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METHOD OF HOT DIPPING METAL COATED OBJECTS

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Fig. 1.

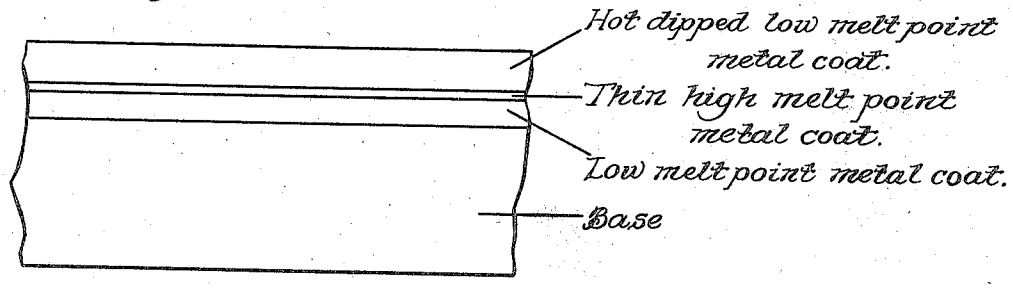
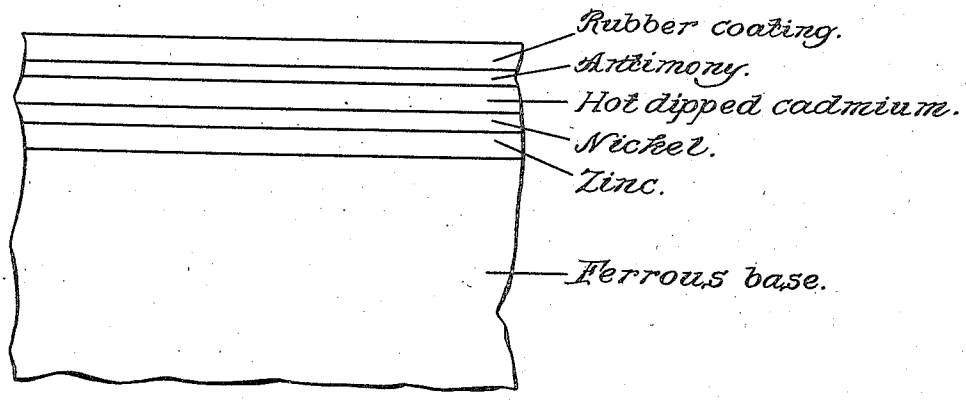


Fig. 2.



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METHOD OF HOT-DIPPING METAL COATED OBJECTS

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18 Claims. (Cl. 91—68.2)

This invention relates to a method of applying a molten coating of metal over another coating of metal normally adversely affected by such a molten coating, and to the objects so produced.

In the production of metal objects it is frequently desirable to apply a second coat over an inner one. Ordinarily the second coat will be of the same metal as the lower one, but this is not always the case. The most economical method at present is to coat with a molten metal, but where this is attempted, dipping the coated base into the molten body dissolves most or all of the lower coating, and it is thus not practicable to build up a thick coat in this manner.

For example, it is frequently desired to increase the corrosion resistance of ferrous base objects by the use of zinc. But attempts to apply more than one coat of zinc by the hot dipping process failed to increase the thickness materially.

In accordance with the present invention a thin layer of an inert metal is deposited on the first coating, then the object may be coated with molten metal without affecting the lower layer. This is illustrated diagrammatically in the drawing in which a base 1 is shown in Fig. 1 provided with a layer of relatively low melt point metal on which is a thin layer of relatively high melt point metal followed by a hot dipped coating of a relatively low melt point metal. Fig. 2 shows diagrammatically a specific embodiment with rubber applied.

The layer of relatively high melt point metal, which may be designated as a flash, is applied by any method not adversely affecting the lower coat. Such methods may be designated as "cold methods", even though they may involve the use of considerable heat, and even though in some instances the metal may be applied in molten or gaseous state, as for example in the sputter processes. Ordinarily, of course, the coating will be applied by electroplating, which will include deposition by substitution. The substitution method is not preferred because it uses up some of the lower coating of metal.

