

1

3,758,314

**AQUEOUS BATH FOR CHEMICAL DEPOSITION
OF DUCTILE COPPER COATINGS**Wolf-Dieter Haack, Berlin, Germany, assignor to
Schering AG, Berlin, Germany

No Drawing. Filed Mar. 2, 1972, Ser. No. 231,362

Claims priority, application Germany, Mar. 9, 1971,

P 21 12 417.4

Int. Cl. C23c 3/02

U.S. Cl. 106—1

5 Claims 10

ABSTRACT OF THE DISCLOSURE

Aqueous bath for the chemical deposition of ductile copper coatings is provided including alkaloid brucine in exceedingly small quantities for use on surfaces.

The invention relates to a chemical copper bath from which ductile copper coatings can be deposited on surfaces, whether metallic or non-metallic.

Copper baths operating without current contain, as a rule, a copper salt, as a source of Cupric ions a complex former, a base, and a reducing agent. It is to be noted that as complex formers there are used oxycarboxylic acids, aminocarboxylic acids, or amino-alcohols, and as reducing agents, notably formaldehyde in alkaline solution. Besides, often also buffer substances, stabilizers and wetting agents are added to the baths as further conventional constituents.

Such copper baths deposit copper directly on catalytically active metals, such as copper or silver, introduced therein. Inactive metals, such as special steel, can be activated beforehand by a brief contact with an aluminum wire. Also non-conductors, such as ceramic or organic plastics, can be provided with a copper coating after suitable pretreatment and activation with finely divided precious metals. The deposition of the copper occurs at first as an auto catalytic process and, once started, the process continues for the duration of the exposure or until the chemical copper bath is exhausted.

The coatings deposited from the known chemical copper baths are, as a rule, coarsely crystalline and show a dull surface. They exhibit high internal stresses and an extreme brittleness, these being a great disadvantage. For thick copper films, as needed for example for the production of flexible conductors or of conductor tracks for printed circuits, these properties, in fact, lead to cracks or blister formations or possibly cause the detachment or separation of the copper film from the foundation or substrate.

Another disadvantage of the known baths, when containing formaldehyde as a reducing agent, is the lively evolution of hydrogen occurring simultaneously with the copper deposition, resulting from the catalytic decomposition of formaldehyde at the freshly formed copper surface into hydrogen and formate, thereby causing an additional consumption of formaldehyde and bases.

This evolution of hydrogen moreover leads to a rather different layer thickness growth on vertical and horizontal surfaces and further causes also the formation of porous coatings, which considerably reduce the quality of the coatings. Additions which appreciably inhibit this extremely disadvantageous hydrogen evolution have not become known until now.

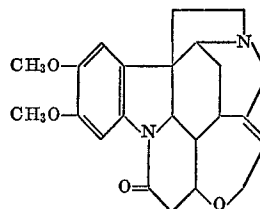
The purpose of the invention therefore is to develop a chemical copper bath for the deposition of ductile, highly elastic copper coatings with a lustrous surface and which can be operated without the disturbing hydrogen evolution.

This is accomplished according to the invention by using an aqueous bath which contains a copper salt, a

2

complex former, a base, a reducing agent and optionally other conventional constituents, and which is characterized by a content of the alkaloid brucine, of the empirical formula $C_{23}H_{26}N_2O_4$, or of soluble salts thereof.

The assumed structural formula of brucine or 10,11 dimethoxystrychnine is as follows:



As soluble salts of brucine there may be named the sulfate, the chloride, or the nitrate.

The use of these additions in chemical copper baths can be effected in concentrations of 0.00003 to 0.003 mole/liter, preferably in the range of 0.0001 to 0.0003 mole/liter, of bath liquid.

The invention has proved particularly advantageous, if the bath contains an aminocarboxylic acid, such as ethylene-diaminetetraacetic acid, or an amino-alcohol, such as triethanolamine, as complex former, and formaldehyde or a compound decomposing to yield formaldehyde, as the reducing agent.

In addition, the baths contain the already stated conventional constituents. If desired, a stabilizer, for example, a mercury-II compound, may be added to increase the stability.

With the copper bath according to the invention, surfaces of metals, plastics, or other materials can be copper-plated in the usual known manner.

For this purpose, the parts to be copper-plated are immersed in the indicated or selected bath and the deposition carried out at a temperature of about 15 to 70° C. until the desired layer thickness is obtained.

Non-metallic surfaces such as those of plastic, require a pretreatment, which can be carried out in the usual manner for example by pickling with chromosulfuric acid, activating in a palladium-II-chloride solution, and reducing with a hydrazine solution.

The copper coatings deposited according to the invention show a uniform layer thickness and are lustrous to highly lustrous and copper-colored. Their surface is pore-free. Even at layer thicknesses of more than 5 microns they are still remarkably ductile.

