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METHOD OF COATING TIN ON COPPER SURFACES

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This invention relates to tin plating, and, more particularly, to tin plating copper articles by chemical reduction. In one of its more specific aspects, this invention relates to tin plating an extended copper surface or base by plating from an aqueous solution containing a soluble salt of tin. The word "copper" as used herein and in the appended claims is intended to include pure copper, commercial copper containing the usual impurities, and copper base alloys.

Tin plating a solid metal body by conventional known methods often results in a dull and rough surface or in a coating thicker than may be required. In the conventional hot dip method, which involves immersing the base material into a molten tin bath, heavy coatings are formed that often are thicker than necessary or desired thereby resulting in an excessive or wasteful use of tin. In addition, a thick coating exhibits a tendency to craze or break. Electroplating is of disadvantage in that extremely careful control is required to avoid loose, spongy deposits, and the tin deposit must be treated in a separate additional step in order to achieve a bright coating. It also is difficult, or almost impossible, to electroplate or hot dip a metal body or base material having an irregular configuration or shape, or the interior surfaces of hollow metal bodies, particularly hollow bodies having a relatively small diameter or of substantial length. In tin immersion plating as a further known method based on a displacement reaction involving displacement of the stannous ion for the free metal of the base material, a bright coating is obtained only where the metal base material is bright.

This invention has therefore as its purpose to provide a tin plated copper article having a substantially continuous, uniform coating of tin deposited by reduction from an aqueous solution containing a soluble compound or salt of tin. The copper article to be tin plated is not restricted to any particular configuration, and includes tin plating the interior wall of tubular or hollow bodies. Equally important, the tin plated copper parts of this invention may be readily wet by solder.

It is known in the art that elemental metal may be precipitated in particulate form from a solution containing a soluble salt of the metal by the action of a reducing agent on the solution. This general concept is employed in the hydrometallurgical precipitation of elemental metal powder, particularly non-ferrous metals, where hydrogen gas is employed as the reducing agent. Reduction of the metal compound or salt and precipitation of the metal normally proceeds at elevated temperatures and at superatmospheric pressures. This method of producing metal powder is particularly useful where a salt of the metal forms a soluble complex ion which may be reduced with a suitable agent, e.g. hydrogen, to yield elemental metal. More recently, it has been proposed to incorporate nucleating sites in the solution of metal salts to further induce precipitation of the metal.

In accordance with the method of the present invention, tin is deposited from a solution of its salt as a substantially continuous, uniform coating on an extended copper surface, and is not precipitated as discrete particles. Elemental tin, or its intermediate product of reduction, such as the oxide, is deposited on an extended copper base

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surface by the action of a reducing gas under pressure on a solution of tin at an effective plating temperature in the presence of the copper base, as explained more fully hereinbelow. The extended copper surface or base, as employed herein and in the appended claims, is defined as a surface, base or substrate or extended dimensions and is particularly of a length and geometric surface area substantially greater than that of discrete particles. The extended surface is not less than about 1/4-inch in its maximum dimension, and is of sufficient thickness to support the coating.

Accordingly, our invention involves depositing a substantially continuous, uniform coating of tin on an extended copper surface from a solution containing a soluble compound of tin having a pH of not less than about 3 by the action of a reducing gas on the solution. The dissolved tin may be present in the solution as either a tin ion, such as the stannous cation, or as a tin containing ion, such as the stannite anion. Suitable compounds of tin for practicing our invention include, for example, stannous sulfate, stannous nitrate, stannous chloride, stannous pyrophosphate, stannous polyphosphate, and alkali metal stannites, for example, potassium stannite and sodium stannite. It should be understood that stannic compounds of tin are also applicable, but require additional reduction to form the deposit. Certain of the tin compounds, upon dissolving in water, exhibit a relatively strong acid pH, in which case, the pH of the solution is adjusted by the addition of a suitable base, for example, ammonium hydroxide, potassium hydroxide or sodium hydroxide. The tin present in solution as a tin ion or tin containing ion is reduced to the elemental metal or its intermediate product of reduction with a suitable reducing gas, preferably hydrogen and in the presence of the extended copper surface.

