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COATING PROCESS WITH ALKALI METAL PHOSPHATE AND ADDED FLUORIDE SALT

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This invention relates to the formation of thin, uniform surface coatings for metals, such as iron, steel, and zinc. These coatings are primarily suitable to increase the life of subsequent applied siccative coatings and also are useful in facilitating drawing operations on iron, zinc and steels, such as in drawing dies.

The successful processes for such coatings, which have been adopted by industry, deal with the use of acid phosphate solutions of zinc, manganese and iron, used as is, or with suitable accelerators. Such a process is described in U. S. Patents Nos. 1,911,726 and 1,888,189. These solutions are all quite acid, having pH's ranging from 2 to 2.5. This is necessary because these phosphates are soluble only in a fairly acid medium. The disadvantages of these solutions are their corrosive action on equipment, dissolution of excessive amounts of iron and consequent heavy sludge formation, due to the formation of insoluble iron phosphates.

The phosphate coatings formed in these processes can be divided into two distinct groups. The heavy ones, ranging from 300 mg.–1000 mg. or over per square foot, and the lighter ones ranging from 150–300 mg. The heavy coatings found adaption in the rustproofing of small parts, such as bolts, and nuts, and larger articles that were not painted. These coatings were sealed with oils or waxes. It was found that these heavy coatings were unsatisfactory paint bases. For this reason, lighter ones were developed. By proper selection of accelerators the coating weights could be controlled to some extent, giving thinner films, which proved good paint bases for sheet metal. The heavier coatings absorbed too much paint, dulling the film, and were less flexible on bending, causing the paint to flake off. However, all these solutions, containing large amounts of zinc and iron, could not be controlled to give much thinner coatings than approximately 150 mg. per square foot.

The phosphates discussed in the art above, are so-called "coating metal phosphates." This means phosphates, the cations of which are metals which enter into the coating proper, such metals as zinc, manganese and iron, thus forming insoluble, more basic phosphates. The alkali metal phosphates are in a different solubility group, in that they are soluble, no matter what the acidity of the solution may be.

Attempts have been made to eliminate the disadvantages outlined above by using these more soluble and cheaper phosphates, such as the alkali metal phosphates. These show possibilities, but as such, do not coat as uniformly and as well as necessary.

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We have found how to utilize the property of these cheaper, more soluble, less acid phosphates, together with a fluoride. These have quite special properties. The fluorides form acid and normal salts, and have the tendency to form insoluble complex compounds.

It is therefore, an object of the invention to provide an inexpensive method of preparing metal for painting using solutions having a pH of 3.0 or over to minimize the dissolution of iron and to eliminate any corrosive action on equipment.

Still another object is to provide a method of the above type by which an adherent coating is provided on iron, zinc or steel surfaces in a relatively short time, the produced coating being effective to improve the drawing properties of the metals thus facilitating its cold drawing in manufacturing operations, increasing the life of the drawing dies and equipment and permitting the making of deeper draws in a single operation than is normally possible without the coatings.

Another object is to provide a method and coating solution of the above type adapted to eliminate the sludge caused by zinc or iron in solution and also adapted to form thinner coatings which are better all around paint bases.

Another object of the present invention is to provide a novel process and coating solution for producing an adherent coating on metal surfaces, such as iron and zinc, by chemical means, the process being readily adapted for use on an economically feasible basis in commercial scale operations.

Other objects of the invention will appear in the following description and appended claims. Before explaining the present invention in detail, it is to be understood that the invention is capable of other embodiments and of being practiced and carried out in various ways. It is also to be understood that the phraseology or terminology employed herein is for the purpose of description and not of limitation.

In using the mono alkali metal or mono ammonium phosphates in conjunction with alkali or ammonium fluorides, or bifluorides, coating solutions can be made up for iron, steel or zinc, which are all buffered and form thin uniform films in a very short time. The solutions are particularly suitable for spray applications in a conventional type of spraying machine, for such parts as automobile bodies, refrigerator panels

and the like. A one minute spray at 140°–150° F. on properly cleaned articles is very adequate.

Immersion application normally requires a longer time, usually from 3 to 10 minutes at 150°–180° F. for best results on steel and one minute or less on zinc.

A certain ratio between the phosphate and fluoride is necessary for best results. For instance, a 1:1 ratio by weight is recommended. The phosphate should not be allowed to drop below 15% of the total coating chemical in solution and may go as high as 95%, at which point the remaining fluoride still exerts its beneficial activating action.

A proper balance is maintained in using a mix of fluoride and acid fluoride. A proper balance is important because too much normal fluoride tends to decrease the acidity, whereas too much acid fluoride gives too much acid for proper coating action.

The above coatings may be rinsed with dilute chromic or phosphoric acid if desired.

The following examples are given to illustrate the invention:

Example I

The following ingredients in the parts by weight indicated were first mixed and then dissolved in water to give a suitable coating solution in accordance with the present invention.

