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CORROSION RESISTANT COATING FOR FERROUS PRODUCTS

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This invention relates to corrosion resistant ferrous products and more particularly to a method for the protection of corrodible ferrous surfaces.

It is well known that some form of protection is necessary to prevent ordinary iron and steel products from rusting under atmospheric as well as marine exposure. The art of chemical treatment has been developed to offer temporary protection, but more particularly to offer a better base for subsequent painting or baked enamel finishing.

Non-ferrous metal coatings such as those of zinc, cadmium, tin, nickel, chromium and lead have commonly been applied to various metal products by galvanic or electrolytic deposition or by spraying or hot dipping. The ability of lead and zinc to withstand atmospheric corrosion has long been known and such coatings are usually applied by hot dipping. In all cases of hot dip coatings on iron and steel, certain numerous microscopic discontinuities known as pores or pin holes are always found despite the best efforts of those skilled in the art. It has been recognized that while heavier coatings reduce porosity, pin holes cannot be eliminated by increasing the thickness of coating metal.

It has been known that where the coating metal is of a nature more corrodible than iron, i. e., more anodic, such as zinc or cadmium, for instance, it is sacrificially corroded in a galvanic couple with iron. In such conditions, pin holes are not considered to be a serious problem until the coating metal in the immediate area of the pin hole is used up. In contrast to the foregoing, where the coating metal is less corrodible than iron or steel, for instance, lead or lead alloys, i. e. cathodic, no galvanic protection is obtained at exposed areas such as pin holes, and corrosion may be accelerated.

It is therefore, a principal object of this invention to provide an improved method for protecting corrodible ferrous metal surfaces. It is another object to provide a method for protecting corrodible ferrous metal surfaces which substantially eliminates pin hole failure of metallic coatings. It is a further object of this invention to provide a method for protecting corrodible ferrous metal surfaces with lead in which the corrosion producing galvanic effect is substantially eliminated. A still further object is to provide a coating which will protect corrodible ferrous metal surfaces from corrosion.

In its broadest aspects, this invention contemplates protection against corrosion of normally corrodible surface, such as that of ordinary iron

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or steel by first applying thereto an adherent coating of lead or a lead alloy and subsequently chemically treating the metal coated surface with an alkaline solution of dichromate and sulphate salts. After treatment with the alkali salt solution the surface is dried and preferably covered with a film forming and drying coating composition such as paint or lacquer.

The adherent lead or lead alloy coating may be applied by any convenient method; however, it is preferable to apply this by hot dipping. The coating should be uniform and may advantageously be from about 0.0002 to 0.001 inch in thickness. Such thickness provides sufficient metal for a complete uniform film as well as for reaction with the chemical treatment as hereinafter described in detail. The lead coating, may, if desired, comprise pure lead or may comprise a lead alloy for instance, containing minor amounts of tin or antimony, or other alloying metals or combinations of these.

The chemical treatment may be accomplished preferably by immersing the lead coated surface in the alkaline salt solution while maintaining same at an elevated temperature. Other methods of applying the solution may be employed if desirable or necessary, such as for instance, spraying. The solution comprises a ternary system in aqueous media of the following components:

(1) An alkali metal dichromate
(2) An alkali metal sulphate
(3) An alkali metal hydroxide

It is preferred from an economic standpoint to use sodium dichromate $Na_2Cr_2O_2.2H_2O$, sodium sulphate Na_2SO_4, and caustic soda NaOH; however, potassium or other alkali metal salts will produce substantially equivalent results. The solution should contain each of the component salts in amount from about 15% to 40% of the total solids content and the concentration should be about from 30 grams to about 120 grams of combined solids per liter. A commercially available wetting agent such as a sodium sulfate derivative of 2-ethyl-hexanol for instance, may be incorporated in the salt solution if desired in amount about 1% more or less.

Apparently, the chemical salt solution as described above reacts to some extent or degree with the lead coated surface. It has been found that an elevated temperature of from about 120° F. to about 170° F. is advantageous; also, the immersion time or contact period may vary widely, for instance, from about 10 seconds to several min-

utes, for instance, 5 minutes, and preferably from about 20 seconds to 60 seconds.

