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PHOSPHATE COATING COMPOSITION AND PROCESS

Montagu Hyams and Andrew Nicholson, London, England, assignors to Parker Rust-Proof Company, Detroit, Mich., a corporation of Michigan

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This invention relates to the coating of ferrous surfaces to improve their resistance to corrosion.

The resistance to corrosion of ferrous surfaces can be improved by treating said surfaces with solutions of acid metal phosphates of metals such as zinc, manganese, cadmium, iron, calcium and barium. In these processes phosphate coatings are formed on the ferrous surface, and the metal present in the acid metal phosphate contained in the coating solution enters into the protective coating. These phosphates have, therefore, been described as "coating phosphates," i. e. phosphates in which the metal present enters into the protective coating.

In British Patent No. 517,049 it is disclosed that protective coatings can be produced rapidly on ferrous surfaces by treatment with a solution which is primarily one of phosphoric acid or a "non-coating phosphate," i. e. a phosphate in which the metal present does not enter into the protective coating, or both and which also contains a small amount of a nitrite, nitrate or sulphite, but which contains at the most only a small quantity of ions of metals which form coating phosphates.

The present invention is based on the discovery that improved results are obtained by using, instead of nitrite, nitrate or sulphite, certain reducible compounds specified below and being certain organic nitro compounds. It is to be appreciated that by no means all reducible compounds are to be regarded as suitable for use in the present invention and that furthermore only certain of the reducible compounds in the broad group specified above are of value.

It is characteristic of all the reducible compounds specified below that coatings are produced in their presence, when used in conjunction with a solution which is primarily one of a "non-coating phosphate" and phosphoric acid and which contains at the most only a small quantity of ions of metals which form "coating phosphates," that are of a quality or density distinct from and superior to those obtainable from the use of such solutions by themselves even after extremely long times of treatment. By their action a coating of increased thickness is formed, which is exactly the opposite of the effect of suitable reducible compounds with "coating phosphates," and the reducible compounds of this invention are therefore to be regarded not as accelerators but as being vital for the coating process.

It is to be appreciated that small amounts of iron and other metal accelerators may be added

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to the solution, as described below but in any event a small amount of ions of metals which form coating phosphates will invariably be present after the solution has been in use for some time, for on treating ferrous surfaces with the solutions of the invention iron partly dissolves. However, the conditions are so controlled that the quantity of "coating phosphate" present in solution is extremely low since, in order that a suitable coating may be produced upon the ferrous surface the pH of the solution must be sufficiently high to favour the precipitation of a ferrous phosphate no less basic than the tertiary phosphate because it has been found by us that ferrous secondary phosphate is unsuitable as a coating constituent, being rapidly converted to powdery ferric phosphate. It has further been found by us that only when ferrous tertiary phosphate is precipitated above 60° C. does it exist in a form which resists far better than any other the tendency to oxidise to ferric phosphate so that we have found that if maximum benefit of our invention is to be obtained the solutions must be used at temperatures exceeding 60° C. and at pH values sufficiently high to satisfy the condition specified above. This minimum pH will depend upon many factors such as temperature and phosphate concentration but we have found from precipitation experiments that a minimum pH of 4.2 will insure the required conditions. Lower pH values than this may well lead to very loose coatings and also to the presence of appreciable amounts of "coating phosphate" in solution.

On treating ferrous surfaces according to our invention iron dissolves incipiently from the surface and a protective phosphate-containing coating is formed in which the metal radical present is derived from the metal being coated, the metal present in the "non-coating phosphate" remaining in solution. In order for this incipient dissolution to take place no pH above a certain maximum for any particular combination of reducible compound and "non-coating phosphate" is permissible. It has been found that in order to derive maximum benefit from our invention this pH should not normally exceed 5.8 and with some combinations should preferably be less than this. The best pH range for each particular reducible compound will be a function of its concentration and temperature of use but all will be found to be most suitable for use within the limits of pH 4.2–5.8.

