------- mg./lit--	40–80
Butanol-modified urea-formol solution ---------- mg./lit--	1–1.5

The coppered pieces obtained from the above Examples 1 and 2 are compared with coppered pieces obtained with conventional baths without the levelling agent; the procedure used for comparing the surface condition of the pieces coppered according to these various methods is the profile test. It proved that in Example 1 the improvement in levelling of the copper deposit obtained in the treated

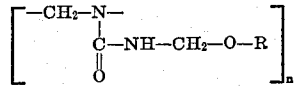
parts is of the order of 30%, and in the case of Example 2 the improvement is of the order of 50%.

These examples clearly show the advantages deriving from the use of these additives in methods designed for covering oxidizable metal parts with protective deposits, notably preliminary to nickel-plating or chromium-plating processes as currently applied to automotive parts. The satisfactory surface condition of the copper deposit thus obtained permits reducing the thickness of the noble metals subsequently deposited thereon while preserving an eventually identical exterior appearance. Under these conditions, this invention is characterized by the economy resulting from the process set forth hereinabove, with the additional advantage resulting from the difference between the cost of the levelling agent of this invention and the additives previously utilized for the same purpose.

Of course, this invention should not be construed as being limited by the composition of electrolytic baths containing such levelling agents but should also be considered as comprising all articles provided with a deposit obtained from such baths.

What is claimed as new is:

1. An aqueous acid electrolytic coppering bath containing a copper salt, a brightener, and a surface tension agent, further comprising a leveling agent having the general formula:



wherein n is an integer in the range of about 500 to about 1000 and the —O—R linkage is a derivative of a compound selected from the group consisting of: aliphatic alcohols having 4–8 carbon atoms, benzyl alcohol, and esters resulting from the reactions of a glycol with an acid selected from the group consisting of phthalic acid, malonic acid and maleic acid.

2. The coppering bath of claim **1**, wherein the modified urea-formaldehyde resin is a sulfonated modified urea-formaldehyde resin, for facilitating its solution in the aqueous acid bath.

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U.S. Cl. X.R.

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