The addition of 0.00003 mole/liter of brucine to the copper bath inhibits the evolution of hydrogen very effectively, and at the same time the potential of an immersed copper electrode becomes more negative by several hundred millivolts. Higher concentrations of brucine completely inhibit the evolution of hydrogen. The deposition potential then lies typically at between -900 and -950 mv., as measured against an Ag/AgCl/saturated KCl reference electrode.

Additions of brucine to chemical copper baths also inhibit the copper deposition to a lesser degree. Spontaneously formed copper seeds are greatly hindered in their growth by the inhibitor brucine and can no longer decompose the bath.

The following examples describe and illustrate some of the copper baths provided according to the invention. Their application is demonstrated in comparison with a known bath.

3

EXAMPLE 1

(a) Copper was deposited on a copper plate from a known bath of the following composition:

0.025 mole/liter copper-(II)-sulfate
0.06 mole/liter triethanolamine
0.10 mole/liter formaldehyde
pH 13.0 (adjusted with sodium hydroxide)

The rate of deposition was about 3.2 $\mu\text{m.}/\text{h.}$ at 25° C., and the deposition potential was -370 mv. (measured against Ag/AgCl/saturated KCl at 25° C.). Appearance of the coating: dull, copper-colored. There was intensive hydrogen evolution.

(b) To a bath of the same composition there was added 0.00025 mole/liter of brucine. The rate of deposition was about 1.4 $\mu\text{m.}/\text{h.}$ at 25° C. and the deposition potential was -920 mv. (measured against Ag/AgCl/saturated KCl at 25° C.). During the deposition no appreciable hydrogen evolution was observable. Appearance of the coating: highly lustrous, copper-colored.

EXAMPLE 2

(a) A known bath of the composition

0.04 mole/liter copper-(II)-sulfate
0.048 mole/liter ethylene-diamine-tetraacetic acid
0.27 mole/liter formaldehyde
pH 12.8 (adjusted with sodium hydroxide)

when operated at 50° C. at a deposition potential of about -600 mv. (measured against Ag/AgCl/saturated KCl at 50° C., released) 1.1 mole of hydrogen per gram-atom of deposited copper.

(b) To a bath of the same composition as described under 2(a) above, there was added according to the invention 0.00016 mole/liter of brucine.

At a deposition potential of about -935 mv. (measured against Ag/AgCl/saturated KCl at 50° C.) no evolution of hydrogen was measurable with the bath.

In this bath, a plastic plate of an acrylonitrile-butadiene-styrene graft polymer was immersed. The plate was pretreated by pickling with chromosulfuric acid, activating in palladium-(II)-chloride solution, and then reducing with hydrazine solution and kept immersed for 6 hours in the copper bath according to the invention at 50° C.

There was formed a firmly adhering, gapless coating of semi-lustrous, copper-colored appearance. The layer thickness was 13 $\mu\text{m.}$

4

EXAMPLE 3

From a bath according to the invention of the following composition

5 0.04 mole/liter copper-(II)-sulfate
0.05 mole/liter ethylene-diamine-tetraacetic acid
0.20 mole/liter formaldehyde
0.00016 mole/liter brucine
0.00001 mole/liter mercury-(II)-chloride
10 pH 12.8 (adjusted with sodium hydroxide)

a copper coating was deposited on polished special steel which was activated by brief contact with an aluminum wire.

After 5 hours of exposure in the chemical bath at 60° C., the layer thickness of the copper coating was 19 $\mu\text{m.}$ This coating showed a dull, light brown appearance and could be pulled off the special-steel as a foil.

Due to its surprising ductility, the foil could be rolled up with a radius of curvature of less than 0.5 mm., without any crack formation occurring.

What is claimed is:

1. In an aqueous bath for the deposition of copper coating on an immersed object, the bath containing a source of cupric ions, a complex former for said ions, and a reducing agent effective for reducing said ions to metallic copper in the presence of said object, the improvement which consists in said bath containing brucine in a concentration of 0.00003 to 0.003 mole per liter.

2. In a bath as set forth in claim 1, said reducing agent being a source of formaldehyde.

3. In a bath as set forth in claim 2, said brucine being present in said bath as a water soluble salt.

4. In a bath as set forth in claim 2, said complex former being ethylenediamine tetraacetic acid or triethanolamine.

5. In a bath as set forth in claim 4, said concentration being 0.0001 mole to 0.0003 mole per liter.

References Cited

UNITED STATES PATENTS

3,457,089 7/1969 Shipley et al. ----- 106-1
3,661,597 5/1972 Gulla ----- 106-1

LORENZO B. HAYES, Primary Examiner

U.S. Cl. X.R.

117-47 A, 130 E