CORROSION RESISTANT IRON OR STEEL
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9 Claims

ABSTRACT OF THE DISCLOSURE

Corrosion resistant ferrous metal articles are produced by treating the articles with iron phosphate prior to applying a strongly adherent coating of a copolymer of an olefin such as ethylene and an ethylenically unsaturated carboxylic acid such as acrylic acid.

This application is a continuation-in-part of our copending application Ser. No. 339,074 filed Jan. 21, 1964, now abandoned.

This invention relates to inhibiting the corrosion of metals. More particularly, this invention relates to inhibiting the deterioration of metal surfaces, specifically ferrous metals, by coating said surface with a highly adhesive polymeric material. In another aspect, this invention relates to the treatment of metal surfaces prior to the application of a protective coating to render the coating more effective.

It is well known that surfaces of metals normally tend to oxidize or rust when exposed to moisture and oxygen. Various methods have been suggested to promote better protection against corrosion and rust formation. The art is familiar with methods which propose the use of thin films of an oil-base material such as lanolin, petroleum jelly, and the like. However, such methods have not been entirely satisfactory.

Less desirable is the presence of an oily protective surface where an overcoat of paint, lacquer, or the like is to be applied. Rigorous cleaning methods must be employed to prepare the surface for the application and retention of said overcoats. When such materials are removed from metal surfaces, the protective effect of the oily materials is eliminated. These corrosion inhibitors, therefore, show definite disadvantages. It is also known that various lamineers have been produced to protect metal surfaces. Thermoplastic materials have been extruded, sprayed, or bonded to metallic surfaces to provide corrosion-resistant surfaces; however, when the protective layer is damaged, e.g., scratched, exposing the base metal, corrosion of the metal not only takes place where exposed but usually penetrates under the coating causing eventual widespread failure.

It is an object of this invention to provide a coated metal substrate, more particularly, a coated ferrous metal substrate, that resists and retards corrosion. It is another object to provide a method for treating metallic surfaces to inhibit corrosion of, and rust formation on, said metallic surfaces. It is a further object to provide coated metals that have a lesser tendency to be corroded yet remain highly receptive to paints, lacquers, and the like. A more specific object of this invention is to provide a metal, more particularly, a ferrous metal, resistant to rust and corrosion, wherein said metal is coated with a highly adhesive polymeric material, the interface of which is air-tight and corrosion-resistant.

Various other objects, advantages, features and variations of the invention will become apparent from the following description.

The above and other objects are accomplished in accordance with the invention, which comprises coating the surfaces of treated metals, especially ferrous metals, with a polymeric film composition which comprises a polymer of an olefin such as ethylene, propylene, butene-1, and the like and an ethylenically unsaturated carboxylic acid, particularly characterized in that the metal surface is one which has been treated with iron phosphate before applying the polymer coating.

Accordingly, in a preferred embodiment of the present invention, an iron phosphate-treated metal surface is employed as the metal substrate to which is applied a coating of an adhesive polymeric material. An example of such a treated metal is "Bonderite 1000" treated steel, which comprises a steel substrate which has been treated with an iron phosphate aqueous solution which generates a protective coating on the steel surface. While the technique for treating a metal surface with iron phosphate is not necessarily a part of the present invention, a typical treatment which can be used includes the steps of subjecting a metal article to an alkaline cleaning solution such as caustic soda or the like followed by rinsing in hot water. The alkaline cleaning solution can contain softening and/or wetting agents if desired. The resulting cleaned metal article is then contacted with a "Bonderite 1000" treating solution comprising phosphoric acid and iron phosphate which produces a substantially insoluble iron phosphate coating on the surfaces of the metal article. The iron phosphate-treated metal article is then given a cold water rinse which can optionally be followed by a rinse in hot water containing a small amount of chromic acid. To this specially treated and dried surface is applied a layer of an olefin-unsaturated carboxylic acid polymer.

