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PHOSPHATE COATING OF METAL ARTICLES

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This invention relates to the production of phosphate coatings on metal articles, and relates more particularly to a phosphatizing liquid and a method of phosphatizing employing an organic liquid as the vehicle for the phosphoric acid in lieu of the water of the conventional aqueous phosphatizing solution.

The production of phosphate coatings on metal articles is today widely employed for the purpose of protecting the metal against oxidation and providing a surface properly conditioned for paint finishes. In present phosphatizing processes employing an aqueous phosphatizing solution, the metal must be thoroughly clean before phosphatizing, as any rust or a thin film of oil or even a fingerprint may cause an unsatisfactory phosphate coating or may produce a non-uniform appearance of the final product. Metal articles to be phosphated are therefore usually thoroughly cleaned to remove all traces of rust, and, to afford protection during the operations preceding phosphatizing, are usually coated with a film of rust preventive oil, called slushing oil, or with some proprietary oily product adapted to perform a similar protective function. When ready for phosphating, the metal articles are (1) degreased by solvent or vapor degreasing, this degreasing step employing an oil solvent such as trichlorethylene or perchlorethylene. Following degreasing, the metal articles are usually (2) cleaned in a hot, mildly alkaline aqueous cleaning solution, (3) thoroughly rinsed twice in hot water, and (4) phosphatized by being either sprayed with or dipped in the hot aqueous phosphatizing solution. After the phosphate coating is thus applied to the metal articles, they are (5) again rinsed in hot water, (6) subjected to a passivation treatment in hot dilute chromic acid solution intended to prevent creep of rust under any accidental break in the final paint film, (7) again thoroughly rinsed in hot water, and (8) dried in hot air, after which the articles are (9) painted, usually by spraying with paint and then baking. If the painting step does not immediately follow the drying step, the articles must be kept dry or they may oxidize. The process above described is sometimes abbreviated by omitting the passivation treatment (step 6) and the preceding and subsequent rinses (steps 5 and 7).

The aqueous phosphatizing solution used in a process such as just described may comprise about 2% of a mixture of free phosphoric acid, zinc phosphate and an oxidizing agent such as a nitrate or a chlorate, frequently termed an accelerator. The free phosphoric acid reacts with the metal of the article and with oxygen from the air or from the oxidizing agent or both to form an adherent coating of insoluble metallic phosphate. This phosphate coating protects the metal somewhat, but its primary function is to serve as a bond for the paint finish. The zinc phosphate of such an aqueous phosphatizing solution is used to improve the grain structure of the phosphate coating, and may act as a catalyst. The phosphate coating obtained improves as the temperature of the solution is raised, and the solution is therefore used as near the boiling point as may be convenient.

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We have discovered that improved results and great economy of operation may be achieved by substituting an organic phosphatizing liquid for the aqueous solution above described, while at the same time modifying the process in a number of particulars later discussed. The active phosphatizing agent may be the commercial phosphoric acid known as the 85% syrup, and the zinc phosphate and the accelerator of the aqueous solution are unnecessary, although they may be used if desired. According to the preferred form of our invention, the phosphoric acid syrup is dissolved in a volatile organic solvent, preferably a 50–50 mixture of acetone and carbon tetrachloride. The concentration of syrup in the solvent may range from 1% to 7%, but we prefer 3%, although there is not much difference in results anywhere in the range from 2% to 4%. Immediately following the conventional degreasing step, the organic phosphatizing liquid is applied by dipping or by spraying. After being dipped or sprayed, the metal article dries in air at room temperature almost instantly, due to the volatility of the solvent employed, leaving a very thin film of metal phosphate on the metal article. A conventional solvent recovery system may advantageously be employed, connected either to a hood over the dipping tank or to the usual spray booth, thus enabling the acetone and carbon tetrachloride to be recovered and reused. The metal article may be painted immediately, or, if more convenient, may be stored for a reasonable period before painting without requiring any special precautions in storage. Tests have shown that polished steel panels so phosphated may be stored for as long as one month under ordinary room conditions without exhibiting any signs of rust and without impairing the subsequent paint finish. As is customary with aqueous phosphatizing, the paint is preferably sprayed on the phosphatized article and then baked.

