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3,832,291

## METHOD OF PREPARING SURFACES FOR ELECTROPLATING

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No. Drawing. Original application Aug. 20, 1971, Ser. No. 173,645, now Patent No. 3,751,289. Divided and this application Mar. 23, 1973, Ser. No. 344,101 Int. Cl. C23b 5/20

U.S. Cl. 204—40

1 Claim

### ABSTRACT OF THE DISCLOSURE

This invention relates to adherent copper films formed by immersion, or electrolytically on metallic objects from an aqueous solution of (1) a nonoxidizing acid, (2) a copper salt of a nonoxidizing acid, and (3) a polyether exhibiting at least 5 ether oxygen atoms per molecule; to processes for coating said films; and to compositions for the deposition of said adherent copper films.

This application is a divisional application of co-pending application Ser. No. 173,645, filed Aug. 20, 1971, now U.S. Pat. 3,751,289.

This invention relates to a method of treating metal prior to copper plating. More specifically, this invention relates to the application of thin adherent copper deposits or film prior to the electrodeposition of relatively thick copper deposits from plating solutions.

Because loose, nonadherent, displacement films of copper are formed on iron, steel, and zinc when these basis metals are immersed in acid copper baths, a cyanide copper or a nickel strike plate has, according to the prior art, been required before plating from an acid copper bath.

For example, when acid copper baths are used for plating steel or ferrous articles such as automobile bumper bars, hubcaps, printing rolls, etc., a preliminary copper strike from a cyanide bath or a nickel strike from an acidic nickel plating bath is first used to avoid poorly adherent immersion deposits before acid copper plating.

After strike deposition from a cyanide bath, the work must be thoroughly rinsed, dipped in a dilute solution of hydrochloric or sulfuric acid to neutralize any undissolved alkaline material, and rinsed again before plating in the acid bath. After nickel strike or nickel chloride immersion dip, thorough rinsing is required to prevent the drag-in of chloride into the acid copper bath. Neither the cyanide copper strike nor the nickel strike produce deposits in deeply recessed areas such as the inside of tubes; consequently a loosely adherent copper deposit forms in these areas on subsequent plating from an acid copper bath.

It is an object of this invention to provide an adherent copper film on metallic objects which effects good adhesion of subsequent copper deposits from copper plating baths, even in deeply recessed areas such as the inside of tubes. It is another object of this invention to provide an adherent copper film such that the work does not have to be rinsed between the strike or immersion dip and the acid copper plating baths, as is necessary after conventional strikes. It is an object of this invention to prevent formation of badly adherent copper electrodeposits. Other objects of this invention will be apparent from the following description.

This invention is directed to a process for coating metal surfaces with a copper film prior to the electrodeposition of copper from copper plating baths comprising treating said metal surface in a solution containing 0.01 to 10 grams per liter of a copper salt of a nonoxidizing acid; 0.1 grams per liter to 500 grams per liter of a non-

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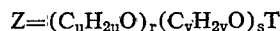
oxidizing acid; and 0.1 to 100 grams per liter of a polyether containing at least 5 ether oxygen atoms per molecule, thereby obtaining a copper film effecting good copper plate adherence on basis metals from copper plating baths. Copper salts operable in the practice of this invention include copper sulfate, copper fluoborate, and copper phosphate.

Copper pretreatment baths of this invention are distinguished from aqueous acidic copper plating baths by their deficiency of copper. Typical amounts of copper include about 0.025 to 2.5 grams per liter as metallic copper (preferably 0.025 to 0.625 grams per liter); or 0.1 to 10 grams per liter as  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  or  $\text{Cu}(\text{BF}_4)_2$  (preferably 0.1 to 2.5 grams per liter).

Polyethers which may be used according to the process of the invention have at least 5 ether oxygen atoms and include polyethers of the formulae:



where R' is a monovalent radical such as H, alkyl, alkenyl, alkynyl, alkylaryl, arylalkyl or a heterocyclic radical; and R'' is a m-valent aliphatic, aromatic or heterocyclic radical;  $m=2$  to 100; and



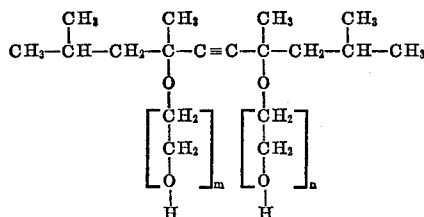
where  $u$  and  $v=0$  to 4, but at least one of  $u$  or  $v$  must be greater than zero;  $r+s=6$  to 1000; and  $\text{T}=\text{H}$ , alkyl, benzyl,  $-\text{SO}_3\text{M}$ ,  $-\text{C}_u\text{H}_{2u}\text{SO}_3\text{M}$ ,  $-\text{PO}_3\text{H}_2$ , or



Suitable polyethers which may be used according to the invention include polyethers set forth in Table I. The polyether additives may be employed in effective amounts, typically 0.1 to 100 grams per liter and preferably 1 to 25 grams per liter to give good adhesion properties.