The polymer used in this invention comprises a copolymer of a major proportion or at least about 75 percent by weight of an olefin such as ethylene, propylene, butene-1, and the like and not more than about 25 percent and preferably from about 4 percent to about 25 percent by weight based on the copolymer of an acidic comonomer selected from α,β-ethylenically unsaturated mono- and polycarboxylic acids and acid anhydrides having from 3 to 8 carbon atoms per molecule, inclusive, and partial esters of such polycarboxylic acids wherein the acid moiety has at least one carboxyl group and the alcohol moiety has from 1 to 20 carbon atoms. Specific examples of such comonomers are acrylic acid, methacrylic acid, crotonic acid, fumaric acid, maleic acid, itaconic acid, maleic anhydride monomethyl maleate, monoethyl maleate, monomethyl fumarate, and monomethyl fumarate.

The copolymer is preferably a polyethylene graft copolymer consisting essentially of high density polyethylene and an unsaturated carboxylic acid. This copolymer, because of its particular adhesive properties, provides excellent protection for metal surfaces. The preferred graft copolymer has a trunk or base of polyethylene having attached thereto polymer chains of an ethylenically unsaturated carboxylic acid monomer which is capable of addition polymerization and which polymer chains are chemically attached to, or combined with polymer molecules of the trunk or base polymer.

The graft copolymers may be prepared by known methods such as reacting unsaturated carboxylic acids with a normally solid homopolymer of an olefin such as ethylene at temperatures from about 65° to 170° C. and at atmospheric, subatmospheric, or superatmospheric pressure. The reaction is preferably carried out at temperatures above the crystalline melting point of the polyolefin and in the absence or substantial absence of air. Excellent adhesive properties are provided in the graft copolymer when the unsaturated acid is present in an amount from about
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4 percent to 25 percent and, preferably, about 6 percent to about 12 percent by weight.

Graft copolymers produced by other techniques such as water dispersion, extrusion, and the like may be used in this invention. Low density polyethylene-20\% acrylate graft copolymers and ethylene-acrylic acid random copolymers also have been found to show good adhesive properties. High density polyethylene-acrylic acid graft copolymers show a lesser tendency toward moisture transmission and, for that reason, are preferred. The copolymers can optionally contain solid fillers in the form of a powder which can serve as stabilizers, inhibitors, colorants and the like, if desired. Exemplary fillers include carbon black, calcium carbonate, calcium silicate, etc.

In accordance with this invention, a ferrous metal substrate treated with iron phosphate and coated with the specified copolymer exhibits a surprising and unusually effective resistance to corrosion when compared with closely related metal phosphate treated surfaces having coatings of the same copolymer. While the bonding of protective coatings of thermoplastic materials to metals is generally known and used in the art, the iron phosphate treated ferrous metal surface exhibits an unexpected high degree of resistance to corrosion when it is provided with a protective coating of the olefin-acidic comonomer polymer as evidenced by data obtained from actual runs and herein reported. These data also show that iron phosphated ferrous metal substrates coated with the graft copolymer form a more corrosion resistant coating than does an untreated steel surface coated with the same copolymer.

The copolymer may be applied to one or both sides of the treated metal substrate by various methods, one of which comprises laying a film of extrusion cast copolymer of about 1 to about 4 mils in thickness on one side of a treated metal plate. The lay-up thus assembled is placed in a molding press at pressures of about 10 to 400 p.s.i. and temperatures of about 130\° C to 220\° C, for approximately two minutes. The press is cooled to below 100\° C, and the prepared plate removed. Adhesive properties, as measured by a standard peel test, were found to increase somewhat linearly with an increase in fabrication temperature. Other methods such as fluidized bed, electrostatic powder spraying plus oven curing, and extrusion coating may also be used.

Laboratory tests show this prepared plate to be suitable, among other things, as a base for epoxy-based paints which are used as primers in the automotive paint industry. The graft copolymer coating appears to be little affected by drying heats of such paints (350\° F. or 177\° C. for 30 minutes).

