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LEAD COATING PROCESS

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This invention relates as indicated to lead coatings, and more particularly to protective coatings for metal surfaces subject to corrosion, especially iron, steel and ferrous alloys.

The tendency of the less noble metals to revert to their naturally occurring states has been recognized since their first employment, and many different methods have been adopted in an attempt to prevent, arrest or inhibit such corrosion or "rusting." It has been estimated that the annual monetary loss due to corrosion in the United States alone is in excess of \$5,500,000,000. Of course, indirect losses due to escape of such materials as oil, water, natural gas and other fluids from corroded pipe lines and losses due to down time in transportation facilities and manufacturing plants are difficult to appraise accurately. It should also be appreciated that construction members and processing equipment, for example, are regularly over-designed to compensate in part for anticipated corrosion. Very large industries have developed providing methods and materials for protecting metal surfaces, including paints, varnishes, lacquers, phosphate coatings, tin plating, galvanizing, and other plating procedures such as the electroplating of zinc, cadmium, copper and nickel. Cathodic protection of pipe lines and the like has recently been developed on a large scale. Obviously, in view of the tremendous quantity of ferrous metals in use, any method of protecting the same even slightly more effectively than methods currently employed would result in a comparable extremely large annual dollar saving.

Each of the known methods of protecting ferrous metal surfaces has certain inherent deficiencies and each such method will ordinarily be employed only in certain selected fields of use. Protective organic coatings, which include the paints and lacquers, are reasonably effective as long as the protective film is not broken, but they tend to be rather expensive and often their cost is justified on the basis of their decorative qualities equally with their protective qualities. The application of metallic coatings both by hot dipping and electroplating is also an old art. The less noble metals such as zinc are generally anodic with respect to iron in most environments and are classified as sacrificial. The protective coating gradually corrodes away and affords considerable protection as long as a continuous film remains. There are situations, however, where zinc as well as lead, tin, cadmium and aluminum will reverse its potential with respect to iron and consequently the position in the electromotive series cannot be wholly relied upon as an infallible index for predicting the galvanic behavior of metallic couples in all environments. Coatings of non-sacrificial metals such as nickel and copper may also form galvanic cells with iron although the current flow is in the opposite direction to that in the case of the sacrificial metals, resulting in accelerated corrosion of the base metal wherever the coating is broken or porous. Relatively thick coatings of such non-sacrificial metals are accordingly commonly employed.

Hot dip methods of applying protective metal coatings have certain advantages over similar coatings electrode-

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posited but also display certain inherent weaknesses. Thus, hot dip galvanized steel may develop cracks when flexed due to the formation of a hard zinc-iron alloy which is brittle and has poor adhesive properties. The hot dip method and the electroplating method both tend to produce coatings rather non-uniform in thickness.

It is accordingly a principal object of the present invention to provide a protective lead coating for metal surfaces subject to corrosion, particularly iron, steel and the ferrous alloys.

Another object is to provide such coating which will be considerably less expensive than other coatings commonly employed for a like purpose.

A further object is to provide such coating and method of application of the same which will be adapted to substantially all sizes and shapes of articles to be protected and will afford a predictable uniform degree of protection.

Still another object is to provide such coating which will not interfere with subsequent working of the article or the application of other decorative coatings and the like but instead will facilitate the same.

Other objects of this invention will appear as the description proceeds.

To the accomplishment of the foregoing and related ends, said invention then comprises the features herein-after fully described and particularly pointed out in the claims, the following description setting forth in detail certain illustrative embodiments of the invention, these being indicative, however, of but a few of the various ways in which the principle of the invention may be employed.

Briefly stated, our invention comprises the provision of a continuous lead coating on the metal surface to be protected by chemical displacement from a bath containing the lead ion in solution. More particularly, we have found that a remarkably effective lead coating may be deposited on ferrous surfaces from a bath having a pH less than 7 and containing one or more aliphatic mono-basic hydroxy acids.