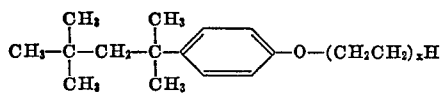
The polyethers of this invention may be derived from 1,2 olefin oxides such as ethylene oxide, propylene oxide, 1,2, butylene oxide, etc.; from 4- and 5-membered ring cyclic ethers such as oxetane, 2,3-dichloromethyloxetane, etc.; from glycidyl esters and ethers such as allyl glycidyl ether, glycidyl acetate, and phenyl glycidyl ether and mixtures of the foregoing.

TABLE I

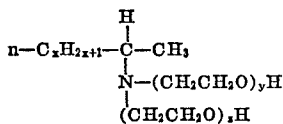
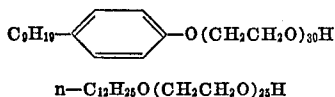


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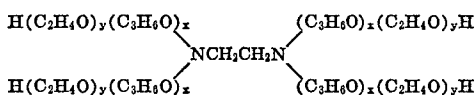
wherein  $m + n = 30$ , or wherein  $m + n = 15$ , or wherein  $m + n = 10$ ;



wherein  $x = 9-10$ , or wherein  $x = 30$ , or wherein  $x = 40$ ;



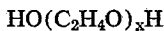
wherein  $x = 9-12$ , and  $y + z = 15$ ;



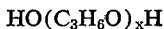
wherein  $x$  is about 3 and  $y$  is about 3-4;



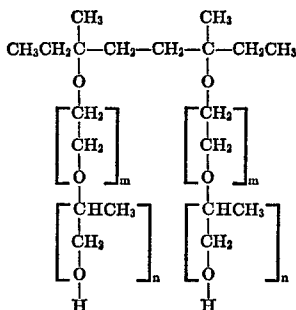
wherein  $x$  is about 13;



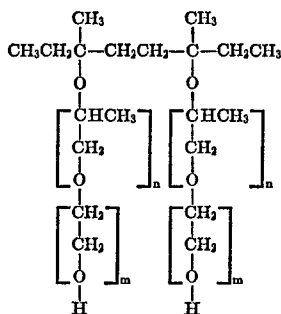
wherein  $x$  is about 33;



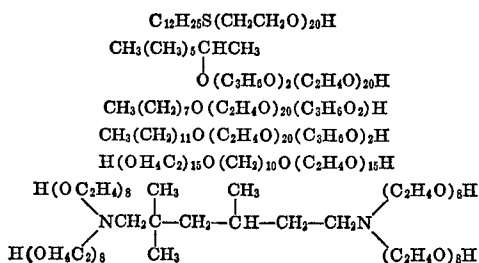
wherein  $x$  is about 12;



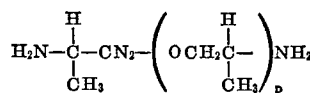
wherein  $m =$  about 12-15 and  $n =$  about 1-2;



$m =$  about 12-15 and  $n = 1-2$ ;



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5 where  $p =$  about 5-6 or 16.

The basis metals which are treated by the pretreatment process of this invention are preferably ferrous metals such as steel, iron, etc., although most common metals and their alloys can be pretreated with Applicant's copper films for subsequent copper plating.

Advantages obtained by the practice of this invention include:

1. Excellent adhesion of subsequent copper deposits over a wide concentration range of the constituents of the invented solution used as an immersion dip prior to copper plating.

2. The concentration ranges and the reliability were greatly increased by making the work cathodic and using the invented solution as a strike bath.

3. In contrast to cyanide or nickel strikes one can get good adhesion even if current is not used. Therefore, we can get good adhesion even in very deeply recessed areas such as the inside of a tube.

4. Work does not have to be rinsed between the strike or immersion dip of this invention and the acid copper plating bath, as it does after conventional strikes. It may be cycled directly from the coating solution of this invention to the plating bath.

