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METHOD OF COATING METALS WITH LEAD

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My invention relates to a method of coating metals with lead. It relates particularly to the coating of iron, steel, and other metals and alloys with lead, although it is not necessarily limited to the coating of the metals particularly enumerated.

Metals such as iron, steel and the like are subject to corrosion by the atmosphere. In the past, various methods have been adopted for the retardation or prevention of such corrosion. One of the most common methods of the prior art is to paint the surface of the iron, steel or other metal to be protected. However, this type of protection is temporary in nature and, as soon as any of the paint fails or wears off, the metal corrodes or rusts.

Another prior art method frequently used for protecting metals has involved the formation of an insoluble coating such as a phosphate film, this film being ordinarily supplemented by a covering coat of paint, lacquer, or the like. Here also, the protective coating is of a temporary nature.

Considerable effort has been devoted to the protection of metals of the type in question by covering them with a metal that is more resistant to corrosion. For example, zinc has been utilized as a covering coating for iron or steel, being normally applied by the hot galvanizing process, although both electroplating and the drydust or sherardizing process are used to a limited extent. The hot processes have certain drawbacks. For example, there is a tendency towards the formation of a brittle intermediate alloy layer between the iron and zinc which frequently results in rupture or flaking off of the coating when the coated metal is subjected to deforming processes in fabricating or the like. Electrodeposited zinc coatings are expensive to apply, and have to date found only limited use. One disadvantage is that such coatings can be applied only to relatively simple shapes. A zinc surface also possesses the disadvantage that it cannot be covered with an adherent coating of paint.

Considerable effort has also been devoted to the covering of metals of the type in question with tin or with terne, which latter is an alloy usually containing about 12 to 25 per cent of tin and the remainder lead. Processes of this type are relatively expensive because of the cost of the coating metal.

Some methods have also been utilized in the prior art for covering the metal to be protected with a coating of lead. The methods thus far used have been subject to certain drawbacks which have placed considerable limitation upon their use. Applying lead by hot-dipping results in a coating which is unduly thick and which is also of irregular thickness at different areas. It is extremely difficult to secure a coating free of pinholes and other surface imperfections. Lead has not been applied electrolytically to any great extent because of the poor quality of coating and because a lead coating can be more easily produced by hot-dipping than by electrodeposition. Likewise, the apparatus required for electrodeposition, the current costs and various factors render the electrodeposition processes unduly expensive.

There are various other drawbacks of the above-described processes for protecting metals of the types in question. Likewise, various other coatings for such metals have been utilized but these other coatings possess the same or other drawbacks as those indicated above. In other words, these prior art processes and coatings all have serious limitations, either from a technical or economic standpoint.

One object of this invention is to provide a protective coating for iron, steel, or other metals or alloys which will be more readily applied and which will be more effective than prior art coatings.

Another object of this invention is to provide a cheap and effective coating which will adequately protect metals of the type in question from corrosion.

Another object is to provide a cheap and effective coating that can be applied to articles of complicated shape or design, or to the inside of tubing, pipe and similar articles.

Another object of this invention is to provide a protective coating of such a character that lacquers, paint and other coating may be applied thereover.

Another object of this invention is to provide a simplified method for coating metals of the type in question with lead, with consequent advantages which will appear as this description progresses.

Still further objects of this invention will appear in the following description and claims.

This application is a continuation in part of my co-pending application S. N. 152,810, filed July 9, 1937.

One phase of this invention consists of the fact that I have discovered that iron, steel, copper, zinc, galvanized iron and other metals and alloys can be coated with a uniform and adherent film of lead by immersing them in certain aqueous baths containing lead. A bath that I have found satisfactory is an aqueous solution containing a lead salt and a metal cyanide. In the preparation of the bath any of a large number of ionizable lead compounds may be used, for example lead oxide, plumbite, cyanide, acetate, chloride, hydroxide, tartrate, oxalate, citrate, nitrate, sulphate, etc. Likewise, any soluble metal cyanide, for example, cyanides of the alkali-metals or alkaline earth-metals are suitable.

The amount of lead in the coating bath may vary within fairly wide limits. For example, in coating iron and steel I have found that it may vary within the limits 0.1 to 10 grams per liter. A bath containing less than 0.1 gram per liter is quickly exhausted and offers no economic advantage. I may in some cases use more than 10 grams per liter although the coatings are usually not so good. When steel is coated in a bath operated at 175 to 200 degrees F. I prefer to use from 3 to 5 grams per liter while at room temperature I prefer to use from 1 to 3 grams per liter, although the concentrations are not critical.

The amount of metal cyanide required depends on the metal to be coated, the temperature of the bath, and to some extent on the amount of additional substances contained in the bath. When a bath containing only a lead compound and sodium cyanide is used for coating iron or steel at 180 to 200 degrees F. the amount of sodium cyanide should preferably be greater than 15 grams per liter. When, in addition to the lead compound and sodium cyanide, a similar bath contained 100 grams per liter of sodium hydroxide, I have used as little as 5 grams per liter of sodium cyanide at 180 to 200 degrees F. and as little as 15 grams per liter at room temperature. The upper limit for aqueous sodium cyanide baths appears to be the saturated solution. Thus, concentrations of from 5 grams of metal cyanide per liter (computed as sodium cyanide) to the amount required to saturate the solution may be employed.

