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CORROSION RESISTANT COATING FOR METAL SURFACES

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This invention relates to the art of producing corrosion-resistant coatings on the ferrous, zinc, cadmium and other metal and alloy surfaces.

The invention relates more particularly to a process for accelerating the production of phosphate coatings upon the surfaces of these metals. Furthermore, the invention relates to the attaining of phosphate coatings superior to similar coatings previously produced in the art.

It is well known that in order to obtain the best protective coatings, metallic surfaces must be thoroughly cleaned of greases, oils, dirts, acids and the like before the application of acid phosphate solutions capable of reacting with the metal surface to provide an adherent phosphate coating thereon. Various cleaning compositions have been suggested for this purpose. It has been discovered that a mineral acid solution is undesirable as a cleaning or pickling agent, since the acid solution appears to passivate the metal surface to greatly diminish the formation of the protective phosphate coating as well as to hinder the complete coverage of the metal surface. Further, strong alkalies have been found not to be entirely satisfactory since it is extremely difficult to completely remove the alkali film from the surface of the metal. When the metal carrying a thin film of alkali solution thereon is introduced into the acid phosphate coating solution, the formation of a protective coating is hindered. In addition, the alkali film neutralizes the acidity of the phosphate coating solution, thereby requiring the replenishing of the acid at frequent intervals.

The object of this invention is to provide a composition capable of simultaneously cleaning and activating metal surfaces for the subsequent formation of protective phosphate coatings at an accelerated rate as well as with optimum surface coverage.

A further object of the invention is to provide for stabilizing an activating agent to prolong the effective life thereof.

A still further object of the invention is to provide for combining a disodium phosphate and metal compound activating agent with amine soap in order to provide for a longer active life for the activating agent.

Other objects of the invention will in part be obvious and will in part appear hereinafter.

According to this invention, an activating agent composed of disodium phosphate combined with a compound of a metal selected from the group consisting of titanium, zirconium, tin, and arsenic is associated with an amine soap in order

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to prolong the effective life of the activating agent. The amine soap is preferably, but not necessarily, present as an emulsifying agent for a hydrocarbon solvent dispersion present with the activating agent for the purpose of simultaneously cleaning the metal surfaces.

The activating agent is prepared by adding to an aqueous solution of disodium phosphate a water soluble compound of one of the multivalent metals, titanium, zirconium, tin and arsenic. Suitable water soluble metal compounds are titanium tetrachloride, titanium trichloride, titanium hydroxide, titanium potassium oxalate, zirconium chloride, arsenic oxides, tin chlorides, and tin sulphates. Obviously, other water soluble compounds of the metals may be employed. The aqueous solution is evaporated to dryness at temperatures above 60° C. with slow heating. The residue after all the water is driven off is finely pulverized in order to facilitate dissolving in water for subsequent use. The proportion of the multivalent metal in the dried residue may vary from 0.005% to 20% by weight of the whole. Hereafter, it will be understood that the term "disodium phosphate combined with a compound of a multivalent metal selected from the group consisting of titanium, zirconium, tin and arsenic" denotes the combination of disodium phosphate and the multivalent metal compound in an aqueous solution and evaporating to dryness.

It is believed that the addition agent prepared by combining disodium phosphate with one of the metal compounds described produces a certain amount of colloid. The presence of the colloid apparently determines the activation of ferrous and zinc metal surfaces to which an aqueous solution of the disodium phosphate and metal compound is applied. It has been found that if the aqueous solution of the activating agent is permitted to stand for more than one day, metal articles dipped therein are not activated to the extent they would be activated if immersed in the well stirred, freshly made solution. Stirring or spraying the solution appears to maintain the colloid in suspension and successful activation of the metal surfaces is secured for prolonged period of time of use.

There are many applications wherein it is not convenient or practical to continually stir the activating solution or to apply it to the metal members in the form of a spray. For example, the solutions may be used infrequently, or in small tanks, or the scope of use is so small as not to justify expensive spray equipment. The problem,

therefore, of maintaining the effectiveness of the activating solution is critical in such applications. However, even in large scale use, it is often more economical to dispense with spray equipment and use only still tanks. It has been discovered that an amine soap applied to the aqueous solution of the activating agent has the unexpected property of maintaining the colloidal portion of the activating agent in suspension indefinitely whereby the activity of the solution does not change even though the solution is in a tank where no stirring or agitation is present. The solution with the amine soap may be employed after a week's non-use with successful results.