The aliphatic mono-basic hydroxy acids such as glycolic, lactic and gluconic acid form soluble lead salts which do not require the presence of ammonium or alkali metal salts as solubilizers. Since these lead salts are highly soluble, it is possible to obtain a high lead ion concentration, and the hydrolysis of iron is repressed as the result of the presence of the hydroxy groups. Other examples of such acids are glyceric and erythronic which, however, are relatively expensive.

Lactic acid may be selected as a particularly suitable aliphatic mono-basic hydroxy acid for our purpose inasmuch as it is relatively inexpensive and commercially available in large quantities. It was found that a water bath containing lead lactate should be maintained at a pH of from about 2.5 to about 5.0 and preferably 3.4 to 4.2 and the lead ion concentration should be maintained in the range of from about 50 to about 250 grams per liter. Where the lead ion concentration is considerably below that indicated, the lead coating deposited on a ferrous article immersed in the bath will be found to be relatively coarse in crystalline structure, poorly adherent to the base metal and lacking in malleability and ductility. More satisfactory deposits were obtained utilizing lead ion concentrations of from about 100 to 250 grams per liter but when concentrations exceeding 300 grams per liter were employed the resultant coatings were found to have poor adhesion to the base metal, and the rate of deposition was appreciably reduced and the surface was non-uniformly coated. In general, it was found that for consistently satisfactory results under normal operating conditions it is desirable to maintain a lead ion concentration of from about 90 to about 140 grams per liter.

Utilizing a water solution of lead lactate having a lead ion concentration of 120 grams per liter, it was found that a lead coating of maximum thickness could be deposited at a temperature of approximately 170° F. and a pH of 4.2. As a general working range, however, for commercial operation a pH of 3.8+ or -0.2 may readily be maintained and affords excellent results.

It has also been found that whereas an increased operating temperature tends to accelerate the deposition of the lead from solution the ultimate thickness of the coating obtainable will be somewhat less than when the deposition takes place at a lower operating temperature. Since the rate of deposition is reasonably rapid at 170° F. and a considerably thicker coating is ultimately obtainable than when the bath is operated at a temperature of, for example, 200° F., it is contemplated that the normal operating temperature will range between approximately 170-190° F., as indicated, in the case of the lead lactate bath. A satisfactory deposit may be obtained from a solution at boiling point but it will not be as thick as when a lower temperature is employed and such operating conditions are obviously relatively impractical. Temperatures in the upper end of this range will ordinarily be employed only when speed is of the essence and a temperature below 155° F. will seldom be employed where a reasonable rapid rate of production is desired. Nevertheless, if the article to be coated may be left in the bath for an extended period (e. g. overnight) then a reasonably satisfactory coating may be achieved at room temperature (70° F.) or even somewhat lower.

It has, of course, been generally known prior to this invention that lead as well as other metals could be plated out of solution by chemical displacement but commercially acceptable coatings have not previously been obtained by this process. In the past such coatings have been extremely thin, coarse of texture, poorly adherent, and full of pin-holes, rendering any protection afforded very slight.

Addition agents

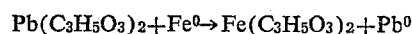
While an excellent lead protective coating can be obtained by carefully following the teachings of this invention without the employment of special addition agents, much less care need be exercised when addition agents of the type commonly added to electroplating baths for the purpose of ensuring sound metallic deposits are employed. Typical addition agents include: Carbohydrates such as the simple sugars, dextrose, maltose, sucrose and lactose; and the more complex carbohydrates such as dextrin and the starches were found to function satisfactorily. Both animal and vegetable proteins such as casein, bone glue, albumin, gelatin and zein served equally well. Some organic acids such as tannic, pyrogalllic, salicylic and gallic also produced the desired effect as addition agents. Special classes of chemical compounds such as aldehydes, furfurals, phenols, cresols, aloin, goulac, licorice, resorcinols, naphthols, gums and amines served as satisfactory addition agents. The concentration of addition agent in all cases was very small, usually in the range of 0.1 to 1 gram per liter of solution. Greater or less amounts could be used, but in most cases, the concentrations indicated were preferred for commercial operation.