The extreme simplicity of this organic phosphatizing process as compared to the aqueous phosphatizing processes now in use will be at once apparent. The nine steps of the full aqueous process described above are reduced to three: (1) degreasing, (2) phosphatizing by dipping or spraying and practically simultaneous air drying, and (3) painting. No elevated temperatures are required in the combined phosphatizing and drying step. As we shall show hereinafter, it is even possible under some circumstances to eliminate the degreasing step.

Metal articles phosphatized by our organic phosphatizing method, and then painted, show superior results in the standard salt spray accelerated test as compared to similar articles produced by either the full or the abbreviated aqueous phosphatizing methods described above. With our process, the paint does not peel along the edges of the conventional scratch, nor is there any evidence of creep. The paint remaining after the salt spray tests shows superior adhesion with our process, this having been determined by subjecting the various panels to a prescribed brushing procedure.

While the organic vehicle we employ is more expensive than the aqueous vehicle of former methods, the superior product obtained and the savings effected by the elimination of steps and the simplification of the remaining steps, more than counterbalance the increased material cost, which cost may be greatly lessened by using conventional solvent recovery methods as above described. Moreover, the fact that our organic phosphatizing liquid may be applied at ordinary room temperature and the accompanying drying may also be effected at room temperature, enables the necessary apparatus to be decidedly simplified, although heat may be used in our process if desired.

In the conventional aqueous process, the hydrogen which is liberated as a result of the reaction between the phosphoric acid and the metal, apparently tends to adhere to the metal and prevent further reaction. One purpose of the oxidizing agents or accelerators is to react with this hydrogen and thus speed up the phosphatizing reaction by removing the hydrogen from the reaction zone. In our process, no such hydrogen difficulty is experienced, making it unnecessary to employ oxidizing agents, although, as stated above, they may be used without doing any harm. We have found that zinc phosphate is entirely unnecessary in our process, but, like the accelerators, it may be employed if desired. The phosphate coating obtained by our preferred process is so much better than that obtained by the conventional aqueous phosphatizing processes, that, even without the paint finish, it affords a very substantial degree of protection to the metal. The chromic acid passivation treatment, designed to prevent creep, is rendered unnecessary by the superior phosphate coating we obtain.

One of the advantages of our preferred process as described above, is the wide applicability of the process to different metals. We have obtained excellent results not only with steel articles, but with articles made of cast iron, zinc die-cast metal, aluminum-zinc die-cast metal containing only a small proportion of zinc, and German silver. Pure aluminum and cadmium-plated articles cannot be satisfactorily phosphated, either by our process or by conventional aqueous methods.

The organic vehicle employed in our process should be one in which phosphoric acid is soluble in the proportion in which it is to be employed, and the vehicle should preferably also be sufficiently volatile so that the remaining film will evaporate promptly at room temperature from the metal article after dipping or spraying. The commercial phosphoric acid 85% syrup contains about 15% of water, and if this material is to be used as the source of phosphoric acid, which is desirable from the cost standpoint, the organic vehicle employed must also be compatible with the resulting small amount of water in the final mixture. It is probable also that a small amount of water is necessary in the phosphatizing liquid in order to permit the phosphoric acid to ionize.

Acetone ideally meets all of the foregoing requirements, and may be used alone with entirely satisfactory results, but its low flash point (−10° C.) makes its use rather dangerous in commercial operations, creating a possible explosion hazard. We therefore prefer to mix carbon tetrachloride with the acetone in order to raise the flash point and decrease the hazard. The carbon tetrachloride is used solely as a flash inhibitor, its function being to raise the flash point of the mixture to the desired extent. As is necessary, carbon tetrachloride is compatible with acetone without destroying the ability of the acetone to dissolve the phosphoric acid. The phosphoric acid syrup is not soluble in carbon tetrachloride alone, but is sufficiently soluble in a mixture of acetone and carbon tetrachloride.