The thickness of the coating is such that from a heat capacity standpoint it has a negligible insulating effect. Why such a thin coating should insulate the metal beneath it is not known. It is possible that the metal maintains a shell which prevents the lower material from running off even though melted and even though the shell may not be entirely continuous.

Surprisingly enough, the coating of inert metal—which is ordinarily a high melt point metal—is effective even though it is almost immeasurably thin. As a result the amount of the inert metal is so little that it does not adversely affect corrosion resistance or other properties of the composite object.

For example, a ferrous base, such as a tire bead reenforcing wire having a diameter of .037 inch may be dipped in molten zinc to apply a galvanized zinc coating. Such a coating is ordinarily about 0.00017 inch in thickness, or contains about 10 grams of zinc per kilogram of wire. An electroplating of copper is then put upon the galvanized wire to the amount of about 12 grams of copper per kilogram of wire. This coat is thus of the order of 0.0001 inch in thickness. The wire may then be again immersed in zinc, and a second coating of about 10 grams per kilogram applied thereon, without affecting the first coating. In this case, the copper apparently produced an intermediate area of brass during the immersion.

The invention is particularly applicable to the production of multiple coats by the hot dipping process, and is applicable to coating with any metal by the hot-dip process upon any other thin coating of metal which ordinarily is adversely affected by the hot dip.

The invention is applicable to a very large number of combinations of metals, primarily being used where it is desired to put a coating of metal by the hot-dip process upon another metal having a similar or lower melting point. However, in many instances it is impossible to plate by the hot-dip process a metal of relatively low melt point upon a metal which has a considerably higher melting point due to the formation of undesirable products. For instance, cadmium, cannot be plated upon zinc in the ordinary hot method due to the formation of a watery alloy, even though the melting point of cadmium is very considerably below that of zinc.

The following table shows a number of examples of the process:

Inner coating	Intermediate coating	Outer coating
Hot zinc	Copper	Hot cadmium.
Hot zinc	Antimony	Hot cadmium.
Hot zinc	Nickel	Hot cadmium.
Hot zinc	Cobalt	Hot cadmium.
Hot cadmium	Cobalt	Hot zinc.
Hot tin	Copper	Hot lead.
Hot zinc	Cobalt	Hot lead.
Hot zinc	Nickel	Hot lead.
Hot zinc	Nickel	Hot tin.
Hot zinc	Iron	Hot zinc.
Hot zinc	Chromium	Hot tin.
Hot zinc	Cobalt	Hot tin.
Hot zinc	Nickel	Hot lead.
Hot zinc	Chromium	Hot cadmium.
Hot zinc-antimony	Nickel	Hot lead.
Lead-arsenic (hot or cold)	Nickel	Hot lead.
Heavy electro-zinc	Nickel	Hot cadmium.
Hot zinc-electro-zinc	Nickel	Hot cadmium.
Hot lead-electro-lead	Copper	Hot lead.

In all of the above cases, the original coat consisted of about 10 grams per kilogram of wire of .037 to .093 inch diameter, the intermediate coat was electroplated and was of the order of .4 to .8

gram per kilogram, and the outer coat was approximately 10 grams per kilogram. For other diameter wires coating of similar thickness are employed. Other metals such as antimony, chromium, silver, and the like may be used as an intermediate coating, the amounts required varying for the various metals. Antimony, for example, may require about 12 grams per kilogram, owing to its low melting point. In the case of readily oxidizable metals, care should be taken to avoid oxides in order that subsequent coats may adhere.

The process affords a very desirable method of putting tin upon an object. For example, copper was applied at the rate of .02 ounce per square foot over a hot tinned brass strip, and additional hot tin was then applied over the copper.