Due to the low acidity of the bath dissolved iron is precipitated immediately as coating with-

out forming more than a negligible amount of sludge. This means that chemical consumption, scaling of steam coils and clogging of spray jets are reduced to a minimum. Sludge is also far less than when "coating phosphates" are employed since "non-coating phosphates" do not precipitate out insoluble phosphate due to dissociation when heated or neutralised as do equilibrium solutions of "coating phosphates."

Examples of "non-coating phosphates" as specified above are those of the alkali metals such as the sodium and potassium phosphates, as well as those of ammonium. Mixtures of these phosphates may be employed. The "non-coating phosphates" are in many cases cheaper and more readily available than the "coating phosphates" and as explained above in using them no substantial amount of sludge is formed. A copper, nickel or other metal accelerator may be incorporated in the solution. The most suitable concentration of such phosphate for use has been found to lie within the range 0.05 to 0.25 molar.

The coating solutions of the invention may be sprayed on to the metal surface to be coated, or the metal may be immersed in the solution to which wetting agents or thickening agents may with advantage be added to facilitate the coating action.

Not all organic nitro compounds have been found suitable for use in our invention. Some, such as m-nitraniline and 2:4 dinitro-diethyl aniline, were found to be insufficiently soluble to render suitably active concentrations. Others, such as nitromethane and nitroguanidine, which are particularly effective in conjunction with "coating phosphates," were found to be ineffective for the purpose of the present invention. Those organic nitro compounds which are used in accordance with the present invention are given below in decreasing order of preference together with the most suitable ranges of concentration for use.

Organic Nitro Compound	Concentration, Percent
m-nitrobenzene-sulphonic acid	0.05–0.25
o-nitro-chlorbenzene-p-sulphonic acid	0.5 –2
3:nitrophthalic acid	0.02–0.1
m-nitrobenzoic acid	0.02–0.1

Hydroxylamine and its salts have been found to be very suitable for use in the present invention, optimum concentrations being 0.1–0.5% in the case of the hydrochloride.

Reducible materials other than those specified above are inferior to those specified for use for the purpose of the present invention. Thus various well known oxidising agents such as permanganates have been found to be ineffective whilst others such as hydrogen peroxide and hypochlorite have been found to yield substantially nothing but dust when used in controllable amount. Oragnic reducible compounds such as trichloracetic acid and quinone, active in conjunction with "coating phosphates," were found to be ineffective for the purpose of the present invention.

If the compounds of this invention are used substantially below the lower limit of concentration recommended above the necessary change in coating quality or density over that obtainable without their use for maximum benefit cannot be attained even after very prolonged periods of processing. If used substantially above the upper limit of concentration recommended above the compounds of the invention will cease to produce a coating of any description or yield mainly loose dust on the surface. Mixtures of suitable compounds may be used in which case their effect may be regarded as additive.

The precise concentration of suitable reducible compound recommended for use in any given situation will depend upon the temperature, pH and time of treatment. In general the higher the temperature and the longer the time of treatment the lower the concentration of organic nitro compound, hydroxylamine required or desirable, whilst the reverse is true in the case of pH. Usually higher concentrations of reducible material are permissible with consequently more efficient coating action in the presence of wetting agents, thickening agents or agitation of the solution. The general criterion in deciding the correct concentration of organic nitro compound, hydroxylamine for producing coatings on ferrous surfaces for the subsequent application of paints, lacquers or like materials is to select any concentration within the limits specified heretofore which will give a uniform adherent coating associated with not more than 10–20 mg./sq. ft. of loose coating.

The coatings of the invention, after rinsing in water and drying, are eminently suitable for use as a base for paints, lacquers or like materials and also for oils but it is of advantage to rinse the coatings produced with a dilute solution of chromic, phosphoric or oxalic acid, or with a dilute solution of an iron, chromium or aluminium salt, for instance ferrous sulphate, ferric nitrate, chromium sulphate or nitrate, or aluminium sulphate or nitrate, or with a solution containing a mixture of these substances prior to drying and the application of paints, lacquers, oils or like materials. The concentration of the rinsing solution is suitably from 7–21 ozs. of the acid or salt in 100 gallons of water, although more concentrated solutions may be employed, and the temperature of the rinsing solution is preferably from 150°–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 the paint applied to the coating to blister is reduced.