Since some impurities such as traces of certain sugars commonly found in commercial grades of acids contemplated herein such as lactic acid may themselves serve the purpose of "addition agents," such less expensive grades may be preferred to chemically pure acids although a supplemental addition agent will also ordinarily be added. Of course, contaminants which would interfere with the displacement reaction or deleteriously affect the coating will be avoided. The precise manner in which such addition agents operate to achieve the improved results has never been wholly understood in

the electroplating art and is equally mysterious here. Their presence, however, definitely permits the obtaining of satisfactory coatings throughout a wider range of operating conditions, serving to inhibit grain crystallization.

Iron build-up and control

Of course, as the lead is deposited on the ferrous surface a corresponding amount of iron will pass into solution and in due course of time a substantial change in the composition of the solution will result. A probably reaction mechanism can be written as follows:



The theoretical weight of lead thus deposited may be computed by multiplying the increase in weight of the article being plated by a factor of 1.37. By actual test it is found that the reaction yield is nearly 100%, a factor of 1.38 being obtained.

Plating of lead by chemical displacement from a solution prepared from the aliphatic mono-basic hydroxy acids continues satisfactorily despite a considerable build-up of ferrous ion concentration and this greatly facilitates control of commercial operations. Thus, for example, at a temperature of 185° saturation will occur at a concentration of about 25 to 30 grams per liter of ferrous ion, the ferrous lactate beginning to crystallize and precipitate. However, 100 grams per liter or approximately one pound per gallon of lead can be deposited before ferrous ion saturation occurs. While satisfactory lead deposits are obtained from solutions saturated with ferrous ion, nevertheless subsequent rinsing operations are somewhat facilitated if crystallization of ferrous lactate during operation is avoided. Ferrous lactate is readily soluble in cold water and is therefore not a serious problem even when crystallization does occur. Its removal from the plating bath may be conveniently achieved by cooling the bath, whereupon a large proportion will precipitate and may be removed by decanting or, preferably, by filtration.

Commercial operating conditions

In preparing the bath or solution, a lead acid concentrate of any of the water soluble aliphatic mono-basic hydroxy acids may be used. After the concentrate has been prepared, it may be diluted to any lead ion concentration desired between 50 and 400 grams per liter of lead ion but the preferred concentration will ordinarily be about 120 grams per liter. By way of illustration, a concentrate having 500 grams per liter of lead ion may be prepared as follows:

A slurry of 585 grams PbO (litharge, 85% lead) in 375 ml. of water is prepared and while agitating slowly 526 ml. of lactic acid (85%) are added, increasing agitation as the acid addition nears completion. Some heat may be required completely to solubilize the lead oxide or hasten such solution. A clear solution of lead lactate is obtained having a density of about 1.665 grams per ml. or 13.9 pounds per gallon. This concentrate may be diluted as desired or added to an operating bath to maintain the strength of the latter. A typical preferred solution might contain:

Components	Gms./Liter	Lbs./Gal.
Lead oxide (mono).....	140.0	1.17
Lactic acid (80%).....	168.0	1.40
"Addition agent".....	0.1-1.0	-----
Water to make up to volume.		

The above formulation will contain approximately 120 grams per liter of lead ion. Inasmuch as the ingredients are commercially available at reasonable prices and the method of preparation of the solution is simple, the cost of the bath is very low. Obviously, a feasible method to

reclaim the lactic acid from the ferrous lactate produced could further greatly reduce this cost.

To control the lead ion, it is necessary only to analyze for iron in solution, and determine the specific gravity. The following chart illustrates the effect of accumulated iron on the solution at given concentrations of lead ion.

