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CORROSION RESISTING RUBBER COATED ARTICLE

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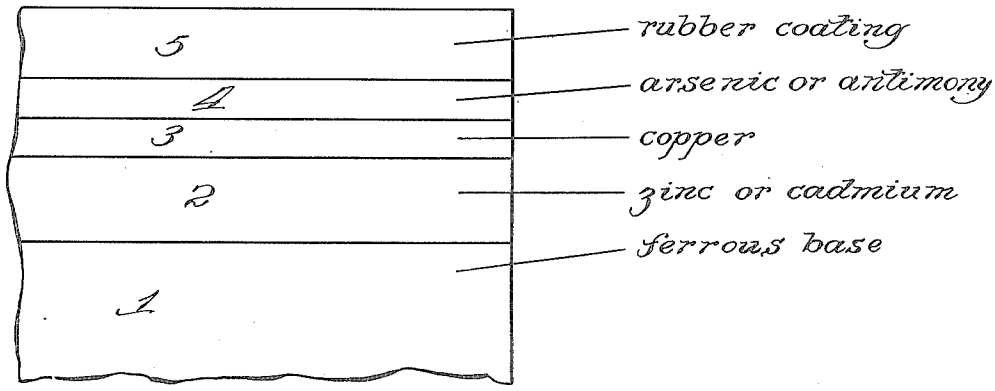

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CORROSION RESISTING RUBBER COATED ARTICLE

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Continuation of application Serial No. 749,467, October 22, 1934. This application July 19, 1935, Serial No. 32,298

16 Claims. (Cl. 91—68.2)

This invention relates to the manufacture of corrosion-resisting rubber coated articles and particularly to ferrous base metals which are plated with rubber adhesion-promoting metals and corrosion-resisting metals.

It has heretofore been known that steel objects coated with brass could be vulcanized directly to rubber. Likewise, steel objects which have been coated first with zinc and then with copper, may be vulcanized directly to rubber. In either case, however, the metal is considerably more subject to corrosion than is the case with a ferrous object which has simply been galvanized.

The problem of increasing the corrosion resistance has been extremely difficult due to the fact that any additional material added upon the base would naturally interfere with the adherence of the base to the rubber.

It has now been discovered that the corrosion resistance of a ferrous object galvanized with zinc and then plated with copper may be increased from 100–200%, without impairing the adherence to rubber, by electro-depositing upon the surface thereof a very thin coating of a metal of the class consisting of antimony or arsenic.

It is preferred that the zinc be applied by the hot dip method, since by so doing an iron-zinc alloy is formed at the junction of the zinc and iron and a much more corrosion-resistant coating is obtained. Electroplated coatings of zinc give corrosion-resistance, but only about 50% of those obtained by galvanized zinc. Electroplated brass, however, gives negative results with an antimony coating, the corrosion-resistance actually being decreased thereby.

The invention is illustrated diagrammatically in the drawing, in which 1 represents a ferrous metal base; 2, the original layer of zinc deposited thereon; 3, the original layer of copper upon zinc; 4, the corrosion-resisting layer, and 5, the rubber vulcanized thereto.

As an example of the invention, a ferrous base, such as a steel tire bead reinforcing wire, or a flexible steel strip, is first cleaned and is then galvanized with zinc. A preferred zinc coating is of the order of 1/4,000th to 1/11,000th of an inch in thickness. The galvanized base is then electrolytically plated with copper either by electrodeposition or electroplating. The proportion of zinc to copper is usually from 6 to 30 parts of zinc to one part of copper, and the thickness is of the order of 1/60,000th to 1/240,000th of an inch, generally being about 1/100,000th of an inch. Preferably the copper content is .75 to 1.20 grams per kilogram of wire of .037 inch thickness. A preferred process of producing a copper and zinc-coated article is described in my application 665,425, filed April 10, 1933, now Patent No. 2,002,261, dated May 21, 1935.

After copper-plating the object is transferred immediately to a bath containing an electrolyte of antimony or arsenic.

In the case of antimony, a satisfactory bath may be prepared by dissolving three ounces of sodium cyanide in one gallon of warm water, dissolving ½ ounce 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 copper-zinc coated material is immersed in the bath for a short period. The period of immersion should be sufficient to produce a coating of from 0.1 gm. of antimony per kg. of wire to .35 gm. of antimony per kg. of wire. Above .35 gm. per kg. the adherence of the rubber to the wire begins to be noticeably impaired. A preferred range is .11 to .19 gm. per kg., .15 gm. per kg., being preferred. These figures are for tire bead wire having a diameter of .037".

Tire bead wires, for which the invention is primarily intended, have a typical composition as follows:

	Per cent
Carbon	.65
Manganese	.80
Phosphorus	.015
Sulfur	.025
Silicon	.095

Balance is iron with traces of impurities.

For a coating having a weight of .15 gm. per kg. of a .037" wire the thickness is originally in the order of 1/613,000th of an inch. After leaving the plating bath the object is washed in cold water, then in hot water, and is quickly dried by hot air.

A zinc-copper coated steel tire bead reinforcing wire so treated will show 150–200% greater corrosion resistance as measured in a salt spray than a similar wire without the antimony coating. The adherence to rubber in each case will be almost identical.

In the case of arsenic, solutions may be prepared from the trisulfide in substantially the same molecular proportions shown for the antimony trisulfides. The arsenic increases the corrosion resistance by more than 150%. In each case the adherence to rubber is unimpaired.

