Method of Coating Cupreous Metal with Tin

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Our invention relates to a method of coating metals and alloys with other metals. More particularly, it relates to a method of coating metals and alloys with other metals by an immersion process, without the use of an electric current from an outside source and without a contact metal within the bath to be utilized.

In our United States Patent No. 2,159,510 issued May 23, 1939, we disclosed an immersion process for coating copper or its alloys with tin. The process of the present invention is likewise applicable to coating copper and its alloys with tin, although it is also applicable to coating other metals and alloys with tin or other metals. Although the sodium cyanide-sodium stannite bath and the process disclosed in the United States Patent No. 2,159,510 work successfully, we have found that a process employing an immersion coating bath containing thiourea possesses a number of advantages over the process disclosed in said patent.

One of the objects of our invention is to produce coatings of tin, antimony, bismuth, silver, lead, molybdenum, and other metals on copper, iron, steel and other metals and alloys by a simple immersion process.

Another object of our invention is to obtain coatings of tin on copper or its alloys or on copper or copper alloy-coated articles by a simple and relatively inexpensive immersion process wherein the coating may be produced in a relatively short time.

Another object of our invention is to produce coatings of the type indicated which will be sufficiently thick and will have adequate covering characteristics.

Other objects of our invention will appear from the following description and claims.

The invention will be described first by outlining it as it applies to the deposition of a coating of tin on copper by immersion. However, it is to be understood that this example is only illustrative and that our invention is not limited thereto. Other examples will be given in the description following which will show that our invention is also applicable to the deposition of a coating of metals other than tin on metals other than copper.

We have found that in immersion coating, it is desirable that the metal to be plated be in the form of a complex so that too high a concentration of free ions does not exist in the bath. In coating metals with tin, it is usually necessary to have the tin in the stannous condition. Thiourea is a strong complex former and also a reducing agent. We have discovered that baths containing thiourea, tin, and an acid produce bright adherent coatings on copper when the latter is immersed in a solution thereof. We have also discovered that coatings are effected even if the original bath is made from stannic tin. While we do not wish to be bound by any specific theory, we are of the opinion that thiourea forms a stable complex with tin and, because of its potency as a reducing agent in acid solutions, part of the tin is reduced to the stannous condition in which form it is effective to make immersion coatings. Also, as is well-known, stannous tin oxidizes readily in solution. We believe that the thiourea reduces stannic tin, formed in this manner, back to the stannous condition. Furthermore, as will be shown later in this description, the bath life is much longer in the case of thiourea-containing baths.

It is only necessary to make a solution of a tin salt, thiourea and an acid, and to immerse a piece of copper in the solution. Almost immediately a coating of tin forms on the copper and the thickness increases with increased time of immersion. Coatings are formed at ordinary room temperatures, although higher temperatures, even to the boiling point, can be employed.

As specific examples of baths that produced satisfactory coatings of tin on copper, the following are given as illustrative of those tried in the investigation leading to this invention.

A bath was made containing 45 grams per liter of thiourea and 5.0 grams per liter of stannous chloride, SnCl2·2H2O. To this was added sulphuric acid in amounts varying from 1 to 100 grams per liter. Each bath was effective in producing immersion coatings of tin on copper at room temperature.

In another series the SnCl2·2H2O was kept constant at 5.0 g./l. and the sulphuric acid at 20 g./l. The thiourea was varied from 1 to 100 g./l. Effective coatings were obtained at concentrations of thiourea above 10 grams per liter. A concentration of 5 g./l. of thiourea was ineffective at room temperature.

In still another series the concentration of thiourea was kept constant at 50 g./l.; the concentration of sulphuric acid constant at 20 g./l.; and the SnCl2·2H2O varied from 0.5 to 100 g./l. All baths yielded satisfactory coatings, although when the concentration of SnCl2·2H2O was 20 g./l. or above some tin complex precipitated from the bath.
A bath made of 50 g./l. of thiourea, 20 g./l. of sulphuric acid and 5 g./l. sodium stannate; i.e., with tin added in the stannic condition, gave satisfactory coatings even at room temperature.

Coatings are deposited rapidly. As an example, a thiourea bath containing 5.0 g./l., SnCl₂·2H₂O deposited tin at room temperature to the extent of 0.015 gm. per sq. dm. in 5 minutes, 0.029 in 15 minutes and 0.033 in 30 minutes. The deposit in 24 hours was 0.23 g./sq. dm. The rate of deposition varies with the bath composition.

Baths made of thiourea are quite stable. For example, baths containing 45 grams of thiourea, 5.00 g./l. SnCl₂·2H₂O and from 5 to 50 g./l. H₂SO₄ were still effective even after standing open exposed to air for more than a month.

Coatings may be put on copper-coated articles as well as on the metal itself. For example, a tin immersion coating may be put on copper-clad steel. The copper can be put on the steel by any of the various methods, including electroplating and immersion.

It is obvious, of course, that immersion-coated articles may be heat-treated. For example, copper coated with tin may be heated to form an alloy layer. This unit, if desired, can again be immersed in the tinning bath to give an exterior tin coating.

The advantages of this invention will be obvious to those skilled in the art. The advantages discussed in the United States Patent No. 2,159,810 for tinned copper are also applicable to this invention. A particular and specific advantage of this present invention, however, is the stability of the baths. Another advantage is that many metals, other than tin, can be plated by an immersion process from baths containing thiourea. A further advantage is that tin may be plated from baths initially made with stannic tin.

In the foregoing examples, stannous chloride was disclosed as a source of tin. Other tin salts, soluble in the solution used, are likewise applicable. For example, we may use stannous sulphate or sodium stannite. Likewise, sulphuric acid was given as an example of an acid. Other acids, for example, hydrochloric, can be used.

Having thus described our invention, what we claim is:

1. The method of forming an adherent tin coating on a cuprous surface, said method comprising contacting said cuprous surface with an aqueous acidic solution for a time sufficient to deposit the desired amount of tin coating, and thereafter removing said surface from contact with said solution, said solution containing, per liter, acid equivalent to that obtained from 1 to 100 grams of concentrated sulphuric acid, from 10 to 100 grams of thiourea, and dissolved tin equivalent to that obtained by the addition of from 0.5 to 20 grams of SnCl₂·2H₂O.

2. The method of forming an adherent tin coating on a cuprous surface, said method comprising contacting said cuprous surface with an aqueous acidic solution for a time sufficient to deposit the desired amount of tin coating, and thereafter removing said surface from contact with said solution, said solution containing, per liter, from 1 to 100 grams of concentrated sulphuric acid, from 10 to 100 grams of thiourea, and dissolved tin equivalent to that obtained by the addition of from 0.5 to 20 grams of SnCl₂·2H₂O.

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