As another example of the invention a hot galvanized wire bead reenforcing wire having a coating of approximately 11 grams of zinc per kilogram of wire was electroplated with .25 gram of copper per kilogram of wire. An outer coat of cadmium was then applied by the hot-dip process, the temperature of the cadmium bath being about 100 degrees higher than the melting point of the cadmium. By this means about 10 to 11 grams of cadmium per kilogram of wire was applied.

In case of tire bead reenforcing wires the wire may be coated with zinc, then with copper, then with zinc, and again with a coat of copper to which rubber is vulcanized. In such a case the second layer of copper is of the order of 0.00001 of an inch, and by alloying with the zinc becomes rubber adherent. The first coating of copper may be of the order of .0001 inch in thickness.

As a further example of the invention, a ferrous tire bead having a diameter of .037" or other ferrous base object may be galvanized with zinc, electroplated with a flash of nickel, and then a hot-dipped layer of cadmium applied to the nickel, followed by a thin layer of antimony or arsenic on the cadmium. A wire so coated has extremely high corrosion resistance, particularly to corrosion of the type of which the salt spray is typical.

The thickness of the galvanized zinc coating will ordinarily be sufficient to provide about 10 gm. of zinc per kg. of wire. A satisfactory nickel coating contains about 0.12 gm. of nickel per square foot of surface. Considerably thicker coatings, however, will not adversely affect the product. Nickel may then be electroplated to the amount of .1 to 1.5 gm. of nickel per kg. of wire, and the wire is then admixed in molten cadmium which will apply a coating of about 10 gm. per kg. of wire, and will not adversely affect a lower coating of zinc. It is preferred to wipe all hot-dipped coatings.

Antimony may then be applied to the cadmium from an electrolytic solution of the metal, such as is described in my co-pending application Serial No. 32,298, filed July 19, 1935.

It may be prepared, for example, by dissolving 3 oz. of sodium cyanide in 1 gallon of warm water, dissolving ½ oz. of antimony trisulfide in the solution, and then heating to 120° F. The solution is preferably maintained at about this temperature during the reaction. The coated material is then immersed in the bath for a short period, normally long enough to produce a coating of the order of 0.1 gram to .35 gram of antimony per kilogram of wire. Normally, an immersion of 3 to 10 seconds is sufficient. The coating of antimony will be of the order of .005 oz. of antimony per square foot of surface. The article is preferably washed in cold water and then carried while still wet to a bath of boiling water, and is then air-dried while still hot, the air-drying taking place rapidly enough to prevent corrosion.

The antimony not only increases the corrosion resistance of the material to which it is applied, but when plated in a thin layer, is particularly valuable in connection with articles which are to be vulcanized to rubber, inasmuch as it apparently alloys itself with the cadmium in such a manner as to produce a rubber-adherent material.

In the case of the zinc-nickel-lead coating heretofore described, the zinc coating may be hot dipped, followed by electroplating. The coating may also be entirely electroplated, if desired. Its thickness may vary from .0001 inch upward, but normally will not exceed .004 inch. The weight per unit area of zinc will thus be approximately one to forty grams of zinc per square foot of area covered. This thickness will apply not only to wires, but also to flat and other ferrous surfaces.

The nickel coating may then be applied from a suitable electroplating bath and ordinarily will have a thickness of the order of 1/600,000 to as high as 1/1000 of an inch, or about .016 gram to 9.6 grams per square foot of surface. The thinner coatings are preferred.

An outer coating of lead may then be applied, either by the hot dip process, or by the electrolytic process, or by the hot dip process followed by electroplating. The thickness of the lead will vary from about 1/15,000 to 1/1,000 of an inch or, expressed in weight per unit area, from about .25 to 3.75 grams per square foot of surface covered.

An iron base so coated with zinc, nickel and lead has extremely high corrosion resistance, particularly in acid atmospheres.

It will be appreciated that the flash coating of high melt point metal interposed between the two hot-dipped coats may, in general, so alloy itself with one or both of the coats, that it loses its identity as an individual layer. The claims therefore must be interpreted from the standpoint of the time of application of the various coats.