We have found that dilute solutions of chromic acid, or solutions containing hexavalent chromium, are particularly effective in this respect and give a most surprising increase in corrosion resistance. As little as 0.005% chromic acid in the rinse will bring about a marked improvement, but this improvement becomes even more marked as the concentration of chromic acid is increased up to around 0.25%. Beyond this concentration no substantial improvement in corrosion resistance is discernible whilst the coatings tend to become very stained. The most useful concentration of chromic acid for use with coatings of the invention has been found to lie between 0.02–0.1% CrO_3, the rinsing solution preferably being applied for a period of up to one minute at 150°–180° F.

The invention is illustrated by the following examples:

Example 1

A solution in 100 gallons of water of 15 lbs. sodium dihydrogen phosphate, 1 lb. sodium salt of m-nitro-benzene-sulphonic acid and 2 ozs. wetting agent (e. g. sodium lauryl sulphate) and

sufficient caustic soda to give a pH of 5.0 was employed. A copper accelerator was added to the solution, in concentration of 0.0002 to 0.012% calculated as copper.

The solution was placed in a spray machine and heated to about 170–180° F. and sprayed onto the metal to be coated for a period of about 1 minute.

The metal surface, after withdrawal from the processing solution, was rinsed in hot water, followed by immersion for ½ minute in a solution of 10 oz. chromic acid in 100 gallons water maintained at 160° F. before final force drying.

By this treatment dark, adherent, even, hard, corrosion resistant coatings of some 100 mg./sq. ft. were obtained upon ferrous surfaces which are eminently suitable for use as a base for paints, lacquers or like materials.

Comparable results were obtained by immersing the metal in the heated solution for 2–4 minutes. A nickel or iron salt may be used instead of the copper salt as accelerator.

Example 2

In a process otherwise as described in Example 1 a solution was employed containing in 100 gallons of water 15 lbs. sodium dihydrogen phosphate, 5 lbs. o-nitro-chlorbenzene-p-sulphonic acid and 2 ozs. wetting agent (e. g. sodium lauryl sulphate) and sufficient caustic soda to give a pH of 4.6.

By this treatment dark, adherent, even, hard corrosion-resistant coatings of some 100 mg./sq. ft. were obtained upon ferrous surfaces which were eminently suitable for use as a base for paints, lacquers or the like materials.

Example 3

In a process otherwise as described in Example 1 a solution was employed containing in 100 gallons of water, 15 lbs. of 75% phosphoric acid, 3 lbs. hydroxylamine hydrochloride and sufficient ammonium hydroxide to give a pH of 4.8.

By this treatment very dark, adherent, even, hard corrosion-resistant coatings of some 150–200 mg./sq. ft. were obtained upon ferrous surfaces which were eminently suitable for use as a base for paints, lacquers or like materials.

The invention includes the novel treating solutions as well as their use in the treatment of metallic surfaces.

We claim:

1. A process for the production of phosphate coatings on ferrous surfaces in which process the surface is treated with a coating solution consisting essentially of at least one substance selected from the group consisting of phosphoric acid, ammonium phosphate and the alkali metal phosphates, said phosphate being present in a concentration of 0.05 to 0.25 molar, at least one reducible compound selected from the group consisting of m-nitrobenzene-sulphonic acid in an amount of .05 percent to .25 percent, o-nitrochlorbenzene-p-sulphonic acid in an amount of .5 percent to 2 percent, 3-nitrophthalic acid in an amount of .02 percent to .1 percent, m-nitrobenzoic acid in an amount of .02 percent to .1 percent, and the salts thereof in a concentration equivalent to the concentration of the corresponding acid said solution being maintained at a temperature above 60° C. and containing sufficient alkaline material to produce a pH within the range of 4.2 to 5.8.