46% mono sodium phosphate
27% sodium fluoride
27% sodium bifluoride

In coating metals with the above ingredients, 17 pounds of the above dry mix were used per 100 gallons of processing solution at 160° F. The solution was tested for acid strength by titrating a 10 ml. sample with N/10 of sodium hydroxide, using phenolphthalein indicator. The end point was a permanent pink and was reached with about 15 ml. of sodium hydroxide. This is called a 15 point solution. The pH as measured with a standard glass electrode was 4.25.

Example II

The following ingredients in the parts by weight indicated were first mixed and then dissolved in water to form another suitable coating solution.

20% mono ammonium phosphate
40% sodium fluoride
40% sodium bifluoride

In preparing a coating solution using the above ingredients, 20 pounds of the above dry mix were used for each 100 gallons of solution. The pH of the solution was found to be 4.3, measured with a standard glass electrode.

Example III

The following ingredients in the parts by weight indicated were first mixed and then dissolved to form a suitable coating solution in accordance with the present invention.

90% mono potassium phosphate
5% sodium fluoride
5% ammonium bifluoride

In employing the above ingredients, 17 pounds of the dry mix were used per 100 gallons of solution. Suitable coatings were obtained on steel and zinc articles which were immersed or subjected to a spray of this coating solution for three and one minute periods, respectively, at 150° F. The pH of this solution was found to be approximately 4.4. By varying the relative amounts of the above constituents, the pH of the solution may be varied up to 5.5, using more normal fluoride and less bifluoride.

Example IV

The following ingredients in the parts by weight indicated were first mixed and then dissolved in water to form another suitable coating solution.

45% mono ammonium phosphate
35% sodium fluoride
20% sodium bifluoride

In employing the above ingredients in a coating solution, 20 pounds of the above dry mix were employed per 100 gallons of final solution. The pH of this solution was found to be 5.3. Care should be exercised to maintain a pH for the final processing bath of between 3.0 and 5.8. Too low a pH gives too much pickling, whereas, too high a pH, naturally, stops all the action. This may be accomplished by changing the relative proportions of the fluoride and bifluoride.

In the prepartion of the coating solution, any combination of alkali or acid compounds of the activators may be employed, so balanced as to give the solution a pH between 3.0 and 5.8. For example, a suitable amount of sodium fluoride may be combined with a suitable portion of sodium bifluoride, or hydrofluoric acid, to provide the desired balance.

The exact chemical reactions of the above solutions are not known, but undoubtedly fluoride ions activate the metal surface in these comparatively high pH coating solutions. The coatings thus formed are combinations of phosphates and oxides, with traces of insoluble halogen, and are improvements over the coatings obtained with straight phosphates, and permits operation of the process at pH's much higher than have been possible heretofore.

The coatings obtained by the method of the present invention are thin and uniform, weighing only 25–100 mg. per square foot. They are ideal bases for subsequent organic finishes, especially when a final rinse application of chromic acid and di-chromates, or phosphoric acid is used. These rinse acids are used in very low concentration, .05% to .10% solution by weight and are allowed to dry onto the coating.

The coatings of the present invention have also been found particularly suitable to facilitate drawing operations, by increasing the life of the draw dies and equipment and also by permitting deeper draws in a single operation.

The term "alkali metal" in the subsequent claims includes the alkali metals and also ammonium.

Having thus described our invention, we claim:

1. In a method for coating metal surfaces, such as iron, steel, zinc and alloys thereof, the novel step of subjecting the metal to the action of an aqueous coating solution which essentially consists of an alkali metal phosphate, and an alkali metal fluoride until a coating is formed on the surface of the metal, the concentration of the phosphate in the solution being between 15 and 95 percent by weight of the total chemical in solution, said solution having a pH between 3.0 and 5.8.

2. In a method for coating metal surfaces, such as iron, steel, zinc and alloys thereof, the novel step of subjecting the metal to the action of an aqueous coating solution which essentially

consists of an alkali metal phosphate, and an activator comprising alkali fluorides and alkali acid fluorides, until a suitable coating is formed thereon, the concentration of the alkali fluoride and alkali acid fluoride being balanced to maintain the pH of the solution between 3.0 and 5.8, the concentration of the phosphates in the solution being between 15 and 95 percent by weight of the total chemical in solution.

3. A method for coating metal surfaces such as iron, steel, zinc and alloys thereof comprising the steps of subjecting the metal to the action of an aqueous coating solution which essentially consists of an alkali metal phosphate, having therein an alkali fluoride until a coating is formed on the surface of the metal, removing the metal from the coating solution and thereafter rinsing the coated surface with a dilute acid of the group consisting of chromic and phosphoric acids, the concentration of the phosphates in the solution being between 15 and 95 percent by weight of the total chemical in solution, said solution having a pH between 3.0 and 5.8.

4. In a method for coating metal surfaces such as iron, steel, zinc and alloys thereof, the novel

step of subjecting the metal surface to the action of an aqueous coating solution which consists essentially of an alkali metal phosphate and an alkali metal fluoride, until a coating is formed on the surface of the metal, the said phosphate and the said fluoride being present in a one-to-one ratio by weight, and the solution having a pH between 3.0 and 5.8.

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