The following description illustrates the method of practicing this invention: The metal to be coated is properly cleaned by means well known to the art. It is then preferably pickled. Pickling is not an essential step in this invention, although in most instances I prefer to carry out the pickling operation. The metal is then immersed in the coating solution bath.

Immediately on immersion, a lead coat forms though a more prolonged immersion results in a heavier coating. For some purposes, I may wish to permit the article to remain in the solution for a period of 30 minutes or even longer. Present indications are that the period of immersion may range from two minutes to one hour, although this depends somewhat on the metal being coated and the particular bath being used. For coating iron or steel the minimum time is preferably about 5 minutes.

The temperature at which the bath is operated is not critical. Thus, iron, steel, copper, brass, etc., may be coated in solutions having any temperature from atmospheric to boiling.

After the coated article is removed from the coating bath, it may be rinsed or washed by means well known to the art. Articles of complicated shape and design can be coated by my process.

It is not essential in practicing this invention to add to the bath substances other than a metal cyanide and a lead compound. However, I have discovered that improved coatings and better operating conditions are obtained on adding certain other ingredients to the coating bath. The members of the first class of these substances which I may add appear to act as accelerating agents in the formation of the coating. The members of the second class of substances which I may add apparently influence the rate and uniformity of coating. The functions of the two types of addition agents are thus distinct and different.

Of these additional ingredients those of the first class are added in substantial amount and form one or more of the major constituents of the bath. Included in this group are such substances as alkali hydroxides, tartrates, oxalates, silicates, citrates, etc. When one or more of these substances are added to the bath the lead coatings obtained are heavier and thus more corrosion-resistant than lead coatings obtained from a bath containing only a lead compound and a metal cyanide. Some of the substances of this group also prevent the formation of a bath sludge by preventing the precipitation of insoluble lead salts. They thus prevent both contamination of the lead coating with floating sludge particles and loss of lead from solution by precipitation.

The amount of a substance of the first group, such as alkali hydroxide, tartrate, etc., which is used is to some extent arbitrary. In general the higher the concentration of, for example, sodium hydroxide, or of sodium potassium tartrate, with constant cyanide and lead concentrations, the smoother and heavier were the lead coatings obtained on steel at 180 to 200 degrees F. for a given time of immersion. These substances may substitute for a part, but not for all, of the cyanide. For by increasing the sodium hydroxide, for example, from 10 to 100 grams per liter the amount of sodium cyanide required to produce substantially equivalent lead coatings on steel at 180 to 200 degrees F. was decreased from about 35 to about 10 grams per liter. With no cyanide present no lead coatings were obtained.

The members of the second class of beneficial compounds are added to the bath in small amounts only, i. e. traces to about 2.5 grams per liter. Included in this group are sulphonated derivatives of naphthalene, soaps and soap-forming acids, thiourea and its derivatives, glues, gelatins, etc. When correctly used these substances increase the density, smoothness and corrosion resistance of the lead coatings. They furthermore stabilize the bath so that the lead coatings obtained are of uniform quality. The beneficial effects are retained to some extent even with the smallest measurable concentrations. Only small amounts of these substances are required in order to obtain the greatest benefit. It is undesirable to add too much because many of them when used in excess form precipitates which are detrimental in the operation of the bath. In cold baths best results are obtained with concentrations from 0.01 to 0.25 gram per liter; in hot baths with not over about 2.5 grams per liter.

In some instances I have found it desirable to employ the substances included in this second group by submerging the article to be coated in a solution containing the substance before immersing it in the lead coating bath.

The following are examples of baths successfully used:

I. For coating iron or steel at 180–200 degrees F.:

	Grams per liter
Lead nitrate	6
Sodium cyanide	100

II. For coating iron or steel at 180–200 degrees F.:

	Grams per liter
Lead monoxide	5
Sodium hydroxide	100
Sodium cyanide	10
Nekal BX (sulphonated derivative of naphthalene)	2.5

III. For coating iron or steel at room temperature:

	Grams per liter
Lead monoxide	1.5
Sodium hydroxide	100
Sodium cyanide	50
Nekal BX	0.05

IV. For coating copper or zinc at room temperature:

	Grams per liter
Lead monoxide	3
Sodium hydroxide	100
Sodium cyanide	25

The metal coated with lead may be used in that condition. For example, lead-coated iron or steel may be used to make roofing, automobile gasoline tanks, cans or other containers and in general can be used in any place where lead or terne plate is now used. I may also coat screen wire in this manner, and the product so made can be used on windows, doors, and for other purposes.

