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2,956,901

COPPER COATING COMPOSITION AND METHOD OF COATING

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6 Claims. (Cl. 117—50)

The invention relates to coating surfaces with copper and more particularly relates to a composition and process of spray metallizing conductors and non-conductors with chemically reduced copper.

An object of this invention is to provide a simple and inexpensive process of providing a smooth, uniform coating of copper.

Another object is to provide copper solutions and reducer solutions particularly suitable for spray metallizing.

A further object is to provide copper solutions particularly suitable for making printed circuits.

These and other objects and advantages are accomplished by spraying an aqueous solution of copper cyanide containing at least 2 grams per liter of solution of ethylenediamine tetracetic acid (EDTA) or its sodium or potassium salts, or where no EDTA is used, the solution should contain an alkaline metal cyanide, such as sodium or potassium cyanide in a molar ratio of alkali metal cyanide to copper cyanide of between approximately .2 and 2.89. The copper solution is used in conjunction with a reducer solution in such manner that the solutions converge on the article to be coated.

We have found in order to reduce copper from a copper cyanide complex and obtain a suitable coating on the article that the molar ratio of alkali metal cyanide to $\text{Cu}_2(\text{CN})_2$ must be below approximately 2.89. The lower limit is the lowest ratio in which the $\text{Cu}_2(\text{CN})_2$ will dissolve and is approximately .2. At above the molar ratio of 2.89, any excess of free NaCN will prevent the reduction of copper. In order to have high speed of reduction with maximum thickness of copper coating, the preferred ratio is approximately 2.5.

We have obtained satisfactory results with concentrations of copper cyanide ranging from approximately 2 to 12 grams per liter of solution, and alkali metal cyanide from about 2.0 to 10 grams per liter, but the latter may be omitted when EDTA is present.

The range of EDTA, or its alkali metal salts, is about 2 to 12 grams per liter, but it may be omitted entirely when the alkali metal cyanide is present.

We prefer to use a minor proportion, such as .25 to 1.2 grams per liter of an anionic surface active agent in the copper solution. A suitable surface active agent is sodium lauryl sulphate. However, any of the anionic agents are suitable, particularly the fatty alcohol sulphates.

The reducing solution which we have found gives highly satisfactory results with the copper cyanide solution is an alkaline solution of an alkali metal hydrosulphite, such as sodium or potassium hydrosulphite.

The hydrosulphite can be present in between approximately 10 to 50 grams per liter of solution with between approximately 2 to 15 grams per liter of an alkali metal hydroxide.

Preferably, an alkali metal nitrite is also present as a stabilizer for the hydrosulphite, particularly when the copper solution and reducer solution are air atomized by spraying with air through nozzles. A suitable con-

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centration of nitrite is 5 to 10 grams per liter. The molar ratio of $\text{Na}_2\text{S}_2\text{O}_4$ to NaNO_2 can range from .3 to 2.0 for good operation.

The temperatures of the solutions can vary widely. Satisfactory results have been obtained with metal solutions at 68° F. to 180° F., and reducer solutions at 68° F. to 140° F.

For cold spraying of plastics, that is, temperatures of 60° F. to 100° F., we obtain preferred results by sensitizing the plastic surface with 2 to 10 grams of SnCl_2 per liter of aqueous solution, preferably containing .5 to 2 grams per liter of sodium lauryl sulphate, or other fatty alcohol sulphate. The plastic is then rinsed with water and then sprayed with 2 to 10 grams of silver nitrate per liter of aqueous solution, also preferably containing .5 to 2 grams per liter of sodium lauryl sulphate or other fatty alcohol sulphates; then without rinsing, the plastic is sprayed with the copper salt solution.

For metals or hot spraying of plastics, the results are about the same without the sensitizer.

In general, the higher the temperature is, the faster is the rate of deposition and the thicker and more opaque the coating.

The spray application can be done by air atomization of solutions, air pressure feed of spray nozzles, or hydraulic pressure in spray nozzles.

The following examples are given to illustrate the invention:

EXAMPLE I

Solution make-up

Metal solution:

Sodium cyanide (NaCN)	1 lb., 8 oz.
Copper cyanide ($\text{Cu}_2(\text{CN})_2$)	2 lbs.
Sodium lauryl sulphate	2.75 oz.
Water to make 1 gal.	