Corrosion tests were conducted on various metal substrates coated with graft and random copolymers. The ASTM Method B117, 577, Method of Salt Spray (Fog) Testing was employed to evaluate corrosion resistance. A scribe mark is made through the coating and into the metal substrate. Samples are exposed to heat of about 90\° F. and a fog made by atomizing a 5 percent salt solution (weight of NaCl in water) said exposure being conducted in an enclosed cabinet. Exposure time is ten days, after which an evaluation is made as to the distance the corrosion penetrates beneath the coating and away from the scribe mark. Such an evaluation correspondingly indicates the degree of loss of adhesion during the exposure period. The width of failure is an indication of corrosion penetration and is defined as the total width of the lesion across the scribe mark.

The following examples are illustrative of the invention and are not intended to limit the scope thereof.

**EXAMPLE 1**

(a) A test panel of steel, treated with iron phosphate (Bonderite 1000) to an extent of approximately 130 mg./ft.\textsuperscript{2}, was covered with a film of a high density polyethylene-acrylic acid graft copolymer containing about 10 percent acrylic acid and being 1–1.5 mils in thickness. Slip sheets of “Mylar” polyester film were placed above the graft film and below the metal plate to prevent adhesion to the molding press. The plate was placed in a press for two minutes at 200\° C and at a pressure of up to 100 p.s.i. The press was cooled to below 100\° C. and the bonded plate removed. A scribe mark was made through the coating and into the base metal. The sample thus prepared was placed in an enclosed cabinet and subjected to a 5 percent salt spray corrosive solution for a period of ten days. In accordance with the ASTM Method B117 577, Width of failure after ten days was \(\frac{1}{8}\) inch.

(b) A sample was prepared and tested as in (a) above with the exception that the copolymer layer was increased to 2 mils thickness. Width of failure was less than \(\frac{1}{16}\) of an inch.

(c) A sample was prepared and tested as in (a) above except that only the copolymer layer was increased to 4 mils in thickness. Width of failure was less than \(\frac{1}{32}\) of an inch.

(d) Two samples were prepared and tested as in (a) above except that to the copolymer was added 20 percent and 40 percent respectively, of wollastonite (CaSiO\textsubscript{3}) filler and coating thickness was 3 and 4 mils respectively. Width of failure for each sample was about \(\frac{1}{64}\) of an inch.

In a series of control runs made to illustrate the improved and unexpected result obtained with the iron phosphate treatment, single test panels of the same type as those used and described in Example 1 were given a zinc phosphate treatment to an extent of about 200 mg. per square foot of surface area. The test panels were then coated with films of high density polyethylene-acrylic acid graft copolymer of the same type and by the same technique as that described in Example 1.

**Control a**

In this control run, the conditions of testing were the same as those used in Example 1(a). The copolymer film contained about 10 percent acrylic acid, and was about 1–1.5 mils in thickness. The width of failure after 10 days exposure was measured and found to be \(\frac{1}{4}\) inch. This represents a width of failure 4 times greater than that obtained with the iron phosphate treatment.

**Control b**

In this control run, the copolymer film was 2 mils thick and the width of failure after 10 days exposure was found to be \(\frac{1}{4}\) inch. This represents a width of failure 4 times greater than that obtained with the iron phosphate treatment of Example 1(b).

**Control c**

In this control run the copolymer film was 4 mils thick and the conditions employed the same as those of Example 1(c). The width of failure was measured and found to be \(\frac{1}{8}\) inch thick. This also represents a failure 4 times greater than that obtained with the iron phosphate treatment in Example 1(c).

**Control d**

Two zinc treated plates were laminated to separate films of the same composition and by the same technique that described in Example 1(d). The widths of failure for each after 10 days exposure was about \(\frac{1}{4}\) inch and about \(\frac{1}{4}\) inch, respectively. This represents widths of failure 2 and 4 times greater, respectively, than the corresponding iron phosphate treated plates described in Example 1(d).

In another control run, a test panel of black iron was coated with the graft copolymer as in Example 1(a). Corrosion and adhesion loss was so great that the sample was removed from the cabinet within five days.

In still another control run, a test panel of body stock iron was coated as in the preceding control run. Width of
failure was $\frac{1}{2}$ to $\frac{3}{4}$ of an inch, completely failing the test.