Pb++ Conc., Gms./L.	Specific Gravity @ 185° F. Containing X Gms./L. of Iron					
	0	5	10	15	20	25
132.....	1.140	1.150	1.160	1.170	1.180	1.190
128.....	1.135	1.145	1.155	1.165	1.175	1.185
124.....	1.130	1.140	1.150	1.160	1.170	1.180
120.....	1.125	1.135	1.145	1.155	1.165	1.175
116.....	1.120	1.130	1.140	1.150	1.160	1.170
112.....	1.115	1.125	1.135	1.145	1.155	1.165
108.....	1.110	1.120	1.130	1.140	1.150	1.160
104.....	1.105	1.115	1.125	1.135	1.145	1.155
100.....	1.100	1.110	1.120	1.130	1.140	1.150

Although this method is not infallible, control can be exercised within 5% which is adequate for commercial operation. If, for example, by analysis, the iron was determined to be 10 grams per liter and the specific gravity was determined to be 1.135, the column to the left indicates the presence of 112 grams per liter of lead ion. If the initial concentration was 120 grams per liter, the operator would know that 8 grams per liter of lead had been deposited and needed to be replaced to maintain the initial strength of the solution.

The solution may desirably be prepared initially in the form of a concentrate having from 1000 to 200 grams per liter of lead ion, a greater concentration affording a too thick syrupy solution, difficult to handle, and a lower concentration being relatively ineffective to replenish a depleted bath as well as containing an unnecessary amount of water if the solution is to be shipped. A range of from 800 to 500 grams per liter is better for practical purposes and a concentration on the order of 800 is preferred.

One of the interesting features of the novel coating solution of this invention is its versatility in mode of application. Satisfactory deposits can be obtained by immersion, brushing on, flow coating, and spraying. The last-named method is often especially advantageous since much of industry is geared to spray coat various types of materials for chemical surface treatment of metals as phosphating, chromating, and the like. The mode of application will generally be dictated by the facilities available and the size and shape of the articles to be coated. Insofar as we are informed, the deposition of a metal coating by chemical displacement from a spray application has never before been successfully achieved.

As might be expected, the rate of deposition is greatest at the start of the operation and gradually lessens with time. The solutions may be prepared so that peak reaction equilibrium producing maximum thickness of coating will occur in five, ten or fifteen minutes, for example. Sound deposits having a thickness of 0.0003 inch are easily obtainable and deposits having a thickness of 0.0005 to 0.00075 inch may be obtained when employing properly adjusted solutions. Coatings of such thicknesses are much heavier than any obtainable by prior methods and are ample effectively to protect the underlying ferrous surface from corrosion.

It will, of course, be appreciated that before the work is coated it should first be free of all oil, grease and dirt. Such prior cleaning operation may, for example, include vapor degreasing or preferably treatment with a chemical cleaner such as the commercially available alkali, emulsion or two-phase cleaners. Following such cleaning operation, the work should be thoroughly rinsed in water, and if free of rust and scale it need not be acid pickled. If pickling should be required, however, the work will again be thoroughly water rinsed after completion of the pickling operation. It will then be conveyed to the processing tank or spray booth where metallic lead is deposited thereon

to the desired predetermined thickness. Subsequently, the work will be rinsed first in cold water and then in hot water to facilitate drying, forced warm air drying being preferred.

The lead coated article may receive supplemental surface treatments such as chromating, oxalating, sulphating and phosphating in dilute solutions. Under proper conditions, the lead may be bright-flowed which further enhances its corrosion retarding ability. As a rule, however, these various supplemental treatments will be found unnecessary. More frequently, the finished coated article will merely be painted or oiled, the surface being particularly suited therefor.

Corrosion and weathering tests have shown ferrous articles coated in accordance with the present invention to be exceptionally resistant to corrosion. Ferrous articles lead coated in accordance with this invention will withstand approximately 48 to 120 hours in the conventional salt spray test cabinet and, if oiled, considerably longer.

The employment of lead coatings to facilitate deep drawing operations and the drawing of wire, and particularly the drawing of steel wire, has been suggested since it has been determined that lead is a lubricant in such drawing operations superior to the usual greases, oils, soaps, emulsions, etc., but such other methods have been generally adopted in the industry for the reason that no economical method of applying the lead coating has previously been available. Thin lead coatings may also serve efficiently as a bearing metal in other applications.