One method for prolonging the effective life of the activating agent is to prepare a mixture of equal parts of disodium phosphate combined with the metal compound, a fatty acid, such as oleic acid, and an amine, such as triethanolamine, with sufficient water to make a fluid paste. The triethanolamine and oleic acid react at once to form a soap. The mixture is then admixed with water in quantities sufficient to produce an activating aqueous solution having from 0.01% to 5% disodium phosphate. The aqueous solution will remain active for a week or more when used as a still bath in which ferrous and zinc metal surfaces are immersed. From 15 seconds to one minute is all the time required to activate the metal surfaces in such solution. The activating agent may be admixed with the amine soap prepared separately. The aqueous solution may be sprayed or otherwise applied to the metal members than by use in a still tank with good results. The amine soap is particularly advantageous even when used by spraying in case the solution is employed only intermittently.

In preparing the amine soap, numerous alkaline amine compounds capable of reacting with fatty acids to form soaps may be employed. For example, monoethanolamine, diethalonamine, triethanolamine, diethylethanolamine, morpholine, aminoethylethanolamine, trisopropanolamine, propylenediamine, and ammonium hydroxide are suitable amines for this purpose. Various fatty acids in particular acids having more than 12 carbon atoms in the chain may be combined with the amine to form a soap. Particularly successful results may be secured with oleic acid, palmitic acid and stearic acid.

The proportion of amine to the fatty acid may be varied. Good results have been obtained where the proportion of amine has varied from twice the weight of the fatty acid to as little as 15% of the weight of the fatty acid. The soap may be prepared independently by admixing the amine with the fatty acid and then adding to the disodium phosphate activating agent or by adding the fatty acid and amine to the disodium phosphate activating agent in water and thus initiating the soap forming reaction. The proportion of soap to the disodium phosphate activating compound is at least 10% of the weight of the disodium phosphate activating agent. Where extremely dilute solutions of disodium phosphate activating agent are prepared, the proportion of amine soap to the activating agent should be a little greater than where the disodium phosphate compound is employed in proportions of 1% to 2% of the aqueous solution.

The amine soap has been found to be an effective suspending agent not only when added to the aqueous solution solely for this purpose, but likewise when employed in combination with an emulsion type solvent cleaner. The amine soap is a satisfactory emulsifying agent for a hydrocarbon solvent such, for example, as kerosene, fuel oil, or high boiling point naphtha. In the combination with the disodium phosphate activating agent, the amine soap emulsion cleaner stabilizes the activating agent and imparts prolonged life thereto. The following compositions have been prepared and have been found excellent for simultaneously cleaning and activating ferrous and zinc metal surfaces:

Table

	Per Cent by Weight		
	A	B	C
Kerosene	35.46	35.91	65.67
Oleic Acid	7.17	10.07	3.55
Water	47.80	48.41	23.88
Disodium Phosphate Agent	3.98	4.02	4.78
Triethanolamine	3.59	1.57	2.12

Compositions A, B and C may be employed in the concentrated form shown in the table or they may be diluted with water to form an emulsion with as much as 99% water with successful results.

The combined emulsion cleaner and activating solution is conveniently prepared by mixing the fatty acid in the kerosene and dissolving the amine in water and pouring the first into the aqueous amine solution while rapidly stirring. The disodium phosphate activating agent may be put into solution separately with a small amount of the amine and fatty acid added to an aqueous solution of the disodium phosphate activating agent. This last solution may then be admixed with the emulsion cleaner proper.

The proportion of kerosene, fuel oil, or other hydrocarbon solvent in the emulsion may vary considerably. For most practical purposes, the proportion of hydrocarbon solvent should not exceed 70% and be not less than about ½ of 1% by weight of the emulsion to be applied to metal surfaces.

The amine soap will generally exceed the weight of the disodium phosphate.

The combined emulsion cleaner and activating agent forms a complex composition in which the major proportion of the disodium phosphate is in solution in the water with a small proportion of colloid suspended in the water. The hydrocarbon solvent, such as kerosene, forms a dispersed phase while the amine soap is the emulsifying agent for the dispersed kerosene.