An examination of the panels prepared and tested in Example I and controls (a) through (d) after one year of shelf-aging showed results which further support the unexpected increase in corrosion resistance for the iron phosphate treatment. The test panels having the graft copolymer coating on the iron phosphate-treated steel showed no additional corrosion or loss of adhesion from the point of the scribe mark after one year. However, the test panels having the graft copolymer coating on the zinc phosphate-treated surface showed definite signs of continued corrosion activity and loss of adhesion. It was evident corrosion continued beyond the previous measured widths and had progressed to a distance of about $\frac{1}{2}$ inch.

EXAMPLE II

In another series of runs to compare the effectiveness of various metal phosphate treatments on the corrosion resistance of cold rolled steel plates coated with copolymers of ethylene and acrylic acid it was unexpectedly discovered that the iron phosphate treatment produced a coated steel sheet having a relatively high resistance to corrosion. The metal-phosphate treated cold rolled steel sheets were used from the Parker Rust Proof Division of the Hooker Chemical Company, 2177 E. Milwaukee Ave., Detroit, Mich. The polyethylene-acrylic acid copolymer coatings were applied to the steel sheets in the form of a film in the same manner as that described in connection with Example I. At least one scribe mark was made through the copolymer coating and into the base metal on each of the sheets. The sheets were then placed into an enclosed cabinet and exposed to a standard salt spray bath for 10 days according to ASTM Method B117-61. At the end of 10 days, the coated plates were removed and the degree of corrosion observed on the basis of the width of the lesion on both sides of the scribe. The effects of the corrosive atmosphere on the several coated plates with the various metal phosphate treatments are outlined in Tables I through V below.

In each table, HDPE means high density polyethylene; AA means acrylic acid; and $d$ means the thickness of the copolymer film of the individual metal plates. The fractions in the tables indicate the width of the lesion across the scribe after the 10 day salt spray exposure. When expressed as a ratio, it represents the minimum and maximum width of the lesion over the length of the scribe.

### TABLE I

<table>
<thead>
<tr>
<th>Run No.</th>
<th>Type of Treatment</th>
<th>Polymer Coating (HIPDE +10% AA Graft Copolymer)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Iron Phosphate (Bonderite 1000)</td>
<td>54 to 54 in. d=4 mils.</td>
</tr>
<tr>
<td>2</td>
<td>Iron Phosphate (Bonderite 1000)</td>
<td>54 in. d=4 mils.</td>
</tr>
<tr>
<td>3</td>
<td>Zinc Phosphate (Sprs Bond 1000)</td>
<td>54 in. d=4 mils.</td>
</tr>
<tr>
<td>4</td>
<td>Heavy Zinc Phosphate (Parco Compound No. 3)</td>
<td>54 to 34 in. d=4 mils.</td>
</tr>
<tr>
<td>5</td>
<td>Heavy Manganese Phosphate (Parco)</td>
<td>54 to 34 in. d=4 mils.</td>
</tr>
</tbody>
</table>

### TABLE II

<table>
<thead>
<tr>
<th>Run No.</th>
<th>Type of Treatment</th>
<th>Polymer Coating (HDPE +10% AA Graft Copolymer)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Iron Phosphate (Bonderite 1000)</td>
<td>54 in. d=4 mils.</td>
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<td>3</td>
<td>Zinc Phosphate (Sprs Bond 1000)</td>
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</tr>
</tbody>
</table>

### TABLE III

<table>
<thead>
<tr>
<th>Run No.</th>
<th>Type of Treatment</th>
<th>Polymer Coating (HDPE +10% AA Graft Copolymer)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Iron Phosphate (Bonderite 1000)</td>
<td>54 in. d=4 mils.</td>
</tr>
<tr>
<td>2</td>
<td>Iron Phosphate (Bonderite 1000)</td>
<td>54 in. d=4 mils.</td>
</tr>
<tr>
<td>3</td>
<td>Zinc Phosphate (Sprs Bond 1000)</td>
<td>54 in. d=4 mils.</td>
</tr>
<tr>
<td>4</td>
<td>Heavy Zinc Phosphate (Parco Compound No. 3)</td>
<td>54 to 34 in. d=4 mils.</td>
</tr>
<tr>
<td>5</td>
<td>Heavy Manganese Phosphate (Parco)</td>
<td>54 to 34 in. d=4 mils.</td>
</tr>
</tbody>
</table>

