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COMBINATION CLEANING AND COATING SOLUTION FOR METALLIC SURFACES AND METHOD OF FORMING COATINGS THEREWITH

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The present invention relates to a method and material for producing corrosion resistant coatings on metallic surfaces and particularly steel, iron, zinc and aluminum. More specifically, this invention concerns alkali metal phosphate solutions which have been modified with a dispersing agent to impart cleaning properties to the solution to enable the simultaneous cleaning and coating of metallic surfaces.

Ordinarily metal to be coated with a protective chemical coating is preliminarily subjected to cleaning in one or more mechanical or chemical steps. A relatively large proportion of the metal to be coated is only slightly soiled with small amounts of oil, grease, dirt, fingerprints or the like, and the use of separate cleaning equipment and a separate processing step for metal in such condition is expensive and undesirable.

It is therefore the principal object of this invention to provide an alkali metal phosphate solution which is capable of both cleaning and forming a protective phosphate coating on metallic surfaces when applied by spraying.

It has heretofore been proposed that the cleaning properties of phosphate coating solutions could be improved by the addition to such solution of certain surface-active agents or wetting agents. Typical of the wetting agents which have been suggested are the alkali metal salts of the higher alcohols such as lauryl and oleyl alcohols. The use of the heretofore suggested wetting agents in spray applications has been undesirable because of the tendency of such solutions to foam excessively.

In accordance with the present invention, the disadvantage of excessive foam formation may be eliminated and cleaning properties be simultaneously imparted to alkali metal phosphate solutions by the incorporation of certain proportions of the alkali metal salts of lignosulfonate in the solution.

As used in this specification and some of the appended claims, the term alkali metal phosphate solutions refers to aqueous acidic phosphate solutions of the alkali metals including ammonium. For the formation of coatings on the surfaces of such metals as iron, steel, zinc and aluminum, alkali metal phosphate solutions may be operated at acidities varying between a pH of about 4.2 and about 6.0. Although it is not absolutely necessary, alkali metal phosphate solutions may be further modified with such oxidizing agents as chlorates, bromates, nitrites, organic nitro compounds and sulfites. The presence of one of these oxidizing agents in the alkali phosphate solution is particularly effective in increasing the corrosion resistance of the coating and the uniformity of quality of the coatings in continuous commercial production, especially where the substrate metal is ferrous. Proportions of oxidizing agents which may be effectively utilized are given in the table:

TABLE

Oxidizing agent:	Concentration percent by weight
Chlorate ion—ClO_3	.5–4
Bromate ion—BrO_3	.02–2
Sulfite ion—SO_3	.02–.5
Nitrite ion—NO_2	.02–.4
Meta nitrobenzene sulfonate	.04–2

The oxidizing agents of the table are preferably added to the solutions in the form of alkali metal salts, but may be added as the salt of any metal which is not incompatible in the solution, such as zinc, manganese, etc.

In general, conventional wetting agents or surface-active agents function by lowering the surface tension of solutions to which they are added, and at least some such agents possess emulsifying properties as well. In spray applications of alkali phosphate solutions, it is undesirable to appreciably lower the surface tension of the solution because of the increased tendency of such solutions to foam. The alkali metal lignosulfonates, unlike the heretofore used wetting agents, apparently do not lower the surface tension of an alkali metal phosphate solution but do provide added cleaning ability especially for light oil stains, grease stains and the like.

In order to secure improved resistance to corrosion and improved paint adhesion it is necessary to incorporate a minimum of at least .01% sodium lignosulfonate or its equivalent in other alkali metal lignosulfonate in the solution. The upper limit is not critical and excess quantities cause no harm, but for practical reasons proportions above about 2% are not recommended. For the great bulk of metal stock, a proportion of sodium lignosulfonate of about .05%–0.10% is adequate. In solutions containing one of the above given oxidizing agents, better resistance to corrosion and more improved paint adhesion is achieved from solutions containing concentrations of sodium lignosulfonate between .02% and .2% and having a pH between 4.8 and 5.8. The best conditions are .05% sodium lignosulfonate and a pH of about 5.2.

The following examples are given to illustrate both the solutions and method of this invention in somewhat greater detail.

Example I

An alkali phosphate solution was formulated by combining 60 grams of sodium dihydrogen phosphate and sufficient water to form 5 liters. The mixed solution was found to have a pH of 4.9. Separate portions of this solution were modified by adding proportions of sodium lignosulfonate to produce concentrations of 0.01%, 0.02%, 0.05%, 0.10%, 0.20%, 0.50% and 1.0%. A number of 4" x 12" mild steel, zinc and aluminum panels, in the as-received condition, were sprayed for one minute with portions of each of the above baths maintained at 160° F., and rinsed in hot water. The panels were then rinsed in a dilute aqueous chromic acid solution and dried at about 200° F. for 3 to 10 minutes. After drying the panels were painted in accordance with commercial methods. Very little foaming of the spray solution was encountered.

The panels were then subjected to the conventional accelerated salt spray corrosion and humidity scratch tests and the panels resulting from the modified solutions were compared to the panels sprayed with the unmodified basic sodium dihydrogen phosphate solution. After 288 hours in the salt spray chamber (3% sodium chloride fog) the corrosion of the panels from the modified solutions were found to be in every case superior to those from the unmodified solutions. On a similar comparison basis, humidity resistance of the panels from

the modified solution was superior to that of the panels from the unmodified solutions. Within the range of .017 to 1% of sodium lignosulfonate, little difference in the resistance to corrosion or humidity between the various panels could be detected. Panels processed similarly in solutions modified with proportions of sodium lignosulfonate to produce concentrations below .01% did not show a noticeable improvement in corrosion or humidity resistance.