The disodium phosphate renders the water slightly alkaline with a pH of from 8 to 9 and thereby enhances the stability of the emulsion. The amine soap emulsifying agent in turn suspends the activating colloid particles present and thereby prolongs the effective life thereof to one week or more. This co-operation is highly beneficial.

The emulsion of the hydrocarbon solvent with the amine soap is an excellent cleaning composition for ferrous and zinc metal surfaces. The emulsion is readily rinsed and leaves the metal surfaces free of any hydrocarbon solvent or alkali. The emulsion, therefore, produces a surface having the best condition of cleanness. Furthermore, the metal surfaces acquire a high degree of activity for subsequent reaction with an acid phosphate solution to produce phosphate coatings therein.

Cleaned and activated ferrous metal surfaces may be treated with an acid phosphate solution containing, for example, 1000 pounds of water,

10 pounds of an oxidizing agent such as sodium nitrate, 10 pounds of an acid metal phosphate such, for example, as zinc dihydrogen phosphate or manganese dihydrogen phosphate, and 30 pounds of phosphoric acid. Other oxidizing agents, such, for example, as nitrites, may be employed in the solution. The purpose of oxidizing agents is to oxidize or remove bubbles of hydrogen gas which would tend to blanket the surfaces of the metal as the phosphate coating is produced. With an activated metal surface, the solution need be applied for only a period of time of the order of one-half minute to produce an extremely fine and uniform phosphate coating. Under the microscope, the crystalline phosphate coating produced in this brief time is extremely fine and covers substantially the entire metal surface. Without the activating agent, the same metals acquire only a coarse and incomplete crystalline coating.

The acid phosphate solution for producing phosphate coatings on the activated and cleaned metal is modified for treating zinc metal, cadmium and the like, as is well understood in the art.

After a sufficiently good crystalline phosphate coating has been produced on the metal surfaces, the metal is removed from the acid phosphate solution and rinsed with water or subjected to a sealing treatment in a chromic acid solution. A hot aqueous solution of about 190° F. containing 7½ ounces of chromic acid per 100 gallons when applied for a few seconds to the metal surfaces improves the corrosion resistance of the coatings. The heat imparted to the metal by the hot chromic acid solution may be sufficient to dry the metal automatically on exposure to the air.

The metal surfaces may be coated with an organic finish or otherwise treated for final surface requirements. An oil coating may be of benefit in some cases. The corrosion resistance of the phosphate surfaces produced according to this invention is excellent. In combination with an organic finish, phosphate coated zinc and ferrous metal surfaces in accordance with this invention have an excellent life, even under severe atmospheric conditions.

Since certain changes may be made in the above invention and different embodiments of the invention may be made without departing from the scope thereof, it is intended that all matter contained in the above-described disclosure shall be interpreted as illustrative and not in a limiting sense.

I claim as my invention:

1. A composition for use in activating the surface of a metal selected from the group consisting of ferrous, zinc, cadmium metals and alloys in which they form the predominant constituent, for subsequent reaction with phosphate coating solutions consisting essentially of, in combination, disodium phosphate combined with at least one water-soluble compound of a metal selected from the group of metals consisting of titanium, zirconium, tin and arsenic, and a soap of a fatty acid and an amine in an amount of at least 10% of the weight of the combined disodium phosphate and the metal compound.

2. A composition for use in activating the surface of a metal selected from the group consisting of ferrous, zinc, cadmium metals and alloys in which they form the predominant constituent, for subsequent reaction with phosphate coating solutions consisting essentially of, in combination, disodium phosphate combined with at least one water-soluble compound of a metal selected from the group of metals consisting of titanium, zirconium, tin and arsenic, and a soap of oleic acid and triethanolamine in an amount of at least 10% of the weight of the disodium phosphate and the metal compound.

3. A stable aqueous solution for activating the surface of a metal selected from the group consisting of ferrous, zinc, cadmium metals and alloys in which they form the predominant constituent, for subsequent reaction with phosphate coating solutions consisting essentially of, in combination, at least 0.01% by weight of disodium phosphate combined with at least one water-soluble compound of a metal selected from the group of metals consisting of titanium, zirconium, tin and arsenic, at least 0.01% of a soap of a fatty acid and an amine and the balance being water.