Reclamation of aliphatic mono-basic hydroxy acids

A process has been described above whereby a lead coating may be deposited upon an iron, steel or ferrous article by chemical displacement from a solution of a lead salt of an aliphatic mono-basic hydroxy acid. Lead lactate is disclosed as a preferred example of a lead salt suitable for such purpose. As explained, however, the ferrous salt of the aliphatic mono-basic hydroxy acid which is formed by the reaction, gradually accumulates and will periodically be removed, additional lead salt being added from time to time to maintain proper operating concentration. Inasmuch as those aliphatic mono-basic hydroxy acids which are commercially available in any quantity, such as lactic acid, are quite valuable, it is readily apparent that the cost of the chemical displacement reaction may be much reduced if the acid can be reclaimed from the ferrous salt produced, and reused in the preparation of additional lead salt.

It is accordingly another object of this invention to provide a novel method of reclaiming aliphatic mono-basic hydroxy acids from the ferrous salts thereof, and more particularly lactic acid from ferrous lactate.

A further object is to provide such method which will be relatively inexpensive in operation and thus result in a considerable financial saving in the cost of raw materials required for the maintenance of a chemical displacement reaction for the deposition of a lead coating on ferrous articles from a solution of the lead salt of such aliphatic mono-basic hydroxy acid.

Still another object is to provide such method of reclaiming the acid which will also result in reclaiming the iron content in a form having considerable commercial value.

As explained above, a very superior protective lead coating may be produced on the surface of iron, steel and ferrous articles generally by immersing such article in a solution of a lead salt of an aliphatic mono-basic hydroxy acid such as glycolic, lactic and gluconic acid, for example. In a preferred embodiment, a water solution of lead lactate having a lead ion concentration of from about 100 to 250 grams per liter may be employed at an operating temperature of from approximately 170° to 190° F. "Addition agents" of the type commonly added to electroplating baths for the purpose of ensuring

sound metallic deposits may be utilized in very small amounts.

When metallic lead is deposited upon the surface of a ferrous article immersed in a water solution of lead lactate at a temperature of 185° F., for example, a corresponding amount of ferrous lactate is formed. When a considerable quantity of ferrous lactate has accumulated and the solution is then cooled, a very large proportion of the ferrous lactate will precipitate and may be removed by filtration. It will, of course, carry with it a trace of lead lactate. The precipitate is now dissolved in hot water and treated with an excess of sulphuric acid to produce a precipitate of lead sulphate which is filtered out, washed and dried. The filtrate which now comprises the ferrous lactate, lactic acid and sulphuric acid is treated with an excess of an alkaline earth metal hydroxide such as barium or calcium hydroxide, preferably the latter, and the precipitate filtered, washed and dried. This precipitate comprises calcium sulphate and ferrous hydroxide, and the filtrate comprises calcium lactate together with the remaining unreacted calcium hydroxide. Now upon the addition of sulphuric acid, a precipitate of calcium sulphate is formed completely removing the calcium from the solution. This precipitate will also be washed and dried. The filtrate comprises a solution of lactic acid together with any remaining excess sulphuric acid. By adding lead oxide (litharge) to such filtrate, the sulphuric acid is removed as lead sulphate which is filtered out, washed and dried, and the filtrate now comprises a solution of lead lactate ready to be added to the chemical displacement bath to maintain the latter at proper concentration for continued deposition of a lead coating on the ferrous article by chemical displacement.

Based on current market prices, the cost of the necessary indicated chemicals required in the above steps to reclaim one ton of lactic acid is relatively low and the product thus reclaimed is worth approximately \$500 per ton. The margin is more than ample to cover the cost of labor and facilities required and makes the employment of lead lactate or other lead salt of an aliphatic mono-basic hydroxy acid as a source of lead ion for deposition on ferrous articles even more attractive.

The ferrous hydroxide produced may also be heated in the presence of air to form ferric oxide having a substantial value as a pigment and polishing material. As a charge for steel making furnaces, it has a value of approximately \$50 per ton. In view of the foregoing, it will be seen that it is possible to deposit a pound of lead coating by chemical displacement from a lead lactate solution at a material cost much less than would be the case if the lactic acid were not thus cheaply reclaimed.