The concentration of tin in solution will depend to some extent upon the thickness of the tin coating desired. Generally there appears to be no benefit from employing a concentration in excess of about 80 grams of tin per liter, but the concentration of tin in solution should be less than that which a substantial amount would precipitate out in particulate form which may be readily determined by experiment. A concentration of less than about 2 grams of tin per liter is usually too low for obtaining a coating of sufficient thickness or for effecting reduction within a reasonable period of time for obtaining a useful coating. We have found a concentration of about 10 to 50 grams of tin per liter to be generally satisfactory.

Tin is plated onto the extended copper surface from a solution of a dissolved tin compound by treating the solution with a reducing gas, preferably hydrogen. Reduction is generally facilitated by employing a solution at elevated temperatures and maintaining the reducing gas under superatmospheric pressures. Employing a tin-containing solution within the temperature range of from about 200° to 500° F. has been found particularly suitable, and a partial pressure of the reducing gas above the solution of not less than about 50 p.s.i.g. and even as high as 4000 p.s.i.g., or higher, is effective. Although higher temperatures and pressures may increase slightly the reduction reaction, this increase in reaction generally is not sufficient to warrant the higher temperatures or pressures. To effect a substantially uniform adherent coating of tin upon the extended copper surface, we found it especially desirable that reduction and deposition proceed under a substantially quiescent condition, that is, with a substantial absence of turbulence. This procedure is disclosed and claimed in the copending U.S. application to Edward L. Cole and Edwin C. Knowles, entitled "Method of Plating Metals Onto an Extended Surface," Serial No. 112,508, filed, May 25, 1961.

The solution of tin employed in the plating operation of our invention advantageously has a pH of not less than 3, and preferably a pH of from about 5 to 11. A bright tin coating is readily achieved by employing a solution of tin having a pH of from about 7 to 11. Tin plated copper surfaces produced from this solution may be readily wet by solder.

A bath containing an aqueous solution of tin compound in the above described concentration and pH ranges effectively tin plates copper articles of the above character, the tin coating being dense and non-porous and exhibiting uniform adhesion and uniform color. The tin coating produced is of a magnitude in the order of from about 0.5 milligram per square inch of copper surface to 50 milligrams per square inch, which, as calculated, ranges from about 0.00001 inch thick to about 0.002 inch thick. Tin coatings having a thickness in the order of about 0.00001 inch thick to as high as 0.00007 inch thick are particularly useful for numerous applications and attractively economical. However, the coating may be somewhat thinner or thicker than that described depending upon the conditions employed, and particularly the concentration of tin in solution, the pH of the solution, the temperature and the partial pressure at which the hydrogen is maintained.

Although the exact form of the tin coating cannot be determined, the coating as analyzed by X-ray diffraction methods shows that a copper-tin alloy is generally formed, but in many instances a quantity of free tin, usually as β -tin, is deposited. The coating may also be admixed with an intermediate product of reduction of tin, such as stannous oxide or the hydrate with a small amount of unidentifiable material.

The tin plated copper surface of our invention may be particularly useful in many applications where a protective coating is desirable or essential. The extended copper article may be of any configuration, and may include a hollow or tubular conduit. Thus, a copper conduit may be tin plated on the interior wall surface and used in transporting materials that normally attack or corrode copper to a greater degree than tin. In addition, tin plated copper articles prepared in accordance with our invention may be readily wet by solder, and therefore may be particularly useful in joining copper parts, such as copper wire in an electronic device, or copper pipe.

Our invention is further illustrated by the following examples:

EXAMPLE I

In the first of these plating tests, three aqueous baths of stannous sulfate were prepared and the pH adjusted by the addition of ammonium hydroxide. (See Table I). Copper strips measuring approximately 0.5 inch by 4 inches by $\frac{1}{16}$ -inch were cleaned with benzene and acetone, and then washed with a 5% solution of nitric acid, followed by water washing to remove all traces of acid. The strips were dried for several hours at 160° F., cooled, and samples No. 1 and No. 2 were weighed. Each strip was immersed in one of the prepared aqueous baths of stannous sulfate, and placed in an autoclave. The autoclave was flushed with hydrogen to remove air and then pressurized with hydrogen. Test samples No. 1 and No. 2 (see Table I) were treated for 5 hours at 1125 p.s.i.g. and at 355° F. Test sample No. 3 was pressurized at 1000 p.s.i.g. at 300° F. and for 5 hours. The autoclave was depressurized, cooled to room temperature, and the samples removed, washed with water, dried and samples No. 1 and No. 2 again weighed. The composition of the solutions, net gain in weight, and weight of deposit

per unit area of base, and appearance of the samples are shown in Table I, below:

Table I

TIN PLATING COPPER STRIPS FROM STANNOUS SULFATE SOLUTION

Test Sample No.-----	1	2	3
Concentration of tin, grams/liter-----	41-----	40-----	39-----
pH-----	3-----	5-----	7-----
Net gain in weight, grams-----	0.0130-----	0.0116-----	
Weight of deposit, mg./sq. in. of copper-----	3.25-----	2.90-----	
Appearance of tin plate-----	Gun metal luster.	Gun metal luster.	Bright, silvery.

Test sample No. 3 was readily wet by solder which adhered firmly to the treated sample.

EXAMPLE II

An aqueous bath of stannous pyrophosphate was prepared by dissolving 3 grams of stannous pyrophosphate and 6 grams of tetrasodium pyrophosphate decahydrate in 165 milliliters of water. The resulting solution had a tin concentration of 11 grams per liter and a pH of 7. To 15 milliliters of this solution, ammonium hydroxide was added to adjust the pH to 10. A copper strip similar to that used in Example I, was cleaned and weighed, as in Example I. The strip was immersed in the 15 milliliter solution, and placed in an autoclave. The autoclave was flushed with hydrogen and pressured with hydrogen at 1000 p.s.i.g. at 310° F. and for 5 hours. Thereafter, the autoclave was depressurized and cooled to room temperature. The copper strip was removed from the autoclave, washed with water, dried and again weighed. The strip showed a net gain in weight of 0.0083 gram, the weight of the coating being 2.07 milligrams per square inch of copper. The deposit had a silvery cast, and the treated strip was readily wet by solder.

EXAMPLE III

A tinning bath of aqueous stannous pyrophosphate having a concentration of 21 grams of tin per liter of solution was prepared as in Example II. The solution was adjusted to a pH of 9 by the addition of potassium hydroxide.

A 6-inch copper tube having a $\frac{3}{4}$ -inch inside diameter was cleaned first with steel wool, washed with benzene, then acetone, and immersed for one hour in a boiling anhydrous methanol solution. The copper tube was placed in a glass tube and completely covered by the above stannous pyrophosphate solution. The glass tube was then placed in an autoclave, the autoclave flushed with hydrogen, and then pressurized with hydrogen at 1000 p.s.i.g. at 300° F. and for 5 hours. The autoclave was depressurized and cooled to room temperature. The surface of the copper tube had a gun metal luster appearance.

We claim:

1. A method of forming a tin coating on an extended copper surface which comprises contacting said surface with an aqueous solution containing a soluble compound of tin having a pH of not less than 3, and subjecting said solution to a reducing gas under pressure whereby a coating of tin is formed on said surface.

2. A method according to claim 1 wherein the pH of said solution is from about 5 to 11.

3. A method according to claim 1 wherein said soluble compound of tin is a stannous salt.

4. A method according to claim 1 wherein said soluble compound is an alkali metal stannite.

5. A method according to claim 1 wherein the concentration of said tin in said solution is not less than about 2 grams per liter.

6. A method according to claim 1 wherein the solution is maintained at a temperature of from about 200 to 500° F.

7. A method according to claim 1 wherein said reducing gas is hydrogen.

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8. A method of forming a tin coating on an extended copper surface which comprises contacting said surface with an aqueous solution containing a soluble compound of tin, said solution having a concentration of from about 10 to 50 grams of tin per liter and a pH of from about 5 to 11, and subjecting said solution to a reducing gas under pressure while maintaining said solution at a temperature of from about 200 to 500° F.

9. A method according to claim 8 wherein said reducing gas is hydrogen.

10. A method of forming a tin coating on an extended copper surface which comprises contacting said surface with a solution containing a soluble stannous salt having a concentration of not less than 2 grams per liter of stannous cation and a pH of from about 7 to 11, and

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subjecting said solution to a reducing gas under a pressure of not less than 50 p.s.i.g. while maintaining said solution at a temperature of from about 200 to 500° F.

11. A method according to claim 10 wherein said reducing gas is hydrogen.

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