The nonoxidizing acids of this invention are preferably sulfuric acid  $\text{H}_2\text{SO}_4$  and fluoboric acid  $\text{HBF}_4$ . The immersion baths of this invention should be at a temperature of  $10^\circ\text{C}$ . to  $60^\circ\text{C}$ . (preferably  $20^\circ\text{C}$ . to  $40^\circ\text{C}$ .). While this invention is completely operable without the use of current as shown by examples hereinafter, this invention may also be practiced with current for instance a cathode current density of 0.1 to 60 amperes per square decimeter. While agitation is not necessary for the practice of the invention, air agitation, volume agitation, and mechanical agitation may be used with no deleterious effect.

This invention according to one of its aspects, is the deposition of a film of copper from a solution comprising 0.01 grams per liter to 10 grams per liter of a copper salt selected from the group consisting of copper sulfate, copper phosphate and copper fluoborate, 0.1 grams per liter to 500 grams per liter of a nonoxidizing acid, and 0.1 grams per liter to 100 grams per liter of a polyether containing at least 5 ether oxygen atoms per molecule; and after deposition of said strike coating of copper, electrodepositing copper thereon from an aqueous copper plating bath.

Optionally, the copper "strike" of this invention may be deposited electrolytically at a temperature of  $10^\circ\text{C}$ . to  $60^\circ\text{C}$ . with the use of a current density of 1 asd. to 20 asd. The first step, the essence of the invention, is to form a thin, dense, strongly adherent layer or striking coating. Under the above conditions, the strike coating is formed in from 20 seconds to 3 minutes depending upon the current density, the copper ion concentration, and various additives of the strike solution.

For electrodeposition of bright, strongly leveled, ductile copper, the article is transferred from the strike bath of this invention to an aqueous acidic copper plating bath containing chloride ions and organic additives without permitting the article to dry and without rinsing it.

In accordance with certain of its aspects this invention provides a process for electrodepositing bright copper from aqueous acidic baths comprising buffering the metal surface, cleaning by immersing the pretreated metal surface in an organic solvent; electrolytically degreasing said surface electrolytically in alkaline solution; rinsing, immersing in an acid bath thereby obtaining a bright, clean metal surface, depositing on said surface a strike coating of copper from a solution containing 0.01 grams

per liter to 10 grams per liter of a copper salt; 0.1 grams per liter to 500 grams per liter of nonoxidizing acid; and 0.1 gram per liter to 100 grams per liter of a polyether containing at least 5 ether oxygen atoms per molecule; and electrodepositing on said copper film a relatively thicker layer of bright, strongly leveled, ductile copper from a copper plating bath containing suitable combinations of addition agents.

Typical copper plating baths which may be employed to electrodeposit adherent thicker copper over the copper film of this invention include the following:

TABLE II

	Compound	Grams per liter	Perferably grams per liter
Sulfate bath.....	CuSO <sub>4</sub> ·5H <sub>2</sub> O	150-300	220
	H <sub>2</sub> SO <sub>4</sub>	10-110	60
	Cl <sup>-</sup>	( <sup>1</sup> )	( <sup>2</sup> )
Fluoborate bath.....	Cu(BF <sub>4</sub> ) <sub>2</sub>	100-600	224
	HBF <sub>4</sub>	1-60	3.5
	H <sub>3</sub> BO <sub>3</sub>	0-30	15
	Cl <sup>-</sup>	( <sup>1</sup> )	( <sup>2</sup> )

<sup>1</sup> 5-100 mg./l.

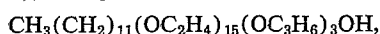
<sup>2</sup> 20-40 mg./l.

The basis metals which may be pretreated with the process of this invention include ferrous metals, such as steel, iron, etc.; zinc and its alloys including zinc-base die-cast articles; nickel, including nickel alloys with other metals such as cobalt, iron, chromium, aluminum, including its alloys.

For the purpose of providing those skilled in the art with a better understanding of this invention, the following examples are set forth.

## EXAMPLE 1

After thoroughly pickling and cleaning a steel panel, 2.5 cm. wide and 20 cm. long, half of it was immersed into an aqueous solution containing 1 gram per liter of cupric sulfate pentahydrate (CuSO<sub>4</sub>·5H<sub>2</sub>O) and 100 grams per liter of sulfuric acid (H<sub>2</sub>SO<sub>4</sub>) and 16 grams per liter of an ethoxylated propoxylated lauryl alcohol (MW 1020), having the following structure



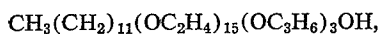
at 24° C., with an applied cathodic potential sufficient to produce an average current density of 8.0 asd. after the panel was half immersed. After 30 seconds the panel was transferred to an acid copper plating bath where it was plated with copper to an average thickness of 75 microns.