2. A liquid composition for the production of phosphate coatings on ferrous surfaces, said composition consisting of an aqueous solution composed of at least one substance selected from the group consisting of phosphoric acid, ammonium phosphate and the alkali metal phosphates, said phosphate being present in a concentration of from 0.05 to 0.25 molar and at least one reducible compound selected from the group consisting of m-nitrobenzene-sulphonic acid in an amount of .05 percent to .25 percent, o-nitrochlorbenzene-p-sulphonic acid in an amount of .5 percent to 2 percent, 3-nitrophthalic acid in an amount of .02 percent to .1 percent, m-nitrobenzoic acid in an amount of .02 percent to .1 percent, and the salts thereof in a concentration equivalent to the concentration of the corresponding acid, said solution containing sufficient alkaline material to produce a pH within the range of 4.2 to 5.8.

3. A liquid composition for the production of phosphate coatings on ferrous surfaces, said composition consisting essentially of an aqueous solution composed of at least one substance selected from the group consisting of phosphoric acid, ammonium phosphate and the alkali metal phosphates, said phosphate being present in a concentration of from .05 to .25 molar, and m-nitrobenzene-sulphonic acid in an amount of .05% to .25%, said solution containing sufficient alkaline material to produce a pH within the range of 4.2 to 5.8.

4. A liquid composition for the production of phosphate coatings on ferrous surfaces, said composition consisting of an aqueous solution composed of at least one substance selected from the group consisting of phosphoric acid, ammonium phosphate and the alkali metal phosphates, said phosphate being present in a concentration of from .05 to .25 molar, and o-nitro-chlorobenzene-p-sulphonic acid in an amount of .5% to 2%, said solution containing sufficient alkaline material to produce a pH within the range of 4.2 to 5.8.

5. A liquid composition for the production of phosphate coatings on ferrous surfaces, said composition consisting of an aqueous solution composed of at least one substance selected from the group consisting of phosphoric acid, ammonium phosphate and the alkali metal phosphates, said phosphate being present in a concentration of from .05 to .25 molar, and 3-nitrophthalic acid in an amount of .02% to .1%, said solution containing sufficient alkaline material to produce a pH within the range of 4.2 to 5.8.

6. A liquid composition for the production of phosphate coatings on ferrous surfaces, said composition consisting of an aqueous solution composed of at least one substance selected from the group consisting of phosphoric acid, ammonium phosphate and the alkali metal phosphates, said phosphate being present in a concentration of from .05 to .25 molar, and m-nitrobenzoic acid in an amount of .02% to .1%, said solution containing sufficient alkaline material to produce a pH within the range of 4.2 to 5.8.

7. A liquid composition for the production of phosphate coatings on ferrous surfaces, said composition consisting of an aqueous solution composed of ammonium phosphate in a concentration of from 0.05 to 0.25 molar, and at least one reducible compound selected from the group consisting of m-nitrobenzene-sulfonic acid in an amount of 0.05% to 0.25%, o-nitro-chlorobenzene-p-sulfonic acid in an amount of 0.5% to 2%, 3-nitrophthalic acid in an amount of 0.02% to 0.1%, m-nitrobenzoic acid in an amount of 0.02% to 0.1% and the salts thereof in a concentration of the corresponding acid, said solution contain-

ing sufficient alkaline material to produce a pH within the range of 4.2–5.8.

8. A process for the production of phosphate coatings on ferrous surfaces which comprises the steps of treating the said surface with a coating solution consisting essentially of at least one substance selected from the group consisting of phosphoric acid, ammonium phosphate and the alkali metal phosphates, said phosphate being present in a concentration of 0.05 to 0.25 molar, at least one reducible compound selected from the group consisting of m-nitrobenzenesulfonic acid in an amount of .05 percent to .25 percent, o-nitrochlorbenzene-p-sulfonic acid in an amount of .5 percent to 2 percent, 3-nitrophthalic acid in an amount of .02 percent to .1 percent, m-nitrobenzoic acid in an amount of .02 percent to .1 percent, and the salts thereof in a concentration equivalent to the concentration of the corresponding acid, said solution being maintained at a temperature above 60° C. and containing sufficient alkaline material to produce a pH within the range of 4.2 to 5.8, continuing said treatment until a coating is formed and thereafter rinsing said coating in a dilute aqueous chromic acid solution.

MONTAGU HYAMS.
ANDREW NICHOLSON.

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