COATING SOLUTIONS DERIVED FROM PEROXY DISULFURIC ACID OR PEROXY DIPHOSPHORIC ACID

Inventors: Richard Elliott Shaw, Windsor; Michael Ware, Penn, both of England

Assignee: Imperial Chemical Industries Limited, London, England

Filed: Aug. 8, 1969

Appl. No.: 848,699

Foreign Application Priority Data
Aug. 16, 1968 Great Britain..................39,268/68

U.S. Cl..........................148/6.15 Z, 148/6.17

Int. Cl.....................................C23H 7/08

Field of Search..................148/6.15, 6.17

References Cited

UNITED STATES PATENTS
2,272,216 2/1942 Lodeesen..............................148/6.15
2,326,309 8/1943 Romig ..................................148/6.15
2,820,731 1/1958 Heinzelman et al.....................148/6.15
3,144,361 8/1964 Klinghoffer............................148/6.15
3,166,444 1/1965 Ehren et al............................148/6.15 X

Primary Examiner—Ralph S. Kendall
Attorney—Cushman, Darby & Cushman

ABSTRACT

An acidic phosphating solution for coating metal surfaces comprising (1) zinc phosphate (2) an acid radical derived from peroxo disulphuric acid, peroxo diphosphoric acid, peroxy diboric acid or peroxy dicarboxylic acid and (3) a conventional phosphating accelerator.

8 Claims, No Drawings
1 COATING SOLUTIONS DERIVED FROM Peroxy Disulfuric ACID or Peroxy Diposphoric ACID

The present invention relates to phosphating solutions and to the use of these solutions in a process of producing improved phosphate coatings on metallic surfaces.

It is well known that a crystalline coating of an inorganic phosphorus compound on metallic surfaces, particularly ferrous, zinciferous and aluminum surfaces. Such a coating is useful in that a subsequently applied paint film has good adhesion to the metal surface and the corrosion resistance of the painted metal surface is improved. The most useful phosphate coatings are normally applied to the metal surface by treatment with an acidic phosphating solution which contains an inorganic phosphate, for example zinc or manganese phosphate and it is common practice to accelerate the coating reaction by including a suitable oxidant in the phosphating solution. Oxidants conventionally employed as accelerators are, for example, sodium nitrite (used either alone or in conjunction with, for example, a chlorate or a nitrate), and hydrogen peroxide.

In order that a paint subsequently applied over the crystalline phosphate coating shall provide a coating which is smooth and of reasonable gloss, and that there shall be good adhesion to the metal surface, it is preferable that the crystalline coating is fine and hard in texture. However, when using the known phosphating solutions, and particularly when applying with or without an accelerator, it has been found that it is useful as accelerators and optionally combined with other known phosphating additives, it has not been possible to obtain the most desirable fine and hard coatings.

We have now found surprisingly that tight, smoother and harder phosphate coatings can be produced on ferrous, zinciferous and aluminum surfaces and that the phosphating process is more amenable to control when there is employed an acidic phosphating solution which contains zinc phosphate, an acid radical derived from peroxy disulfuric acid, peroxy diposphoric acid, peroxy diboric acid or peroxy dicarbonic acid and a conventional phosphating accelerator.

By a conventional phosphating accelerator we mean an oxidant which will by itself effectively accelerate the deposition of a phosphate coating under the normal phosphating conditions, and these accelerators are well known to those skilled in the art. Important example of such oxidants and the preferred conventional accelerators are the alkali metal nitrates and amonium nitrite and hydrogen peroxide. The nitrates are particularly preferred because they lend itself to the coating reaction. Other less effective oxidants include the alkali metal nitrates and chlorates. It has also been found useful to use these accelerators in combination with other accelerators, for example, the nitrates may be used in combination with the chlorates or other accelerates may be used in combination with certain other additives which may serve to improve the performance of the phosphating process, for example glycerophosphate and fluoride ions. These combinations may be present in the new phosphating solutions. The conventional accelerators are to be distinguished from those salts comprising an acid radical derived from peroxy disulfuric acid, peroxy diposphoric acid, peroxy diboric acid and peroxy dicarbonic acid which are known by those skilled in the art to be ineffective as phosphating accelerators by themselves under the normal phosphating conditions, and more particularly they are quite ineffective when a phosphate coating is to be obtained on a metallic surface in a short space of time by spraying the surface with phosphating solution, e.g., at temperatures in the region of 130–140°F for 60 seconds.