Mixtures of acetone and carbon tetrachloride ranging from 60–40 to 44–56 by volume have a flash point of about 54° C., slightly above the flash point of ordinary kerosene. Such mixtures may therefore be safely handled, with only the usual precautions employed in paint spraying operations. The proportions of acetone and carbon tetrachloride may thus be considerably varied without substantially changing the flash point of the mixture. If the carbon tetrachloride be reduced to 30% of the mixture, the flash point drops to 49° C., slightly less than that of kerosene, and this would appear to be about the lower limit of safety. Acetone and carbon tetrachloride by themselves are completely miscible in all proportions, but due to the water included in the commercial phosphoric acid that we prefer to employ, the proportion of carbon tetrachloride cannot be increased beyond 56%, or two liquid phases appear, making spraying impractical. We have been able to observe no conclusive differences, so far as phosphatizing results are concerned, with mixtures of acetone and carbon tetrachloride ranging from 30% carbon tetrachloride up to 56% carbon tetrachloride, as compared with the use of acetone alone. For reasons of economy and convenience, we therefore prefer to use as our organic phosphatizing liquid, a mixture of equal volumes of acetone and carbon tetrachloride, in which is dissolved 3% of commercial phosphoric acid 85% syrup.

It is possible to substitute other organic liquids for the actone-carbon tetrachloride mixture described above. We have found that 3% of commercial phosphoric acid syrup will dissolve in the following volatile organic solvents: methyl alcohol, amyl acetate, methyl acetate, normal-butyl alcohol, secondary-butyl alcohol, isopropyl alcohol, denatured ethyl alcohol, normal-propyl alcohol, and dioxane. All of these solvents are commercially obtainable, and, like acetone, may be used either with or without carbon tetrachloride,

but, for the sake of safety, a flash inhibitor is eminently desirable. These solvents are listed above in their decreasing order of effectiveness, methyl alcohol and amyl acetate producing a slightly less desirable phosphate coating (judged by salt spray paint tests) than our preferred 50–50 acetone-carbon tetrachloride mixture, and the others being successively less effective, but all of them produce a phosphate coating superior to a conventional aqueous phosphatizing process used as a comparison standard.

Solvents having a boiling point substantially higher than that of amyl acetate (148° C.) may be regarded for the purposes of this invention as non-volatile. We have successfully used several such non-volatile organic solvents, such as octyl alcohol (B. P. 195° C.), cyclohexanol (B. P. 161.5° C.) and tri-butyl phosphate (B. P. 178° C.), in all of which phosphoric acid syrup is soluble to the extent of 3%. These non-volatile solvents do not require a flash inhibitor, but have the disadvantage that heat should be used to accelerate the drying step, for example, by blowing hot air over the metal articles to be dried. They also produce somewhat less desirable phosphate coatings than the volatile solvents. However, all of the non-volatile solvents named above produced better phosphate coatings (judged by salt spray paint tests) than a conventional aqueous phosphatizing process used as a comparison standard, and we therefore do not wish to exclude their use from the scope of our invention.

It is also desirable that the organic vehicle be one that has grease and oil penetrating properties. This is true of our preferred acetone-carbon tetrachloride mixture. Where the organic vehicle has this property, it is possible to apply our phosphate coating even through a thin oil film. Thus, we have successfully coated polished steel panels dipped in either lubricating oil or a commercial slushing oil, drained for twenty-four hours, and then sprayed with our preferred organic phosphatizing solvent, without cleaning or degreasing the panels in any way after the oil dip. The panels were then painted in the usual manner. Clean control panels were similarly treated except for the oil dip. The phosphate coatings on the oil-dipped panels, before painting, had a poor appearance, but, judged by salt spray tests after painting, were almost the equal of those obtained on the clean control panels. This suggests the possibility of eliminating the degreasing step in commercial practice where the metal articles to be phosphatized are not excessively coated with oil or grease.

Our above-described low temperature, rapid process results in the formation of an extremely thin phosphate film. This film is frequently so thin that it would easily escape notice by the uninitiated. In the usual phosphatizing processes, the phosphate coating produced is of substantial thickness, being measurable in thousandths of an inch, and is plainly evident to the naked eye. It may very well be that the exceptional results produced by our process are due in part to the extreme thinness of the resulting phosphate film. It seems quite probable that the adhesion between the metal and the metal phosphate and the adhesion between the metal phosphate and the paint are both greater than the adhesion between superposed molecules of the metal phosphate; and, if this be true, the ideal coating would be a uniform layer of metal phosphate just one molecule thick. Another possible explanation is that the thick prior art coatings are

sufficiently porous to hold enough water to affect the paint adherence adversely. Regardless of the correctness of these theories, the fact remains, as pointed out above, that our process produces superior paint adherence, judged by the standard salt spray test, as compared to previous aqueous phosphatizing methods.