Lead-coated iron or steel has excellent resistance to atmospheric corrosion and to accelerated corrosion, such as salt-spray. I have discovered that the resistance to accelerated corrosion in salt-spray is greater than that of most phosphate-coated iron or steel. I have further discovered that a lead-coated surface prepared by the process of this invention is an excellent base for paint, lacquers, and the like. In the present art, refrigerator and automobile bodies are given a phosphate or similar coating before application of paint or lacquer. Exposure tests on lead-coated articles which were painted or lacquered showed that they were equal to or superior to painted or lacquered phosphate-coated articles.

It has also been discovered that lead-coated metal has an excellent surface for subsequent metal surface treatment. For example, a lead-coated article may be covered with a metal by electrodeposition or by hot methods, and the resultant surface is remarkably free from pinholes or other surface imperfections. Among the metals that can be applied to the lead-coated articles by electrodeposition are lead, tin, zinc, copper, cadmium, nickel, silver and chromium. Among the metals that can be applied to these lead-coated articles by hot processses are lead, zinc and tin.

Sheet iron or steel coated by my immersion process has other important advantages. For example, it has improved drawing or forming qualities, apparently due to the fact that the lead acts as a die lubricant. Likewise, a sheet of iron or steel the surfaces of which have been coated with lead by my process can be passed through rolls in the cold condition and the resulting surface is remarkably bright in appearance and uniform in texture.

It will be seen that my invention has resulted in a lead-covered surface which in itself is resistant to corrosion and which, in fact, is pleasing in appearance. Moreover, the surface is suitable for use as a base coat for paints, lacquers, enamels, electrodeposition, or hot-coating of metals or alloys.

Although in the above description I have referred to my process being used mainly for coating iron and steel, my process is not limited thereto. I have, for example, successfully coated zinc, aluminum, copper, brass, bronze, and magnesium by my process. The scope of this invention covers those metals or alloys which when immersed in the coating solution employed are higher than lead in the electromotive series of elements based on the potential of elements in the solution used.

From the above, it will be seen that my invention is a decided improvement in the metallurgical art. I have been able to produce coatings of lead on various metals and alloys of the types indicated by a process which is less expensive and less complicated than prior art processes which have been used for this purpose and which is, therefore, more economical. Furthermore, my process is free from most, if not all, of the drawbacks of the processes of the prior art. For example, I have been able to produce a lead coating on the metals and alloys described without the use of an electric current and have thus effected a material saving in equipment cost. Moreover, the coatings produced by my process are remarkably free of pinholes and other surface imperfections and are a decided improvement in this and other respects over those lead coatings previously produced by prior art methods. The coating can readily be applied to complicated sizes and shapes. Also, as indicated, the lead coatings which I have been able to produce constitute corrosion-resistant films which are a distinct improvement over the phosphate and similar corrosion-resistant coatings.

It is well known that lead is extremely resistant to corrosion and enjoys an enviable position in architectural and other fields. Thus, coatings of lead and tin on sheet iron, i. e. the so-called terne plate, find use in metal containers, especially those used for oil and other non-food products. Lead-coated copper is widely used in the building industry. In the past, many of these metallic articles have been coated with lead by a hot-dipping process. These coatings are characterized by incomplete coverage and by the lack of uniformity in the lead coating as well as by high cost, as indicated above. It is obvious, therefore, that my invention of cheaply applying an effective lead coating to metallic objects is a distinct advance in the art.

Having thus described my invention, what I claim is:

1. The method of forming a coating of lead on the surface of a metal or alloy which comprises contacting said surface with an alkaline aqueous solution containing an ionizable lead compound and at least 5 grams per liter of a compound selected from the class consisting of alkali metal and alkaline earth metal cyanides, for a sufficient time to form a permanent lead coating of sub-

stantial thickness on said surface without the aid of externally applied electric potential, said metal or alloy being from that group of metals which when immersed in said solution have higher electrode potentials than lead.

2. The method of forming a coating of lead on the surface of a metal or alloy which comprises contacting said surface with an alkaline aqueous solution containing an ionizable lead compound, at least 5 grams per liter of a compound selected from the class consisting of alkali metal and alkaline earth metal cyanides and a substance selected from the class consisting of alkali hydroxides, alkali oxalates, alkali tartrates, alkali silicates and alkali citrates, for a sufficient time to form a permanent lead coating of substantial thickness on said surface without the aid of externally applied electric potential, said metal or alloy being from that group of metals which when immersed in said solution have higher electrode potentials than lead.

3. The method of forming a coating of lead on the surface of a metal or alloy which comprises contacting said surface with an alkaline aqueous solution containing an ionizable lead compound and at least 5 grams per liter of a compound selected from the class consisting of alkali metal and alkaline earth metal cyanides, and an organic material effective to increase the density, smoothness and corrosion-resistance of the lead coating, for a sufficient time to form a permanent lead coating of substantial thickness on said surface without the aid of externally applied electric potential, said metal or alloy being from that group of metals which when immersed in said solution have higher electrode potentials than lead.

4. A method as claimed in claim 1, wherein said solution contains from 0.1 to 10 grams per liter of lead.

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