The peroxy acid radicals which are present in the improved phosphating solutions are distinguished from the conventional phosphating accelerators in that they contain the grouping X-O-O-X in which X represents an S, P, or B atom covalently bonded to other atoms. Without in any way limiting the scope of our invention we believe that it is the presence of this grouping which is responsible for the surprising improvement in the quality of coating which is found when the peroxy acid radicals are present together with a conventional accelerator in a phosphating solution containing zinc phosphate. Compounds comprising the peroxy acid radical which contains the grouping X-O-O-X should be distinguished from those “per” compounds, e.g., the peroxides and perchlorates, which do not contain such a link, and those “per” compounds which merely contain hydrogen peroxide of crystallization.

Although the improved phosphating solution may be applied to metallic surfaces by spraying, dipping or flow coating or roller coating it is in the application by spray that particular improvement is found over the prior solutions. Phosphate coatings which are tighter, harder and smoother than the coatings obtained with the prior solutions are obtained when the solutions are sprayed onto metallic surfaces at temperatures in the range 100–140°F. A suitable time period for the spray treatment is 60–90 seconds.

Thus the present invention also provides a process of producing a phosphate coating on a ferrous, zinciferous or aluminum surface in which the surface is treated, preferably by spraying, with an acidic phosphating solution which contains zinc phosphate, an acid radical derived from peroxy disulfuric acid, peroxy diposphoric acid, peroxy diboric acid or peroxy dicarbonic acid and a conventional accelerator as herein defined for such a period of time and at such a temperature as to produce a phosphate coating.

The characteristics of a phosphate coating are commonly determined by visual inspection of the coating and of a subsequent phosphating and, by a simple "scratching" test, for example with a fingernail. We find that the phosphate coatings obtained using the improved phosphating solutions are more resistant to "scratching," e.g., they are less readily marked than are the prior phosphate coatings by a fingernail drawn across the surface, and they yield a smoother and more glossy surface when subsequently coated with paint.

The hardness, tightness and uniformity of the coatings produced when using the present solutions are particularly valuable when an article is to be painted subsequently by electrodeposition. A paint applied by electrodeposition is particularly liable to reflect and even magnify any unevenness of the substrate to which it is applied and the character of the coatings obtained by using the present solutions ensures that the optimum appearance for a given substrate can be achieved.

We also find that the weight of phosphate coating deposited on a metallic surface can be readily regulated by the addition of peroxy acid radical and may be progressively decreased depending upon the proportion of peroxy acid radical present.

The acid radical of the peroxy acid is preferably introduced into the phosphating solution as the alkali metal or ammonium salt of the peroxy acid. In general we find that it is necessary for there to be present at least 0.005 percent of such a salt by weight calculated as the peroxy acid radical and based on the total weight of the phosphating solution but preferably there is present in the phosphating solution 0.01–1.0 percent of the salt by weight calculated as peroxy acid radical based on the total weight of the phosphating solution. Addition of the peroxy acid salt to the phosphating solution may take place at any suitable time, for example just prior to use in the phosphating process or, at suitable times thereafter to maintain the concentration approximately constant and to maintain the desired coating weight on the metal surface.

The acidity of the phosphating solutions and their content of zinc and phosphate ions are based on the conventional phosphating solutions containing zinc phosphate and are well known to those skilled in the art.

The proportion of conventional accelerator which is desirable present in the phosphating solution will depend upon the particular accelerator chosen and upon the coating characteristics required. In general this will be known to those skilled in the art but preferably, and particularly when the application there is using between 0.005 percent and 0.1 percent of hydrogen peroxide (100 vol.) or nitrite by weight based on the total weight of the solution.

The invention is illustrated by the following examples in which proportions are by weight unless otherwise stated.
EXAMPLE 1

An acidic phosphating solution based on zinc phosphate and phosphoric acid was prepared containing 0.2 percent zinc and 0.5 percent phosphate based on the weight of the solution. The solution was divided into four portions (a), (b), (c) and (d) to which were added sodium nitrite and/or ammonium persulphate according to Table 1 below.

Four panels measuring 12"x4" and of steel typical of that used in automobile manufacture were first cleaned by spraying with a mild alkaline cleansing solution for 2 minutes at 160°F and 10 lbs/sq.in. pressure, rinsed in water and then sprayed with a phosphating solution for 1 minute at 130°F and 10 lbs/sq.in. pressure.

The panels were rinsed with water and dried in a blast of warm air. The nature of the resulting phosphate coating is described in Table 1.

