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METHOD OF SIMULTANEOUSLY PHOSPHATING AND CLEANING METAL SURFACES AND COMPOSITION THEREFOR

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This invention relates to improvements in the production of phosphate coatings on ferrous and zinc or zinc alloy surfaces with solutions of the phosphates of sodium, ammonium, potassium, magnesium or organic bases, or mixtures thereof.

The use is known of such solutions either alone or in the presence of suitable oxidizing agents and/or metal accelerators for forming phosphate coatings on ferrous and zinc surfaces.

Such processes are preferably operated at a temperature above 150° F. and within the pH range of 4.2 to 5.8 on ferrous surfaces and 3.5 to 5.0 on zinc surfaces. By their use, due to the low acidity of the bath, dissolved metal is precipitated readily as a coating without forming more than a negligible amount of sludge; consequently such processes have desirable qualities of low consumption of chemicals, and there is little or no scaling of the coils and clogging of the spray jets. Due, however, to their low acidity, these processing solutions exert but little pickling action on the metal surface and have little power to remove soil or act upon greasy surfaces. Another disadvantage associated with this type of process is that the coatings produced sometimes tend to be dusty. It has been proposed to overcome these difficulties by adding wetting agents, but such a procedure has not proved entirely satisfactory.

We have now found that ferrous and zinc or zinc alloy surfaces may be cleaned and coated simultaneously to give improved coatings of high resistance to corrosion by a process in which there is applied to the surface an emulsion of a grease removing solvent in an acidic solution of a phosphate of sodium, ammonium, potassium, magnesium, or of an organic base or a mixture of such phosphates. Phosphate solutions containing accelerators are preferred, such as, for example, chlorates, bromates, sulfites, nitrites, etc. A quantity of accelerator having an effect on the coating action substantially equal to that of about .5 percent to 4 percent chlorate is satisfactory. The grease-removing solvents which we prefer are those which are not very volatile at the processing temperature yet do not possess too high a boiling range; otherwise they tend to adhere to the metal surface and prevent processing. We have found that solvents having a boiling range within the limits of 130° C. to 300° C. are most suitable, and any normal grease-removing solvent within this boiling range and which is compatible with the solution can be used. We prefer to use aromatic hydrocarbons; for example, the fraction known commercially as Solvent Naphtha or aliphatic hydrocarbons such as the paraffin fraction known commercially as Kerosene. The solvent is preferably present in a concentration from 1 to 10 percent of the coating solution. Other suitable solvents are tetrahydro naphthalene, methylcyclohexanone, ethyl benzoate, and orthodichloro benzene.

The maintenance of rapid movement between the solution and the surface to be treated is desirable, and it is, therefore, preferred to spray the solution onto the metallic

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surface. To maintain the grease removing solvent in the state of a stable emulsion during the treatment an emulsifying agent is required. We prefer non-ionic materials as the principal emulsifying agents. Certain anionic active agents, such as petroleum sulphonates and long chain alcohol sulphates, may be used since they are stable within the required pH range of 3.5 to 5.8. Cationic active agents are less desirable mainly because they inhibit the phosphate coating action.

By "non-ionic oil-in-water principal emulsifying agents" we mean that class of surface active agents which is used as the main emulsifying ingredient and which remains substantially unionized in aqueous solution having a pH of 3.5 to 5.8. Examples of such agents which we have found to be particularly effective are the derivatives of ethylene oxide polymers, particularly those containing about 3 to 25 polyoxyethylene groups therein, such as polyoxyethylene derivatives of oleic acid, which are commercially available under the name "Antarox B-100" and "Acco Emulsifier #5," and polyoxyethylene alkyl phenol derivatives, which are available commercially under the name "Antarox A," "Igepal," and "Triton X-100." We have found para iso-octyl phenyl ether polyoxyethylene glycol having nine polyoxyethylene groups in the glycol to be particularly useful. Further suitable non-ionic emulsifying agents include condensation products of oleyl alcohol with ethylene oxide, and a polyethylene oxide chain esterified with lauric acid, available under the names "Emulphor O" and "Brig 30," respectively.

Operation of the process is preferably effected at a temperature above 150° F., but satisfactory coatings can be obtained at room temperature on zinc surfaces given a suitable time of treatment. Working at 130° F. satisfactory phosphate coatings can be produced in from one-half to two minutes spray. It is of advantage to rinse the coatings produced with a dilute solution of chromic, phosphoric, or oxalic acid; with a dilute solution of an iron, chromium or aluminum salt—for instance, ferrous sulphate, ferric nitrate, chromium sulphate or nitrate, or aluminum sulphate or nitrate; or with a solution containing a mixture of these substances. The concentration of the rinsing solution is suitably from 7 to 21 ounces of the acid or salt in 100 gallons water, although more concentrated solutions may be employed, and the temperature of the rinsing solution is preferably from 150° F. to 180° F. A rinsing period of one minute is satisfactory, and by the rinsing the resistance of the metal to corrosion is increased, and the tendency of paint applied to the coating to blister is reduced.