The edges of the panel were ground down to the steel. The copper was easily pulled off the top of the panel but could not be pulled off the bottom half, which had been treated in the above solution, indicating excellent adhesion.

Other panels were done without current in the above treatment solution and/or with water rinsing between the treatment solution and the plating bath and the plated deposits still had excellent adhesion to the panel. However, under some conditions it is advantageous to use current in the treatment solution and water rinse.

## EXAMPLE 2

After thoroughly pickling and cleaning a steel panel, 2.5 cm. wide and 20 cm. long, half of it was immersed into an aqueous solution containing 1 gram per liter cupric sulfate pentahydrate (CuSO<sub>4</sub>·5H<sub>2</sub>O) and 60 grams per liter of sulfuric acid (H<sub>2</sub>SO<sub>4</sub>) and 1 gram per liter of ethoxylated propoxylated lauryl alcohol (MW 1020), having the following structure

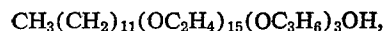


at 24° C., with an applied cathodic potential sufficient to produce an average current density of 8.0 asd. after the panel was half immersed. After 30 seconds the panel was transferred to an acid copper plating bath where it was plated with copper to an average thickness of 75 microns.

The edges of the panel were ground down to the steel. The copper was easily pulled off the top of the panel but could not be pulled off the bottom half, which had been treated in the above solution, indicating excellent adhesion.

## EXAMPLE 3

After thoroughly pickling and cleaning a steel panel, 2.5 cm. wide and 20 cm. long, half of it was immersed into an aqueous solution containing 0.1 grams per liter of cupric sulfate pentahydrate (CuSO<sub>4</sub>·5H<sub>2</sub>O) and 60 grams per liter of sulfuric acid (H<sub>2</sub>SO<sub>4</sub>) and 10 grams per liter of ethoxylated propoxylated lauryl alcohol (MW 1020), having the following structure

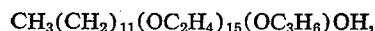


at 24° C., with an applied cathodic potential sufficient to produce an average current density of 8.0 asd. after the panel was half immersed. After 30 seconds the panel was transferred to an acid copper plating bath where it was plated with copper to an average thickness of 75 microns.

The edges of the panel were ground down to the steel. The copper was easily pulled off the top of the panel but could not be pulled off the bottom half, which had been treated in the above solution, indicating excellent adhesion.

## EXAMPLE 4

After thoroughly pickling and cleaning a steel panel, 2.5 cm. wide and 20 cm. long, half of it was immersed into an aqueous solution containing 1 gram per liter of cupric sulfate pentahydrate (CuSO<sub>4</sub>·5H<sub>2</sub>O) and 100 grams per liter of phosphoric acid (H<sub>3</sub>PO<sub>4</sub>) and 16 grams per liter of an ethoxylated propoxylated lauryl alcohol (MW 1020), having the following structure



at 24° C., with an applied cathodic potential sufficient to produce an average current density of 8.0 asd. after the panel was half immersed. After 30 seconds the panel was transferred to an acid copper plating bath where it was plated with copper to an average thickness of 75 microns.

The edges of the panel were ground down to the steel. The copper was easily pulled off the top of the panel but could not be pulled off the bottom half, which had been treated in the above solution, indicating excellent adhesion.

## EXAMPLE 5

After thoroughly pickling and cleaning a steel panel, 2.5 cm. wide and 20 cm. long, half of it was immersed into an aqueous solution containing 1 gram per liter of cupric sulfate pentahydrate (CuSO<sub>4</sub>·5H<sub>2</sub>O) and 100 grams per liter of fluoboric acid (HBF<sub>4</sub>) and 16 grams per liter of ethoxylated propoxylated lauryl alcohol (MW 1020), having the following structure



at 24° C., with an applied cathodic potential sufficient to produce an average current density of 8.0 asd. after the panel was half immersed. After 30 seconds the panel was transferred to an acid copper plating bath where it was plated with copper to an average thickness of 75 microns.