In the case of arsenic, the coating should be from 0.06 gm. to 0.21 gm. of arsenic per kg. of wire. The preferred range is 0.066 gm. to 0.114 gm. per kg.

It is of course obvious that the invention is by no means limited to wires or strips, but may be applied to any other ferrous-base metals which it is desired to coat with rubber.

Instead of zinc, equivalents such as cadmium may be employed, either when eseparately plated or when applied originally as a cadmium brass.

The term "brass" as used herein includes cadmium brass. Mixtures of zinc and cadmium may be employed, and alloys in which zinc and/or cadmium predominate.

When deemed desirable, the galvanized coating may of course be strengthened by additional coatings, either electroplated or otherwise. When it is stated that copper is deposited on the galvanized coating, it is simply meant that copper is deposited on whatever coating is outermost, but that a galvanized coating is next to the iron.

The coating of antimony or arsenic is of course thin enough so that the brass below exerts an influence through it. The coatings are in the order of 1/250,000th to 1/1,000,000th of an inch.

This application is a continuation of my copending application Serial No. 749,467, filed October 22, 1934.

The foregoing detailed description has been 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 claim as new, and desire to secure by Letters Patent, is:

1. In the production of a metallic coated ferrous base article, the steps of separately coating said article with a thin layer of a metal of the class consisting of zinc and cadmium and mixtures thereof, and a layer of copper having a thickness less than approximately 1/60,000th" and of a thickness to alloy throughout with the zinc or cadmium at atmospheric temperature or at the temperature of vulcanization and produce a thin layer of brass thereon, and applying a thin layer of a metal of the class consisting of arsenic and antimony thereon, said layer being thin enough to alloy throughout with the copper.

2. The method as set forth in claim 1, in which the copper layer has a thickness of the order of 1/100,000th".

3. The method as set forth in claim 1, in which the copper has a thickness of the order of 1/100,000th" and the layer of arsenic or antimony has a thickness of the order of 1/750,000th".

4. The method as set forth in claim 1, in which the copper and the arsenic or antimony are applied electrolytically.

5. The method of increasing the corrosion resistance of a ferrous base which comprises hot galvanizing a layer of zinc on said object, electrodepositing a layer of substantially pure copper on the zinc, the thickness of the copper being such as to alloy throughout with the zinc at atmospheric temperature or at the temperature of vulcanization and produce a thin layer of brass thereon, immediately transferring the object to a bath containing a solution of a metal consisting of the class of arsenic and antimony, and electrodepositing a layer of said metal thereon.

6. A ferrous tire bead reinforcing wire having thereon a galvanized coating of zinc, a layer of copper on the zinc, said layer having a thickness less than approximately 1/60,000th" and of a thickness to alloy throughout with the zinc at atmospheric temperature or at the temperature of vulcanization and produce a thin layer of brass thereon, and a thin surface coating consisting originally and substantially entirely of a metal of the class consisting of arsenic and antimony thereon.

7. An article as set forth in claim 6, in which the arsenic or antimony layer has a thickness of the order of 1/613,000th".

8. An article as set forth in claim 6, in which the coating metal is arsenic.

9. An article as set forth in claim 6, in which the coating metal is antimony.

10. An article as set forth in claim 6, in which a rubber coating is vulcanized about said wire.

11. An article as set forth in claim 6, in which the thickness of the arsenic or antimony is from .000001" to .000004".

12. As an article of manufacture, a galvanized ferrous base having a layer of copper thereon of a thickness less than approximately 1/60,000th" and of a thickness to alloy throughout with the zinc at atmospheric temperature or at the temperature of vulcanization and produce a thin layer of brass thereon, and a thin layer thereon originally consisting substantially entirely of a metal of the class consisting of arsenic and antimony.

13. As an article of manufacture, a galvanized ferrous base having a layer of copper thereon of a thickness less than approximately 1/60,000th" and of a thickness to alloy throughout with the zinc at atmospheric temperature or at the temperature of vulcanization and produce a thin layer of brass thereon, and a thin layer thereon originally consisting substantially entirely of a metal of the class consisting of arsenic and antimony, and having a layer of rubber vulcanized thereon.

14. As an article of manufacture, a cadmium galvanized ferrous base having a layer of copper thereon of a thickness less than approximately 1/60,000th" and of a thickness to alloy throughout with the cadmium at atmospheric temperature or at the temperature of vulcanization and produce a thin layer of brass thereon, and a thin layer thereon originally consisting substantially entirely of a metal of the class consisting of arsenic and antimony.

15. As an article of manufacture, a ferrous base having thereon a hot dipped layer of the metal of the class consisting of zinc and cadmium and alloys thereof, and a thin layer thereon of copper, said layer having a thickness less than approximately 1/60,000th" and of a thickness to alloy throughout with the metal of the class consisting of zinc and cadmium and alloys thereof at atmospheric temperature or at the temperature of vulcanization and produce a thin layer of brass thereon, and a thin layer thereon consisting subtantially entirely of a metal of the class consisting of arsenic and antimony.

16. As an article of manufacture, a ferrous base having thereon a hot dipped layer of the metal of the class consisting of zinc and cadmium and alloys thereof, and a thin layer thereon of copper, said layer having a thickness less than approximately 1/60,000th" and of a thickness to alloy throughout with the metal of the class consisting of zinc and cadmium and alloys thereof at atmospheric temperature or at the temperature of vulcanization and produce a thin layer of brass thereon, and a thin layer thereon consisting subtantially entirely of a metal of the class consisting of arsenic and antimony, and having a layer of rubber vulcanized thereon.

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