This application is a continuation in part of my copending applications, Serial No. 749,303, filed October 20, 1934, and Serial No. 30,919, filed July 11, 1935.

The foregoing detailed description is given for clearness of understanding only, and no unnecessary limitations should be understood therefrom, but the appended claims should be construed as broadly as permissible in view of the prior art.

What I regard as new and desire to secure by Letters Patent is:

1. The method of hot-dipping a base coated with a metal attacked by the molten coat which comprises applying a flash coat of an inert metal upon the inner coating by a cold method, and applying the molten metal thereon.

2. The method of coating a base coated with a relatively low melt point metal with a second relatively low melt point metal, which comprises applying a flash coating of a relatively high melt point metal upon the inner coating by a cold method, and applying the outer coating of relatively low melt point metal therein by the hot-dip method.

3. The method as set forth in claim 2, in which the inner and outer coatings are zinc.

4. The method as set forth in claim 2, in which the inner and outer coatings are zinc and the intermediate coating is nickel.

5. A metal-coated object comprising a base, a thin metal coating thereon, a relatively thin intermediate metallic coating thereon, and a hot-dipped outer coating on the intermediate coating, the inner coating being of a metal adversely affected by the molten metal of the exterior coating, and the intermediate coating being inert thereto.

6. A metal-coated object comprising a base, a metal coating thereon, a flash intermediate metallic coating thereon, and a hot-dipped outer coating on the intermediate coating, the inner coating being of a metal attacked by the molten metal of the exterior coating, and the intermediate coating being inert thereto.

7. A metal-coated object comprising a metallic base, a metal coating thereon, a flash intermediate metallic coating thereon, and a hot-dipped outer coating on the intermediate coating, the inner coating being of a metal attacked by the molten metal of the exterior coating, and the intermediate coating being inert thereto.

8. A metal-coated object comprising a base, a coating of relatively low melting point metal thereon, an intermediate flash coating thereon of a relatively high melting point metal, and a hot-dipped outer coating on the intermediate coating of a relatively low melting point metal.

9. An article as set forth in claim 8, in which the inner and outer coatings are of tin.

10. An article as set forth in claim 8, in which the inner coating is of zinc, the intermediate coating is of nickel and the outer coating is of lead.

11. A ferrous base object having a galvanized zinc coating thereon, a flash layer of relatively high melt point metal on the zinc, and a hot-dipped coating of zinc thereon.

12. A ferrous base tire bead reenforcing wire having a galvanized zinc coating thereon, a flash layer of relatively high melt point metal on the zinc, and a hot-dipped zinc coating upon said intermediate layer.

13. A ferrous base article having a zinc coating thereon, the zinc adjacent the iron being hot galvanized, a flash layer of nickel upon the zinc, and a hot dipped lead coating upon the nickel.

14. An article as set forth in claim 8, in which the intermediate coating is nickel.

15. The method of coating a base coated with a relatively low melt point metal which comprises applying a flash coating of a relatively high melt point metal upon the inner coating by a cold method, applying a metal having a melting point of the order of that of the low melt point metal and of the class consisting of zinc, tin, lead and cadmium, thereto by the hot dip method, and applying thereto a metal of the class consisting of arsenic and antimony.

16. A metal coated object comprising a ferrous base, a coating of a relatively low melt point metal thereon, a flash coating of a relatively high melt point metal upon the inner coating, a hot-dipped metal having a melt point of the order of that of the low melt point metal and of the class consisting of zinc, tin, lead and cadmium thereon, and a thin layer of a metal of the class consisting of arsenic and antimony on the hot-dipped coating.

17. An article as set forth in claim 16 in which the outer metal has a thickness of the order of .005 ounce per square foot of area.

18. An object as set forth in claim 16 in which the hot-dipped coating is cadmium and the outer layer is thin enough to alloy throughout with the cadmium layer at an atmospheric temperature or the temperature of vulcanization, and a layer of rubber vulcanized thereon.

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