The edges of the panel were ground down to the steel. The copper was easily pulled off the top of the panel but could not be pulled off the bottom half, which had been treated in the above solution, indicating excellent adhesion.

## EXAMPLE 6

After thoroughly pickling and cleaning a steel panel, 2.5 cm. wide and 20 cm. long, half of it was immersed into an aqueous solution containing 0.5 grams per liter of CuSO<sub>4</sub>·5H<sub>2</sub>O and 100 grams per liter of H<sub>2</sub>SO<sub>4</sub> and 10 grams per liter of ethoxylated propoxylated lauryl alcohol (MW 1020), having the following structure



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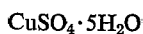
at 24° C. without current. After 20 seconds the panel was dipped into an acid copper plating bath for approximately one second and quickly rinsed in water. Then the panel was dried and a strip of Scotch brand pressure sensitive masking tape 202 was firmly applied to half the width of the panel along its entire length.

The tape was then peeled off the panel. The panel was then examined for bare steel and the tape was examined for copper flakes.

The "tape test" revealed excellent adhesion.

#### EXAMPLE 7

After thoroughly pickling and cleaning a steel panel, 2.5 cm. wide and 20 cm. long, half of it was immersed into an aqueous solution containing 0.5 grams per liter of



and 100 grams per liter of  $\text{H}_2\text{SO}_4$  and 10 grams per liter of polyethylene glycol (MW 1000) having the following structure  $\text{H}(\text{OC}_2\text{H}_4)_{22}\text{OH}$ , at 24° C., without current. After 20 seconds the panel was dipped into an acid copper plating bath for approximately one second and quickly rinsed in water. Then the panel was dried and a strip of Scotch brand pressure sensitive masking tape 202 was firmly applied to half the width of the panel along its entire length.

The tape was then peeled off the panel. The panel was then examined for bare steel and the tape was examined for copper flakes.

The "tape test" revealed excellent adhesion.

#### EXAMPLE 8

After thoroughly pickling and cleaning a steel panel, 2.5 cm. wide and 20 cm. long, half of it was immersed into an aqueous solution containing 0.5 grams per liter of  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  and 100 grams per liter of  $\text{H}_2\text{SO}_4$  and 10 grams per liter of polyethylene glycol (6000) having the following structure  $\text{H}(\text{OC}_2\text{H}_4)_{136}\text{OH}$ , at 24° C., with an applied cathodic potential sufficient to produce an average current density of 2.7 asd. after the panel was half immersed. After 20 seconds the panel was dipped into an acid copper plating bath for approximately one second and quickly rinsed in water. Then the panel was dried and a strip of Scotch brand pressure sensitive masking tape 202 was firmly applied to half the width of the panel along its entire length.

The tape was peeled off the panel. The panel was then examined for bare steel and the tape was examined for copper flakes.

The "tape test" revealed excellent adhesion.

#### EXAMPLE 9

After thoroughly pickling and cleaning a steel panel, 2.5 cm. wide and 20 cm. long, half of it was immersed into an aqueous solution containing 0.5 grams per liter of  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  and 100 grams per liter of  $\text{H}_2\text{SO}_4$  and 10 grams per liter of ethoxylated lauryl alcohol (MW 1286), having the following structure  $n\text{-C}_{12}\text{H}_{25}(\text{OC}_2\text{H}_4)_{25}\text{OH}$ , at 24° C., with an applied cathodic potential sufficient to produce an average current density of 2.7 asd. after the panel was half immersed. After 20 seconds the panel was dipped into an acid copper plating bath for approximately one second and quickly rinsed in water. Then the panel was dried and a strip of Scotch brand pressure sensitive masking tape 202 was firmly applied to half the width of the panel along its entire length.

The tape was then peeled off the panel. The panel was then examined for bare steel and the tape was examined for copper flakes.

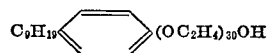
The "tape test" revealed excellent adhesion.

#### EXAMPLE 10

After thoroughly pickling and cleaning a steel panel, 2.5 cm. wide and 20 cm. long, half of it was immersed into an aqueous solution containing 0.5 grams per liter

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of  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  and 100 grams per liter  $\text{H}_2\text{SO}_4$  and 10 grams per liter nonyl phenoxy polyoxyethylene ethanol (MW 1540), having the following structure



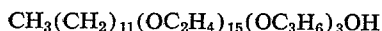
at 24° C., without current. After 20 seconds the panel was dipped into an acid copper plating bath for approximately one second and quickly rinsed in water. Then the panel was dried and a strip of Scotch brand pressure sensitive masking tape 202 was firmly applied to half the width of the panel along its entire length.