The presence of emulsified solvents in the coating solution enables phosphate coatings to be formed on metal surfaces which are too greasy and soiled to allow solutions which do not contain emulsified solvents to attack them and produce satisfactory coatings. Even on clean metal surfaces the presence of the emulsified solvent in the coating solution enables it to wet the metal surface more readily and so produce coatings more even in character with less dust and with greater rapidity.

The invention is illustrated by the following example:

A solution is prepared containing 1.4 percent sodium dihydrogen phosphate and 0.5 percent sodium chlorate. There is then stirred into the solution 2 percent by weight of kerosene which itself contains 5 percent of its weight of para iso-octyl phenyl ether polyoxyethylene glycol. The solution is adjusted to give a pH of 5.0 and is placed in a spray machine and heated to about 160° F. to 170° F. and sprayed onto a greasy ferrous surface for a period of about 1 minute. The metal surface after treatment is rinsed in hot water, followed by immersion for half a minute in a solution of 10 ounces chromic acid in 100 gallons of water maintained at 160° F. before final force drying. By this treatment slightly iridescent, adherent, even,

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corrosion-resistant coatings of approximately 50 mg./sq. ft. are obtained eminently suitable for use as a base for paints, lacquers or like materials.

The same treatment when applied to similarly greasy ferrous surfaces wherein the coating solution does not contain emulsified solvent is found to give substantially no coating.

By adjusting the above solution to a pH of 4.5 excellent coatings can in like manner be obtained upon zinc surfaces.

The invention also includes the solutions referred to above, and these may be prepared at "operational strength," i. e., at a strength suitable for immediate use in the process, or as concentrated chemicals, i. e., at a strength such that they require dilution before use.

We claim:

1. A process for simultaneously cleaning and producing a phosphate coating on the surfaces of metal of the group consisting of iron and zinc and their alloys which comprises the steps of (1) applying to the surface an aqueous solution of an acidic phosphate of an alkali metal in the presence of an accelerator having an effect on the coating action substantially equal to that of about .5 percent to 4 percent chlorate, 1 percent to 10 percent of a hydrocarbon solvent, and a non-ionic oil-in-water emulsifying agent of the polyoxyethylene type having 3 to 25 polyoxyethylene groups therein in an amount sufficient to form a stable emulsion of said solvent, said solution having a pH of from 3.5 to 5.8 and continuing the application until a coating results, and (2) rinsing the coated surface with a dilute solution of chromic acid.

2. A process as claimed in claim 1 wherein the emulsifying agent is para iso-octyl phenyl ether polyoxyethylene glycol having 9 polyoxyethylene groups in the glycol.

3. An aqueous solution for de-greasing and producing a phosphate coating on the surfaces of metal of the group consisting of iron and zinc and their alloys which consists essentially of an acidic phosphate selected from the group consisting of sodium phosphate, potassium phosphate, and ammonium phosphate, and mixtures thereof, an accelerator in an amount having an effect on the coating action substantially equal to that of about .5 percent to 4 percent chlorate, 1 percent to 10 percent of a hydrocarbon solvent having a boiling point within the range of 130° C. to 300° C., a polyoxyethylene derivative type emulsifying agent having 3 to 25 polyoxyethylene groups therein in an amount sufficient to form a stable emulsion of said solvent, said solution having a pH within the range of 3.5 to 5.8.

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4. An aqueous solution for degreasing and producing a phosphate coating on the surfaces of metal of the group consisting of iron and zinc and their alloys, which consists essentially of an acidic phosphate selected from the group consisting of sodium phosphate, potassium phosphate, ammonium phosphate and mixtures thereof, .5% to 4% chlorate, 1% to 10% of a hydrocarbon solvent having a boiling point within the range of 130° C. to 300° C., para iso-octyl phenyl ether polyoxyethylene glycol having 9 polyoxyethylene groups in the glycol in an amount sufficient to form a stable emulsion of said solvent, said solution having a pH within the range of 3.5 to 5.8.

5. A solution for degreasing and producing a phosphate coating on the surfaces of metal of the group consisting of iron and zinc and their alloys which consists of 1.4% sodium dihydrogen phosphate, .5% sodium chlorate, 2% kerosene, .1% para iso-octyl phenyl ether polyoxyethylene glycol having 9 polyoxyethylene groups in the glycol, balance water, the pH of the solution falling within the range of 3.5 to 5.8.

6. A process for degreasing and producing a phosphate coating on the surfaces of metal of the group consisting of iron and zinc and their alloys which comprises the single step of subjecting said surfaces to the action of an aqueous solution of an acid phosphate selected from the group consisting of sodium phosphate, ammonium phosphate, potassium phosphate and mixtures thereof and having a pH in the range of 3.5 to 5.8, 1%–10% of a grease-removing hydrocarbon solvent having a boiling point within the range of 130° C. to 300° C. and a non-ionic emulsifier of the polyoxyethylene type having 3 to 25 polyoxyethylene groups therein in an amount sufficient to form a stable emulsion of said solvent in said solution.

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