The pH of the various solutions was checked just prior to spraying and found to vary between 4.78 and 6.2. One solution having a pH of 6.2 contained .2% sodium lignosulfonate, and the resistance to corrosion was inferior to that of the unmodified solutions operating at a pH of 5.82. All other solutions having a pH of less than 6.0 were satisfactory and produced the above stated improved results.

Example II

To portions of a 12 g./l. sodium dihydrogen phosphate solution, varying quantities of oxidizing agents were added to produce the following concentrations in the solutions: 0.5% ClO_3; 0.3% BrO_3; 0.2% SO_2; 0.7% NO_2 and 0.08% m-nitrobenzene sulfonate. Each of the oxidizing agents was added as the sodium salt. Following the procedure outlined under Example I, sodium lignosulfonate was added to these solutions to produce concentrations of 0.02% and 0.2%. Mild steel panels treated in these solutions under conditions similar to those of Example I were found to have increased resistance to corrosion from salt spray and humidity. The results were comparable to those obtained with the panels of Example I.

Uniformly high quality coatings are formed from alkali metal phosphate solutions containing oxidizing agents when the alkali metal lignosulfonate additive is incorporated in an alkali metal phosphate solution which is used preliminarily in a two-step process. While the greatest commercial advantage is gained by incorporating the dispersing agent of this invention directly in the coating forming solution, the benefits are obtained similarly from the two-step procedure.

Example III

Comparative tests were made on soiled and clean mild steel panels in the following solution variations: (1) A 12 g./l. potassium dihydrogen phosphate solution; (2) A 10 g./l. sodium dihydrogen phosphate solution containing 5 g./l. of ClO_3; (3) solution (1) containing .02% and .2% sodium lignosulfonate; and (4) solution (2) containing 0.02% and 0.2% sodium lignosulfonate. The soiled panels were spotted with light lubricating oil and were slightly dusty. The clean panels were wiped with a dry rag just prior to introduction into the solutions and were substantially free of oil and dust.

After treating the panels in accordance with the method of Example I, the results of the corrosion and humidity tests showed that the coatings resulting from solutions (3) and (4) were definitely superior to the coatings formed in baths (1) and (2).

As used in this specification and in the appended claims, all percentages are by weight.

What is claimed is:

1. A combination cleaning and coating solution for use in the formation by spraying of improved phosphate coatings on the surfaces of iron, steel, zinc and aluminum which consists essentially of an aqueous acidic alkali metal phosphate solution having incorporated therein .01% to 2% of an alkali metal lignosulfonate.

2. A composition of matter for forming by spraying, a phosphate coating on metallic surfaces which consists essentially of an aqueous alkali metal phosphate solution containing an oxidizing agent, and .01% to 2% of an alkali metal lignosulfonate, said solution having a pH of 4.2 to 6.0.

3. A cleaning and coating solution for forming by spraying improved phosphate coatings on metallic surfaces of the group consisting of iron, steel, zinc and aluminum which consists essentially of an aqueous alkali metal phosphate solution containing .02% to .2% alkali metal lignosulfonate, said solution having a pH of 4.2 to 6.0.

4. A solution for spray application to iron, steel, zinc and aluminum surfaces for simultaneously cleaning and forming an improved phosphate coating thereon which consists essentially of an aqueous alkali metal phosphate solution containing an oxidizing agent, and 0.02% to 0.2% alkali metal lignosulfonate, said solution having a pH of 4.2 and 6.0.

5. A solution for spray application to metallic surfaces for simultaneously cleaning and forming a protective phosphate coating thereon, which consists of an aqueous alkali metal phosphate solution containing 0.5% to 4.0% chlorate and 0.02% to 0.2% sodium lignosulfonate, said solution having a pH between 4.8 and 5.8.

6. A method for simultaneously cleaning and forming a phosphate coating on metallic surfaces which comprises the step of spraying the metal surface with a solution consisting essentially of an aqueous acidic alkali metal phosphate solution having incorporated therein .01% to 2% of an alkali metal lignosulfonate.

7. A method for simultaneously cleaning and forming a phosphate coating on the surface of a metal of the group consisting of iron, steel, zinc and aluminum which comprises the step of spraying the metallic surface with a solution consisting essentially of an aqueous alkali metal phosphate solution containing .02% to .2% alkali metal lignosulfonate, said solution having a pH of 4.2 to 6.0.

8. A method for simultaneously cleaning and forming a phosphate coating on the surface of a metal of the group consisting of iron, steel, zinc and aluminum which comprises the step of spraying the metallic surface with a solution consisting essentially of an aqueous alkali metal phosphate solution containing 0.02% to 0.2% sodium lignosulfonate, said solution having a pH of 4.8 to 5.8.

9. A method for simultaneously cleaning and forming a phosphate coating on the surface of a metal of the group consisting of iron, steel, zinc and aluminum which comprises the step of spraying the metallic surface with a solution consisting essentially of an aqueous alkali metal phosphate solution containing an oxidizing agent, and 0.02% to 0.2% alkali metal lignosulfonate, said solution having a pH of 4.2 and 6.0.

10. A method for simultaneously cleaning and forming a phosphate coating on the surface of a metal of the group consisting of iron, steel, zinc and aluminum which comprises the step of spraying the metallic surface with a solution consisting essentially of an aqueous alkali metal phosphate solution containing 0.5% to 4.0% chlorate and 0.02% sodium lignosulfonate, said solution having a pH between 4.8 and 5.8.

11. A method for simultaneously cleaning and forming a phosphate coating on metallic surfaces which comprises the steps of spraying the metal surface with a solution consisting essentially of an aqueous alkali metal phosphate solution containing an oxidizing agent, and .01% to 2% of an alkali metal lignosulfonate, said solution having a pH of 4.2 to 6.0 and thereafter rinsing the coating in a dilute aqueous solution of chromic acid.

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