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METHOD OF TIN PLATING COPPER

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This invention relates to tin plating, and, more particularly, to a method of tin plating copper articles by chemical reduction.

In one of its more specific aspects, this invention relates to tin plating a copper surface or base by plating from an aqueous solution containing a soluble salt of tin and in the presence of a metal selected from the group consisting of aluminum and magnesium. The words "copper," "aluminum" and "magnesium" as used herein and in the appended claims are intended to include the pure metal, the commercial metal containing the usual impurities, and a base alloy of the metal.

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 method for tin plating a copper article with a substantially continuous, uniform coating of tin deposited by reduction from an aqueous solution containing a soluble compound or salt of tin and in the presence of a metal selected from the group consisting of aluminum and magnesium. 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 our copending United States application entitled "Tin Plating," filed December 29, 1960, Serial No. 79,110, of which this application is a continuation-in-part, we describe tin plating copper articles whereby 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 the copper base surface by the action of a reducing gas under pressure on a solution of tin in the presence of the copper base.

We now have found quite unexpectedly that highly desirable tin coatings having a bright, uniform appearance are obtained by tin plating with a solution of tin under the action of a reducing gas and in the presence of a metal selected from the group consisting of aluminum and magnesium, and that the tin plating solutions may be employed over a substantially greater pH range than referred to in our prior application. Although the presence of aluminum or magnesium in association with the copper base is essential to our improved method, no displacement reaction is apparently involved, as explained more fully hereinbelow. In the preferred embodiment of our invention, the copper surface or base to be tin plated is of extended dimensions. An extended copper surface or base, as employed herein and in the appended claims, is defined as a surface, base or substrate of 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 ¼ 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 a copper surface from a solution containing a soluble compound of tin and in the presence of aluminum or magnesium 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, and where desired, the pH of the solution may be 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, and in association with the aluminum or magnesium, 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 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 particular 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 5 to 50 grams of tin per liter to be generally satisfactory. Where desired, a stabilizer, i.e. citrate ion, tartrate ion, urea, etc., may be used to prevent tin from separating out of solution as the oxide.

The copper article to be plated is immersed in a suitable tin solution and in the presence of a metal selected

from the group consisting of aluminum and magnesium. Generally, the aluminum is less susceptible to attack by the hot solution, and therefore is the preferred metal. Although in some instances a change in weight for the aluminum or magnesium may result by reason of the process, this weight change cannot be correlated with the amount of tin deposited out in the elemental state. The process of our invention thus does not involve a displacement reaction wherein a stannous ion in solution is deposited out upon replacement by an aluminum or magnesium ion. However, the presence of aluminum or magnesium is highly beneficial, but this must be accompanied by the action of the reducing gas which apparently is essential in reducing tin from its soluble complex. Intimate contact between the copper article and the aluminum or magnesium is preferred but not essential. It is often convenient or advantageous to employ an aluminum or magnesium hanger in strip or wire form for suspending the copper article in the solution. Where hangers are employed, it is not necessary for the hanger to be completely immersed in the solution. Where desired, the aluminum or magnesium part may be wound or wrapped around one end or section of the copper article, but, of course, the area of the copper article covered will not be tin plated. Good results are obtained when the copper article and aluminum or magnesium part are immersed in the solution but not in contact with each other. The quantity of aluminum or magnesium present for the tin plating process does not appear to be particularly critical, nor is the aluminum or magnesium part restricted to any particular shape or configuration and may include metal wire, plate, bars, balls, ribbon or strips.

Tin is plated onto the 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.

Although the pH of the solution of tin employed in the plating operation of our invention is not particularly critical, we have found it advantageous to employ a pH of not less than about 0.5, and more preferably a pH of from about 0.5 to 12. A bright tin coating is readily achieved by employing a solution of tin having a pH of from about 1 to 11. Tin plated copper surfaces produced in accordance with our invention 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

An aqueous bath of stannous pyrophosphate was prepared by dissolving 6 grams of stannous pyrophosphate and 12 grams of tetrasodium pyrophosphate decahydrate in 165 milliliters of water. The resulting solution had a tin concentration of 21 grams per liter and a pH of 7.