After immersion or treatment, excess solution is drained off or otherwise conveniently removed and the treated surface dried.

The lead coated and chemically treated surface will be found to exhibit remarkable corrosion resistance. The protection may, however, be vastly increased by applying thereon a coating of a film forming and drying surface coating composition such as, for instance, paint or lacquer. The enhanced protection thus obtained is one of the unique features of this invention and is apparently substantially greater than that normally expected from such coating. A synergistic effect on the resistance to corrosion imparted by the lead coated and chemical treated surface and the top film, paint or lacquer, for instance, is definitely indicated.

In order that this invention may be more clearly understood, the following examples are given:

EXAMPLE I

22 gauge cold rolled steel sheets, measuring 5¾" wide and 6' long, were subjected to preliminary degreasing with a customary alkaline cleaner, washing and pickling in a 10% sulfuric acid solution for 10 minutes at about 150° F., followed by washing in water. The sheets were then fed into the entrance rolls of a small coating machine through a one-half inch layer of anhydrous flux containing 80% zinc chloride and 20% sodium chloride, after which the sheet was passed into the molten alloy bath of a composition 2% tin, 98% lead, maintained at a temperature of between 680° F. and 700° F. The coated sheet emerged through exit rolls fluxed with a layer of similar flux to keep the rolls properly tinned. The speed of the rolls and immersion time factor was controlled to produce a thickness of approximately 0.00045" of lead alloy coating metal. The lead coated surface was then immersed in the alkaline chemical treating bath for 30 seconds at about 140° F. removed, the excess solution allowed to drain off and allowed to dry in air. The composition of the chemical treating solution was as follows:

	Grams per liter
Sodium dichromate	18
Sodium sulfate	18
Caustic soda	24
Sodium sulfate derivative (2-ethyl-hexanol)	10

EXAMPLE I*a*

To illustrate the employment of a top coat of a film forming and drying surface coating composition, a part of the sheet steel lead coated and chemically treated as in Example I was given a coat of commercial lacquer applied by spraying.

EXAMPLE I*b*

To further illustrate the employment of a top coat of a film forming and drying surface coating composition, a part of the sheet steel lead coated and chemically treated as in Example I was given a coat of commercial red lead paint applied by brushing.

EXAMPLE II

Cut sections of 16 mesh iron fly screen, 6" wide and 6' long, were degreased with a proper commercial cleaner, washed and then pickled in a 5% hydrochloric acid solution at room temperature for a few minutes. The screening was then fed into the entrance rolls of a small coating machine through a one-half inch layer of anhydrous 80% zinc chloride-20% sodium chloride flux, after which the screening passed into the molten alloy bath of a composition 2% tin, 98% lead, maintained at a temperature of between 680° F. and 700° F. The screening emerged through exit rolls which were kept well tinned by a thin layer of similar flux contained in a flux box and prevented from getting onto the roll nips by means of end baffles. The coated screen was then placed in the alkaline chemical treating solution similar to that described in Example I for about 30 seconds at about 140° F. and removed, drained and allowed to dry in air.

EXAMPLE III

It will be understood that in addition to the ferrous sheet and wire mesh screening shown in Examples I and II, this invention is also adapted to the treatment of small ferrous parts. A basket of cleaned small parts was immersed through a proper flux into molten coating bath of 2.25% tin, 2% antimony lead alloy for a period of time and at a temperature also similar to that described in Example I. Upon removal from the molten bath, the basket of parts was set in a suitable centrifuge and revolved at a speed of about 500 R. P. M. which was effective in throwing off the flux and excess metal clinging to the parts. After about 5 seconds of centrifuging, resulting in a layer of lead alloy coating metal of about 0.0003 inch thickness, the basket of coated parts was removed and dumped into running, cold water and the parts washed for a few minutes. They were then immersed in the chemical treating solution described in Example I a similar period of time and at a similar temperature and then centrifuged to remove excess treating solution and dried in air.