<table>
<thead>
<tr>
<th>Phosphating solution</th>
<th>Calculated on the weight of the solution</th>
<th>Coating wt., mg/dm²</th>
<th>Characteristics of coating produced</th>
</tr>
</thead>
<tbody>
<tr>
<td>(a)</td>
<td>0.03</td>
<td>100</td>
<td>Smooth, soft.</td>
</tr>
<tr>
<td>(b)</td>
<td>0.06</td>
<td>160</td>
<td>Rust stained</td>
</tr>
<tr>
<td>(c)</td>
<td>0.03</td>
<td>100</td>
<td>Very tight, hard and strongly adherent</td>
</tr>
<tr>
<td>(d)</td>
<td>0.03</td>
<td>100</td>
<td>Very tight, hard and strongly adherent</td>
</tr>
</tbody>
</table>

When the panels were subsequently coated by electrodeposition as in Example 1 and stoved, panel (d) showed the best final appearance.

EXAMPLE 2

An acidic aqueous phosphating solution based on zinc phosphate, phosphoric acid and zinc nitrate was prepared containing 0.16 percent zinc, 0.7 percent phosphate and 0.5 percent nitrate. The solution was divided into four portions (a), (b), (c) and (d) to which were added sodium nitrite and/or ammonium persulphate according to Table 2 below.

Each of the four portions of phosphating solution were applied to a separate steel panel (cleaned as in Example 1) according to the method of Example 1. The nature of the of the resulting coating is described in Table 2.

<table>
<thead>
<tr>
<th>Phosphating solution</th>
<th>Calculated on the weight of the solution</th>
<th>Coating wt., mg/dm²</th>
<th>Characteristics of coating produced</th>
</tr>
</thead>
<tbody>
<tr>
<td>(a)</td>
<td>0.03</td>
<td>300</td>
<td>Smooth, soft.</td>
</tr>
<tr>
<td>(b)</td>
<td>0.06</td>
<td>300</td>
<td>Smooth, soft.</td>
</tr>
<tr>
<td>(c)</td>
<td>0.03</td>
<td>100</td>
<td>Rust stained, negligible coating.</td>
</tr>
<tr>
<td>(d)</td>
<td>0.03</td>
<td>100</td>
<td>Tight, hard, strongly adherent.</td>
</tr>
</tbody>
</table>

When the panels were subsequently coated by electrodeposition as in Example 1 and stoved, panel (d) showed the best final appearance.

<table>
<thead>
<tr>
<th>Phosphating solution</th>
<th>Hydrogen peroxide, 100 vol.</th>
<th>Perphosphate, 2%</th>
<th>Coating weight, mg/dm²</th>
<th>Characteristics</th>
</tr>
</thead>
<tbody>
<tr>
<td>(a)</td>
<td>0.03</td>
<td>0.03</td>
<td>100</td>
<td>Tight, hard,</td>
</tr>
<tr>
<td>(b)</td>
<td>0.06</td>
<td>0.03</td>
<td>120</td>
<td>Rust stained,</td>
</tr>
<tr>
<td>(c)</td>
<td>0.03</td>
<td>0.03</td>
<td>100</td>
<td>More tight and</td>
</tr>
<tr>
<td>(d)</td>
<td>0.03</td>
<td>0.03</td>
<td>100</td>
<td>(c) by scrape</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>test.</td>
</tr>
</tbody>
</table>

When the panels were subsequently coated by electrodeposition as in Example 1 and stoved, panel (d) showed the best final appearance.

What is claimed is:

1. An acidic phosphating solution which contains zinc phosphate, an acid radical having the grouping X-O-X, where X is selected from the group consisting of S, P, O, B or C and derived from peroxy disulphuric acid, peroxy diphosphoric acid, peroxy diboric acid or peroxy dicarbonic acid and between 0.005 percent and 0.1 percent, based on the total weight of solution, of a phosphating accelerator selected from alkali metal nitrite, ammonium nitrite and hydrogen peroxide.

2. An acidic phosphating solution according to claim 1 wherein there is present at least 0.005 percent by weight of peroxy acid radical based on the weight of the phosphating solution.

3. An acidic phosphating solution according to claim 1 wherein there is present at least 0.005 percent by weight of peroxy acid radical based on the weight of the phosphating solution.

4. An acidic phosphating solution according to claim 1 wherein there is present 0.01 percent to 1.0 percent of peroxy acid radical based on the weight of the phosphating solution.

5. A process of forming a phosphating coating on a ferrous, zinciferous or aluminum surface which consists in treating the surface with a phosphating solution according to claim 1 for such a period of time and at such a temperature as to produce a coating.

6. A process according to claim 5 wherein the phosphating solution is applied to the metal surface by spraying.

7. A process according to claim 6 wherein the phosphating solution is sprayed onto the metallic surface at a temperature in the range 100—140°F.

8. A process according to claim 7 wherein the metal surface is sprayed with phosphating solution for 60—90 seconds.