Copper strip "A" measuring approximately 1⅛-inch x 2 inches x 1/16-inch, and a second copper strip "B" measuring ½-inch x 2 inches x 1/16-inch, were cleaned with benzene and acetone, and then washed with a 5% nitric acid solution followed by water washing to remove all traces of the acid. The strips were dried for several hours at 160° F., cooled and the samples then weighed. The strips were hung on an aluminum wire suspended across the top of a 150 milliliter beaker containing a sufficient amount of the stannous pyrophosphate solution to immerse the copper strips. That part of the aluminum wire which was in intimate contact with the copper strip was also immersed in the solution and the beaker was placed in an autoclave. The autoclave was flushed with hydrogen to remove air, and then pressurized for 5 hours with hydrogen at 1000 p.s.i.g. and 290° F. The autoclave was depressurized cooled to room temperature and the copper strips removed, washed with water, dried and again weighed. The net gain in weight for copper strip "A" was 0.0135 gram and for strip "B" 0.0071 gram. The aluminum wire showed a loss in weight of 0.0009 gram. Each of the copper strips exhibited a continuous, uniform coating of tin having a bright appearance.

Example II

The procedure outlined in Example I was repeated except that two aluminum hangers were suspended from an aluminum wire stretched across the top of the beaker, and a copper strip was hung from each of the hangers. Each copper strip, and the lowermost part of each aluminum hanger, were immersed in the stannous pyrophosphate. The copper strips, upon treatment, showed a net gain in weight of 0.0131 gram and 0.0099 gram. Here again, a uniform and bright coating of tin was obtained with each copper strip.

Example III

An aqueous solution of stannous pyrophosphate was prepared as in Example I, and the solution was adjusted to a pH of 9 by the addition of potassium hydroxide. Two copper strips, each measuring approximately ½-inch x 4 inches x 1/16-inch were cleaned, dried and weighed

as in Example I. Copper strip "A" was suspended in the tinning solution contained in a tube by means of an aluminum hanger as in Example II. A piece of aluminum wire having a diameter of 0.064 inch and measuring approximately 1½-inches in length was wrapped around one end of the second copper strip "B," and the composite was submerged in the solution contained in a second tube.

The prepared samples were placed in an autoclave, the autoclave flushed with hydrogen and then pressurized with hydrogen for 5 hours at 975 p.s.i.g. and at a temperature of 290° F. The autoclave was depressurized and cooled to room temperature. The treated copper strips "A" and "B," having been washed, dried and weighed upon removal from the autoclave, showed a net gain in weight of 0.0071 gram, 0.0073 gram, respectively. The aluminum hanger and aluminum wire showed substantially no change in weight.

Example IV

An aqueous bath of stannous pyrophosphate was prepared by dissolving 6 grams of stannous pyrophosphate and 24 grams of tetrasodium pyrophosphate decahydrate in 165 milliliters of water. The pH of the resulting solution was 9. Three tinning solutions were prepared by placing 9 milliliters of the foregoing solution in separate tubes and, in each case, diluting the tinning solutions with 9 milliliters of water. Three copper strips, all measuring approximately the same as those employed in Example III, were preliminary prepared by cleaning, drying and weighing as in Example I. The first copper strip "A" was suspended in a tinning solution in one of the tubes by means of a magnesium hanger such that the lowermost part of the hanger was also immersed in the solution. With a second copper strip "B," the magnesium ribbon, measuring about $^{13}/_{1000}$-inch x 1½ inches x $^{6}/_{1000}$-inch was wrapped around one end of the copper strip and the sample immersed in a second tube of solution. In a third test, copper strip "C" and an aluminum strip having a diameter of 0.064 inch and measuring approximately 1½-inches in length were placed side by side in a tube containing the tinning solution.

The prepared samples, each in a separate tube, were placed in an autoclave, the autoclave flushed with hydrogen and then pressurized with hydrogen for 5 hours at 1000 p.s.i.g. and 285° F. Upon removal from the autoclave followed by cleaning, drying and weighing as in Example I, copper strips "A,", "B," and "C" showed a net gain in weight of 0.0079 gram, 0.0669 gram and 0.0129 gram, respectively. The magnesium pieces showed a gain in weight of 0.0075 and 0.0688 gram by reason of oxidation, and the aluminum strip showed a loss in weight of 0.065. In each case there was a bright, uniform coating of tin formed on the copper strips.