Reducer solution:

Sodium hydroxide (NaOH)	1 lb., 5.5 oz.
Sodium hydrosulphite ($\text{Na}_2\text{S}_2\text{O}_4$)	5 lbs., 0.5 oz.
Sodium nitrite (NaNO_2)	1 lb., 11 oz.
Water to make 1 gal.	

The above compositions are for a one gallon concentrated solution of each, which in turn is diluted to make 20 gallons of solution for spraying. The metal and reducer solutions are used in equal volumes in spraying or a batch reduction process.

In the make-up of the metal solution, we use the following procedure:

- (1) Dissolve the required amount of NaCN in water;
- (2) Heat the NaCN solution to about 180° to 200° F.;
- (3) Slowly add the $\text{Cu}_2(\text{CN})_2$ to the above.

The resultant solution is clear and has a residue of undissolved $\text{Cu}_2(\text{CN})_2$ in it. Upon standing and aging, the solution turns a clear blue color and still has the residue. Evidently we are forming a copper cyanide complex in which the $\text{Cu}_2(\text{CN})_2$ is found on both sides of the equation. However, it is well to note that, when any excess of NaCN above the molar ratio of 2.89 is added, copper will not reduce.

Moreover, we have found that the $\text{Cu}_2(\text{CN})_2$ undissolved in the metal solution can be dissolved by the addition of 1 to 2 grams per liter of Tetrine acid (ethylenediamine tetracetic acid), Di-sodium Tetrine, and Tetra-sodium Tetrine. The $\text{Cu}_2(\text{CN})_2$ is dissolved and the solution turns a clear blue without losing its ability to reduce copper.

EXAMPLE II

The solution and procedures are the same as for Example I, except that 2.75 oz. of EDTA is added to

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the metal solution. We may omit the sodium cyanide when EDTA is added, but prefer to use both.

As a specific example of copper coating, the solutions of Example I (or Example II) are sprayed separately at 140° F. at 12 p.s.i. for approximately 5 minutes on an electrical grade phenolic or other plastic laminate, and masked in such a way as to give an electrical circuit by means well known to the art.

We have obtained satisfactory results on aluminum, stainless steel, steel, brass, and plastics. So far as we know, all types of articles can be copper coated with our solutions.

Instead of using a spray process, the article can be coated by dipping into a solution formed by mixing the copper solution and reducer solutions, agitating the solutions, and then removing the coated article. This procedure is not as fast and does not give a coating which is quite as uniform as the spray process.

While we have disclosed certain preferred embodiments of our invention, many modifications thereto may be made without departing from the spirit of the invention; and we do not wish to be limited to the detailed examples, formulas, and proportions of ingredients set forth, but desire to avail ourselves of all changes within the scope of the appended claims.

We claim:

1. The process of coating a surface with copper which comprises mixing together a solution consisting essentially of copper cyanide and a substance selected from the group consisting of 2.0 to 12.0 grams per liter of ethylenediamine tetracetic acid, 2.0 to 12.0 grams per liter of the alkali metal salts thereof, and from 2.0 to 10.0 grams per liter of an alkali metal cyanide, the alkali metal cyanide being present in a molar ratio of alkali metal cyanide to copper cyanide of below approximately 2.89,

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and a reducer solution composition, consisting essentially of a solution of an alkali metal hydrosulphite, and contacting said surface with the mixed solution.

2. The process of claim 1, wherein the solutions are sprayed onto the surface.

3. The process of claim 1, wherein the copper solution contains sodium nitrite in a molar ratio of sodium hydrosulphite to sodium nitrite of from .3 to 2.0.

4. The process of claim 3, wherein the copper solution and the reducer solution are separately sprayed and directed toward the surface, so that they converge on the surface to be coated.

5. The process of claim 8, wherein the surface is a plastic and the temperature of the solutions is between 60° F. to 100° F.

6. The process of claim 9, wherein the plastic surface is sensitized with tin chloride.

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UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 2,956,901

October 18, 1960

Arthur M. Carlson et al.

It is hereby certified that error appears in the printed specification of the above numbered patent requiring correction and that the said Letters Patent should read as corrected below.

Column 4, line 13, for the claim reference numeral "8"
read -- 4 --; line 16, for the claim reference numeral "9"
read -- 5 --.

Signed and sealed this 11th day of April 1961.

(SEAL)

Attest:

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Acting Commissioner of Patents