Specimens of the cold rolled steel products of Example I were selected for comparative tests with various forms of other ferrous coated materials commonly used. This test was the standard salt spray test conducted according to the method described in the American Society for Testing Materials Standard, 1944, Part I—Metals, beginning on page 1,843. All panels were 5¾" by about 2" with cut edges of exposed steel protected in the usual manner by red-lead-in-oil paste. Results of this test in which specimens are inclined at an angle of 45° and subjected to a 20% sodium chloride fog at about 95° F. for a number of hours are given in the following tables.

TABLE I

Illustrating the superiority of the protection afforded by the lead coating and chemical treatment method of this invention, as illustrated in Example I, over prior art coating methods.

Salt spray test

Sample	40 hrs.	144 hrs.	430 hrs.
Uncoated Steel	100% rust		
Galvanized steel (0.00063"Zn)	No rust	35% rust	100% rust.
Galvanized steel (0.00105"Zn)	do	5% rust	60% rust.
Lead alloy coated steel	do	do	50% rust.
Steel lead coated and chemically treated according to this invention (Example I)	do	No rust	5% rust.

As indicated above, the method of this invention provided protection only slightly impaired after 430 hours, compared to badly rusted surfaces on lead coated or galvanized sheet.

TABLE II

Illustrating the improved protection afforded by the lead coating, chemical treatment and lacquer combination according to this invention as illustrated by Example I*a*.

Salt spray test

	40 hrs.	430 hrs.
Steel sheet lacquered	100% rust.	
Steel sheet lead coated and chemically treated (Example I).	No rust.	5% rust.
Steel sheet lead coated, chemically treated and lacquered (Example I*a*).	do.	No rust.

Thus the coated treated and lacquered surface showed increased corrosion resistance over that which would have been expected considering the comparative effects of the lacquer alone and the coating plus chemical treatment above.

TABLE III

Illustrating the improved protection afforded by the lead coating chemical treatment and red lead paint combination as illustrated by Example I*b*.

Salt spray test

	40 hrs.	430 hrs.	1500 hrs.
Steel sheet painted with red lead paint.	no rust.	1% rust.	
Steel sheet lead coated and chemically treated (Example I).	do.	5% rust.	
Steel sheet lead coated, chemically treated and painted with red lead paint (Example I*b*).	do.	no rust.	no rust.

The above illustrated the unexpected result obtained in which more than 1500 hours' protection was afforded by the combination of treatments which individually each show less than 400 hours' perfect protection.

The film forming and drying surface coating composition may be applied to any type of surface previously lead coated and chemically treated. Thus the screen of Example II or the small metal parts of Example III may be further protected as for instance by a coating of paint or lacquer if desired. Salt spray tests made on such surfaces showed corrosion resistance generally comparable to those disclosed for metal sheet in Tables I, II and III.

The top coat of lacquer, paint or the like may be applied by conventional methods, such as dipping, brushing, or spraying. Its constitution may be determined by characteristics desired. For instance, the lacquer coating is advantageous where parts are to be subsequently soldered since the lacquer need not be removed prior to this operation. Red lead paint is useful where the ultimate in protection is desirable. Other types of paint or surface coating compositions may be used under conditions where their characteristics are important.

Accordingly, as shown by illustrated embodiments, the invention consists of a novel system of protective coatings on iron and steel products, the method being one which includes applying in combination an improved lead alloy coating and a subsequent novel chemical treatment which protects not only the lead alloy coating, but also exhibits a tendency to render passive the exposed iron and steel areas. For best results, sufficient thickness of lead alloy coating should be present to allow the chemical treatment to effectively exhibit its full protectiveness. The chemical treatment may be considered comparable to an initial corrosion of a lead surface wherein a minute layer of lead is used up in providing an adherent, protective coating which thereafter minimizes further atmospheric attack. As shown by increased corrosion resistance, the chemical treatment effectively seals the pin holes as well as protects the lead alloys surface, and rusting is minimized and substantially eliminated for long periods of time. This is in contrast to prior art metal coatings on ferrous products which on the one hand, in the case of more corrodible sacrificial coating metals rapidly offer themselves to the environment, and on the other hand, in the case of less corrodible coating metals, which generally cause iron to rust more rapidly at the unprotected pin hole areas.