Example V

To 200 milliliters of distilled water was added 10 grams of stannous sulfate and 2 grams of ammonium sulfate. The pH of the resulting solution was adjusted to 1 by the addition of 3 milliliters of sulfuric acid (96% H_2SO_4). A copper strip measuring approximately ½-inch x 4 inches x $^{1}/_{16}$-inch was suspended in the solution by means of an aluminum hanger as in Example II.

The prepared sample was treated in an autoclave as in Example I under a hydrogen pressure of 1000 p.s.i.g. at 310° F. and for 5 hours. The treated copper strip showed a net gain in weight of 0.0221 gram. The copper strip exhibited a bright uniform coating of tin, and was readily wet by solder.

Example VI

To 15 milliliters of the solution prepared in Example I was added 3 milliliters of potassium hydroxide (5% KOH) to bring the solution to a pH of 11. A copper strip measuring approximately ½-inch x 4 inches x $^{1}/_{16}$-inch, having been preliminarily cleaned and weighed as in Example I, was immersed completely in the solution, having been suspended therein by an aluminum hanger as in Example II.

The sample was treated in an autoclave under the same conditions as set forth in Example I. The treated copper strip showed a net gain in weight of 0.0244 gram, the tin coating having a bright, uniform appearance. The treated strip was readily wet by solder.

Example VII

A tinning bath of aqueous stannous pyrophosphate was prepared as in Example I, and the solution adjusted to a pH of 9 by the addition of potassium hydroxide. A 6 inch copper tube having a ¾-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 suspended in a glass tube by an aluminum wire, and the copper tube was completely covered by the above stannous pyrophosphate solution. The lowermost part of the aluminum wire was also immersed in the 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 290° F. and for 5 hours. The autoclave was depressurized, cooled to room temperature and the copper tube removed therefrom. The surface of the copper tube had a bright, uniform coating of tin.

We claim:

1. A method of tin plating at least one surface of a copper article comprising immersing said copper article in an aqueous solution containing a soluble compound of tin and in the presence of a metal selected from the group consisting of aluminum and magnesium, and subjecting said solution to a reducing gas at a pressure of at least 50 p.s.i.g. while maintaining said solution at a temperature of between 200 and 500° F.

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

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

4. A method according to claim 1 wherein said compound of tin is stannous pyrophosphate.

5. A method according to claim 1 wherein said compound of tin is stannous sulfate.

6. A method according to claim 1 wherein said compound of tin is an alkali metal stannite.

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

8. A method according to claim 1 wherein said pressure is between 50 p.s.i.g. and 4,000 p.s.i.g.

9. A method of tin plating a copper article comprising immersing said article in an aqueous solution containing a soluble compound of tin and in the presence of a metal selected from the group consisting of aluminum and magnesium, said solution having a pH of not less than about 0.5, subjecting said solution to a reducing gas at at least a pressure of 50 p.s.i.g. and maintaining said solution at a temperature of between 200 and 500° F.

10. A method according to claim 9 wherein said solution has a concentration of not less than 2 grams per liter and a pH of from about 1 to 11.

11. A method of tin plating a copper article comprising immersing said copper article in an aqueous solution containing a soluble compound of tin and in the presence of a metal selected from the group consisting of aluminum and magnesium, and subjecting said solution to hydrogen at a pressure of at least least 50 p.s.i.g., said solution having a concentration of about 5 to 50 grams of tin per liter and a pH of from about 0.5 to 12 and at a temperature of about 200° to 500° F.

12. A method of tin plating an extended copper article comprising immersing said copper article in an aqueous solution containing a soluble compound of tin and in the

presence of a metal selected from the group consisting of aluminum and magnesium, and subjecting said solution to hydrogen at a pressure of at least 50 p.s.i.g., said solution having a concentration of not less than 2 grams of tin per liter and a pH of from about 0.5 to 12 and at a temperature of about 200° to 500° F.

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