In general, it will be seen that we employ lead salts of aliphatic mono-basic hydroxy acids in water solution having a pH of less than 7. The salts other than lead lactate are best employed in comparable preferred ranges of pH, lead ion concentration, and temperature. The salts of lower molecular weights are preferred as being more readily water-soluble. The desired solution may be made up by dissolving a water-soluble lead salt of an inorganic acid, such as lead nitrate, and then adding the correct amount of the aliphatic mono-basic hydroxy acid but it is preferred to prepare the solution as described above. The pH may be adjusted in the usual way by addition of further aliphatic mono-basic hydroxy acid, or of an ammonium or alkali metal hydroxide such as sodium hydroxide, as may be required. Some complexes may be formed which tend to remain in solution over a wider pH range.

It is possible to pass a current through the bath to electroplate an additional coating of lead, if desired, but a great advantage of our new process is the fact that an excellent coating for most purposes may be obtained without such additional steps.

The aliphatic mono-basic hydroxy acids ordinarily employed to form the lead salt will of course normally be

relatively low molecular weight mono-basic hydroxy fatty acids, more particularly carboxylic acids.

Other modes of applying the principle of the invention may be employed, change being made as regards the details described, provided the features stated in any of the following claims or the equivalent of such be employed.

We therefore particularly point out and distinctly claim as our invention:

1. The method of forming a protective substantial, sound, adherent lead coating on ferrous articles which comprises subjecting such article to the action of a water solution of a lead salt of an aliphatic mono-basic hydroxy acid having a pH below 7 and a lead ion concentration of from about 50 to 250 grams per liter at a temperature of from 155° to 200° F. for a period of time sufficient to deposit a lead coating of at least 0.0003 inch thickness on such article by chemical displacement.

2. The method of forming a substantial, sound, adherent lead coating on ferrous articles which comprises subjecting such article to the action of a water solution of a lead salt of an aliphatic mono-basic hydroxy acid having a pH below 7 and a lead ion concentration of from about 50 to 250 grams per liter at a temperature at least as high as 155° F. for a period of time sufficient to deposit a lead coating of appreciable thickness on such article by chemical displacement, such solution also containing a small amount of an organic soundness-enhancing addition agent for inhibiting grain crystallization, of the type commonly added to electroplating baths.

3. The method of forming a substantial, sound, adherent lead coating on ferrous articles which comprises spraying such article with a water solution of a lead salt of an aliphatic mono-basic hydroxy acid having a pH below 7 and a lead ion concentration of from about 50 to 250 grams per liter at a temperature at least as high as 155° F. for a period of time sufficient to deposit a lead coating of appreciable thickness on such article by chemical displacement.

4. The method of forming a substantial, sound, adherent lead coating on a ferrous article which comprises spraying such article with a water solution of lead lactate having a pH of from 2.5 to 5.0, and a lead ion concentration of from 50 to 300 grams per liter, at a temperature of from 155° to 200° F., for a period of time sufficient to deposit such coating on such article by chemical displacement.

5. The method of forming a substantial sound adherent protective lead coating on ferrous articles which comprises subjecting such article to the action of a water solution of lead lactate having a pH of from about 2.5 to about 5.0, a lead ion concentration of from about 50 to about 300 grams per liter, and an operating temperature of from about 155° F. to about 200° F. for a period of time sufficient to deposit a continuous corrosion-resistant lead coating on such article by chemical displacement.

6. The method of forming a substantial sound adherent protective lead coating on ferrous articles which comprises subjecting such article to the action of a water solution of lead lactate having a pH of from 3.4 to 4.2, a lead ion concentration of from about 100 to about 250 grams per liter and an operating temperature of from about 170° F. to about 190° F. for a period of time sufficient to deposit a continuous corrosion-resistant lead coating on such article by chemical displacement.

7. The method of forming a substantial sound adherent protective lead coating on ferrous articles which comprises subjecting such article to the action of a water solution of lead glycolate having a pH below 7 and a lead ion concentration of from about 50 to 250 grams per liter at a temperature of from 155° F. to 200° F. for a period of time sufficient to deposit a continuous corrosion-resistant lead coating on such article by chemical displacement.

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