The tape was then peeled off the panel. The panel was then examined for bare steel and the tape was examined for copper flakes.

The "tape test" revealed excellent adhesion.

#### EXAMPLE 11

After thoroughly pickling and cleaning a steel panel, 10 cm. wide and 20 cm. long, half of it was immersed into an aqueous solution containing 0.5 grams per liter  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  and 100 grams per liter  $\text{H}_2\text{SO}_4$  and 20 grams per liter ethoxylated propoxylated lauryl alcohol (MW 1020), having the following structure



at 24° C., with an applied cathodic potential sufficient to produce an average current density of 8.0 asd. after the panel was half immersed. After 15 seconds the panel was rinsed with water and transferred to a pyrophosphate copper plating bath and 25 microns of copper was plated on it.

The edges of the panel were ground down to the steel. The copper was easily pulled off the top of the panel but could not be pulled off the bottom half, which had been treated in the above solution, indicating excellent adhesion.

#### EXAMPLE 12

After thoroughly pickling and cleaning a steel tube, approximately 2.5 cm. in diameter and 30 cm. long, the tube was immersed into an aqueous solution containing 0.5 grams per liter  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  and 100 grams per liter  $\text{H}_2\text{SO}_4$  and 20 grams per liter ethoxylated propoxylated lauryl alcohol (MW 1020), having the following structure  $\text{CH}_3(\text{CH}_2)_{11}(\text{OC}_2\text{H}_4)_{15}(\text{OC}_3\text{H}_6)_3\text{OH}$  at 24° C., without current. After 20 seconds the tube was transferred to an acid copper plating bath and plated so that there was an average thickness of 25 microns of copper on the outside of the tube.

The tube was longitudinally cut in half and examined. The copper on the outside of the tube had excellent adhesion to the tube. And further, the inside of the tube also had a uniform adherent coating of copper in it.

#### EXAMPLE 13 (Control)

After thoroughly pickling and cleaning a steel tube approximately 2.5 cm. in diameter and 30 cm. long, the tube was given a strike from a typical cyanide copper strike solution for approximately 5 minutes at about 5.4 asd. The tube was then rinsed with water, dipped in a 2% (by volume sulfuric acid solution, again rinsed with water and transferred to an acid copper plating bath and plated so that there was an average thickness of 25 microns of copper on the outside of the tube.

The tube was longitudinally cut in half and examined. The copper on the outside of the tube had excellent adhesion to the tube. But the copper on the inside of the tube was loose and flaky.

If one wanted to process this tube through other plating baths, e.g. a nickel plating bath, it would be very probable that the copper would flake off from the inside of the tube thereby contaminating the plating solution.

## EXAMPLE 14

After thoroughly cleaning a zinc die cast automobile handle, it was immersed into an aqueous solution containing 1 gram per liter  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  and 60 grams per liter  $\text{H}_2\text{SO}_4$  and 20 grams per liter of an ethoxylated propoxylated lauryl alcohol (MW 1020), having the following structure  $\text{CH}_3(\text{CH}_2)_{11}(\text{OC}_2\text{H}_4)_{15}(\text{OC}_3\text{H}_6)_3\text{OH}$ , at  $24^\circ \text{C}$ ., with an applied cathodic potential sufficient to produce an average current density of 8.0 asd. after the handle was immersed. After 1 minute the handle was rinsed with water and transferred to a pyrophosphate copper plating bath where it was plated with copper to an average thickness of 7.5 microns. The handle was again rinsed with water and then transferred to an acid copper plating solution where an average thickness of 25 microns of copper was plated on it.

Both the appearance of the plated deposit and its adhesion to the basis metal were excellent.

Although this invention has been illustrated by reference to specific embodiments, modifications thereof which are clearly within the scope of the invention will be apparent to those skilled in the art.

I claim:

1. A process for electro-depositing onto metal surfaces an adherent copper strike coating prior to the electro-deposition of copper from copper plating baths comprising electroplating said metal surface in a solution containing 0.01 to 10 grams per liter of a copper salt, 0.1 grams per liter to 500 grams per liter of a nonoxidizing acid, and 0.1 to 100 grams per liter of a polyether containing at least 5 ether oxygen atoms per molecule, thereby obtaining an adherent film effecting good copper plate adhesion of subsequent heavier copper electrodeposits.

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