While this invention has been described and illustrated by the examples shown, it is not intended to be restricted specifically thereto and other modifications and variations may be employed as limited by the following claims.

We claim:

1. Method for protection of a corrodible metal surface which comprises coating said surface with a metal selected from the group consisting of lead and alloys thereof with tin and antimony, said coating being of thickness between about 0.0002 and 0.001 inch, immersing said coated surface in a solution consisting essentially of an alkali metal hydroxide, an alkali metal sulphate and an alkali metal dichromate, the proportions of each being not less than 15% and not more than 40% of the total solids content of said solution, and water in amount to produce between about 30 grams and 120 grams of total solids per liter, at a temperature of from about 120° F. to 170° F. for a period of about 10 seconds to 5 minutes, removing said surface from said solution and drying the same.

2. Method for protection of a corrodible metal surface which comprises coating said surface with a lead tin alloy, said coating being of thickness between about 0.0002 and 0.001 inch, immersing said coated surface in a solution consisting essentially of an alkali metal hydroxide, an alkali metal sulphate and an alkali metal dichromate, the proportions of each being not less than 15% and not more than 40% of the total solids content of said solution, and water in amount to produce between about 30 grams and 120 grams of total solids per liter, at a temperature of from about 120° F. to 170° F. for a period of about 10 seconds to 5 minutes, removing said surface from said solution and drying the same.

3. Method for protection of a corrodible metal surface which comprises coating said surface with a lead antimony alloy, said coating being of thickness between about 0.0002 and 0.001 inch, immersing said coated surface in a solution consisting essentially of an alkali metal hydroxide, an alkali metal sulphate and an alkali metal dichromate, the proportions of each being not less than 15% and not more than 40% of the total solids content of said solution, and water in amount to produce between about 30 grams and 120 grams of total solids per liter, at a temperature of from about 120° F. to 170° F. for a period of about 10 seconds to 5 minutes, removing said surface from said solution and drying the same.

4. Method for protection of a corrodible metal

surface which comprises coating said surface with a metal selected from the group consisting of lead and alloys thereof with tin and antimony, said coating being of thickness between about 0.0002 and 0.001 inch, immersing said coated surface in a solution consisting essentially of an alkali metal hydroxide, an alkali metal sulphate and an alkali metal dichromate, the proportions of each being not less than 15% and not more than 40% of the total solids content of said solution, and water in amount to produce between about 30 grams and 120 grams of total solids per liter, at a temperature of from about 120° F. to 170° F. for a period of about 10 seconds to 5 minutes, removing said surface from said solution and drying the same and applying thereon a coating of a film forming and drying surface coating composition.

5. Method for protection of a corrodible metal surface which comprises coating said surface with a metal selected from the group consisting of lead and alloys thereof with tin and antimony, said coating being of thickness between about 0.0002 and 0.001 inch, immersing said coated surface in a solution consisting essentially of an alkali metal hydroxide, an alkali metal sulphate and an alkali metal dichromate, the proportions of each being not less than 15% and not more than 40% of the total solids content of said solution, and water in amount to produce between about 30 grams and 120 grams of total solids per liter, at a temperature of from about 120° F. to 170° F. for a period of about 10 seconds to 5 minutes, removing said surface from said solution and drying the same

and applying thereon a coating of red lead paint.

6. Method for protection of corrodible metal surface which comprises coating said surface with a metal selected from the group consisting of lead and alloys thereof with tin and antimony said coating being of thickness between about 0.0002 and 0.001 inch, immersing said coated surface in a solution consisting essentially of an alkali metal hydroxide, an alkali metal sulphate and an alkali metal dichromate, the proportions of each being not less than 15% and not more than 40% of the total solids content of said solution, and water in amount to produce between about 30 grams and 120 grams of total solids per liter, at a temperature of from about 120° F. to 170° F. for a period of about 10 seconds to 5 minutes, removing said surface from said solution and drying the same and applying thereon a coating of lacquer.

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