Although we have thus described our invention in considerable detail in the best form of which we are aware, in accordance with the patent statutes, it will be evident that various changes and modifications may be made by those skilled in the art without departing from the spirit of our invention. Accordingly, we desire to be limited only by the scope of the appended claims.

We claim:

1. The process of phosphate coating an article made of metal of the class capable of reacting with phosphoric acid to form a metal phosphate, which comprises wetting the metal article with a phosphatizing liquid consisting essentially of from one to seven percent of concentrated phosphoric acid dissolved in an organic solvent therefor; said organic solvent being capable of being evaporated at a moderate temperature, said phosphatizing liquid having no aqueous phase and containing only a small proportion of water based on its phosphoric acid content; and removing the organic solvent from the wetted article by evaporation, thereby producing on the metal article a thin and substantially dry film of metal phosphate capable of serving directly as a paint-bonding medium.

2. The process as claimed in claim 1 in which the organic solvent is acetone.

3. The process of phosphate coating an article made of metal of the class capable of reacting with phosphoric acid to form a metal phosphate, which comprises wetting the metal article with a phosphatizing liquid consisting essentially of from one to seven percent of concentrated phosphoric acid dissolved in a volatile organic solvent therefor, and carbon tetrachloride; said carbon tetrachloride being present in sufficient amount to raise the flash point of the phosphatizing liquid materially above that of said volatile organic solvent, said phosphatizing liquid having no aqueous phase and containing only a small proportion of water based on its phosphoric acid content; and removing the organic solvent and carbon tetrachloride from the wetted article by evaporation at not substantially above room temperature, thereby producing on the metal article a thin and substantially dry film of metal phosphate capable of serving directly as a paint-bonding medium.

4. The process as claimed in claim 3 in which the volatile organic solvent is acetone.

5. The process of phosphate coating an article made of metal of the class capable of reacting with phosphoric acid to form a metal phosphate, which comprises wetting the metal article with a phosphatizing liquid consisting essentially of from two to four percent of concentrated phosphoric acid dissolved in acetone and carbon tetrachloride; said carbon tetrachloride being present in sufficient amount to raise the flash point of the phosphatizing liquid materially above that of the acetone, said phosphatizing liquid having no aqueous phase and containing only a small proportion of water based on its phosphoric acid content; and removing the acetone and carbon tetrachloride from the wetted article by evaporation at not substantially above room temperature, thereby producing on the

metal article a thin and substantially dry film of metal phosphate capable of serving directly as a paint-bonding medium.

6. A phosphatizing liquid for phosphate coating articles made of metal of the class capable of reacting with phosphoric acid to form a metal phosphate, consisting essentially of from one to seven percent of concentrated phosphoric acid dissolved in an organic solvent therefor, said organic solvent being capable of being evaporated at a moderate temperature, and said phosphatizing liquid having no aqueous phase and containing only a small proportion of water based on its phosphoric acid content.

7. A phosphatizing liquid for phosphate coating articles made of metal of the class capable of reacting with phosphoric acid to form a metal phosphate, consisting essentially of from one to seven percent of concentrated phosphoric acid dissolved in acetone, and said phosphatizing liquid having no aqueous phase and containing only a small proportion of water based on its phosphoric acid content.

8. A phosphatizing liquid for phosphate coating articles made of metal of the class capable of reacting with phosphoric acid to form a metal phosphate, consisting essentially of from one to seven percent of concentrated phosphoric acid dissolved in a volatile organic solvent therefor and carbon tetrachloride, said carbon tetrachloride being present in sufficient amount to raise the flash point of the phosphatizing liquid materially above that of said volatile organic solvent, and said phosphatizing liquid having no aqueous phase and containing only a small proportion of water based on its phosphoric acid content.

9. A phosphatizing liquid as claimed in claim 8 in which the volatile organic solvent is acetone.

10. A phosphatizing liquid for phosphate coating articles made of metal of the class capable of reacting with phosphoric acid to form a metal phosphate, consisting essentially of from two to four percent of concentrated phosphoric acid dissolved in acetone and carbon tetrachloride, said carbon tetrachloride being present in sufficient amount to raise the flash point of the phosphatizing liquid materially above that of the acetone, and said phosphatizing liquid having no aqueous phase and containing only a small proportion of water based on its phosphoric acid content.

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