4. A stable aqueous solution for activating the surface of a metal selected from the group consisting of ferrous, zinc, cadmium metals and alloys in which they form the predominant constituent, for subsequent reaction with phosphate coating solutions comprising, in combination, at least 0.01% by weight of disodium phosphate combined with at least one water-soluble compound of a metal selected from the group of metals consisting of titanium, zirconium, tin and arsenic, at least 0.01% of a soap of oleic acid and triethanolamine and the balance being water.

5. A composition suitable for use for simultaneously cleaning and activating the surface of a metal selected from the group consisting of ferrous, zinc, cadmium metals and alloys in which they form the predominant constituent, for subsequent reaction with phosphate coating solutions composed of a minor proportion of disodium phosphate combined with a water-soluble compound of a metal selected from the group consisting of titanium, zirconium, tin and arsenic, and a major proportion of an emulsion comprising water as the continuous phase and the dispersed phase comprising a liquid hydrocarbon solvent and an emulsifying agent composed of a soap of a fatty acid and an amine.

6. A composition suitable for use for simultaneously cleaning and activating the surface of a metal selected from the group consisting of ferrous, zinc, cadmium metals and alloys in which they form the predominant constituent, for subsequent reaction with phosphate coating solutions composed of a minor proportion of disodium phosphate combined with a water-soluble compound of a metal selected from the group consisting of titanium, zirconium, tin and arsenic, and a major proportion of an emulsion comprising water as the continuous phase and the dispersed phase comprising a kerosene and an emulsifying agent composed of a soap of oleic acid and triethanolamine, the kerosene being in an amount of from ½% to 70% of the weight of the entire composition excluding the water.

7. A stable aqueous solution for simultaneously cleaning and activating the surface of a metal selected from the group consisting of ferrous, zinc, cadmium metals and alloys in which they form the predominant constituent, for subsequent reaction with phosphate coating solutions for the subsequent formation of phosphate coatings thereon, composed of at least 0.01% by weight of disodium phosphate combined with a water-soluble compound of a metal selected from the group of metals consisting of titanium, zir-

conium, tin and arsenic, at least 0.1% by weight of a dispersion of a liquid hydrocarbon solvent and an emulsifying agent for the hydrocarbon solvent composed of a soap of a fatty acid and an amine, and from 50% to 99% by weight of water.

8. A stable aqueous solution for simultaneously cleaning and activating the surface of a metal selected from the group consisting of ferrous, zinc, cadmium metals and alloys in which they form the predominant constituent, for subsequent reaction with phosphate coating solutions for the subsequent formation of phosphate coatings thereon, composed of from 0.01% to 5% by weight of disodium phosphate combined with a water-soluble compound of a metal selected from the group of metals consisting of titanium, zirconium, tin and arsenic, at least 0.1% by weight of a dispersion of a kerosene and an emulsifying agent for the kerosene composed of a soap of oleic acid and triethanolamine, and from 50% to 99% by weight of water.

9. In the process of treating the surface of a metal selected from the group consisting of ferrous, zinc, cadmium metals and alloys in which they form the predominant constituent, for subsequent reaction with phosphate coating solutions the step comprising subjecting the surface to the action of an aqueous solution of disodium phosphate combined with a water-soluble compound of a metal selected from the group consisting of titanium, zirconium, tin and arsenic, and a soap of a fatty acid and an amine.

10. In the process of treating the surface of a metal selected from the group consisting of ferrous, zinc, cadmium metals and alloys in which they form the predominant constituent, for subsequent reaction with phosphate coating solutions

the step comprising subjecting the surface to the action of an aqueous solution composed of disodium phosphate combined with a water-soluble compound of a metal selected from the group consisting of titanium, zirconium, tin and arsenic, a disperson of hydrocarbon solvent, an emulsifying agent for the hydrocarbon solvent composed of a soap of a fatty acid and an amine, and water as the continuous phase.

11. The process which comprises subjecting the surface of a metal selected from the group consisting of ferrous, zinc, cadmium metals and alloys in which they form the predominant constituent, for subsequent reaction with phosphate coating solutions to the action of an aqueous solution composed of disodium phosphate combined with a water-soluble compound of a metal selected from the group consisting of titanium, zirconium, tin and arsenic, a dispersion of a hydrocarbon solvent, an emulsifying agent for the hydrocarbon solvent composed of a soap of a fatty acid and an amine, water as the continuous phase, and thereafter applying an acidic phosphate solution having an oxidizing agent to produce on the metal surfaces a phosphate coating.

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