### TABLE IV

<table>
<thead>
<tr>
<th>Run No.</th>
<th>Type of Treatment</th>
<th>Polymer Coating (HDPE +10% AA Graft Copolymer)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Iron Phosphate (Bonderite 1000)</td>
<td>54 in. d=4 mils.</td>
</tr>
<tr>
<td>2</td>
<td>Iron Phosphate (Bonderite 1000)</td>
<td>54 in. d=4 mils.</td>
</tr>
<tr>
<td>3</td>
<td>Zinc Phosphate (Sprs Bond 1000)</td>
<td>54 in. d=4 mils.</td>
</tr>
<tr>
<td>4</td>
<td>Heavy Zinc Phosphate (Parco Compound No. 3)</td>
<td>54 in. d=4 mils.</td>
</tr>
<tr>
<td>5</td>
<td>Heavy Manganese Phosphate (Parco)</td>
<td>54 in. d=4 mils.</td>
</tr>
</tbody>
</table>

### TABLE V

<table>
<thead>
<tr>
<th>Run No.</th>
<th>Type of Treatment</th>
<th>Polymer Coating (Ethyleno+10% AA Random Copolymer)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Iron Phosphate (Bonderite 1000)</td>
<td>54 in. d=4 mils.</td>
</tr>
<tr>
<td>2</td>
<td>Iron Phosphate (Bonderite 1000)</td>
<td>54 in. d=4 mils.</td>
</tr>
<tr>
<td>3</td>
<td>Zinc Phosphate (Sprs Bond 1000)</td>
<td>54 in. d=4 mils.</td>
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<td>4</td>
<td>Heavy Zinc Phosphate (Parco Compound No. 3)</td>
<td>54 in. d=4 mils.</td>
</tr>
<tr>
<td>5</td>
<td>Heavy Manganese Phosphate (Parco)</td>
<td>54 in. d=4 mils.</td>
</tr>
</tbody>
</table>

By comparing the results of the iron phosphate treatment with the results of the zinc phosphate treatment and the manganese phosphate treatment in Tables I through V it is evident that the iron phosphate treatment produces a surprising and unexpected increase in the corrosion resistance of the coated plates because in most cases the width of the lesion is less than $\frac{3}{4}$ of an inch whereas the width of the lesions for the other phosphate treatments is many times more.

By comparing the results for the high density polyethylene graft copolymers at various levels of acid comonomer content as reported in Tables I through III, it is evident that the metal phosphate treatment is at least twice as good and in most cases is four times or more as good as the zinc phosphate treatment or the manganese phosphate treatment. As evidenced by the data in Tables IV and V, the improvement is even more pronounced with the random copolymer coatings on the iron phosphate treated panels as compared to the zinc phosphate and manganese phosphate treated panels.

In a control run to illustrate the operability and effectiveness of an ethylene-acrylic acid-vinyl acetate terpolymer coating on various metal phosphate treated steel plates, it was learned that the terpolymers are soft and of a rubbery to tacky consistency. This characteristic of the terpolymers makes them unsuitable for use where a smooth and hard polymer coating is required.

The corrosion-resistant steel products of this invention can be used to great advantage in industries such as automotive manufacturing. Rocker panels constructed in accordance with the present invention are protected from internal corrosion, a problem otherwise almost impossible to prevent at present. Fabrication into auto hoods, fenders, and the like provides additional protection where currently used undercoating materials are unsatisfactory. These and other advantages and uses are apparent to those skilled in the art.
What is claimed is:

1. An article of manufacture of ferrous metal treated with iron phosphate and having a copolymer coating intimately adhered thereto, said copolymer coating consisting essentially of at least about 75 percent by weight of an olefin and not more than about 25 percent by weight of an ethylenically unsaturated carboxylic acid having 3 to 8 carbon atoms per molecule, inclusive.

2. The article according to claim 1 wherein the polymer coating comprises a random copolymer of ethylene and acrylic acid.

3. The article according to claim 1 wherein the polymer coating comprises a graft copolymer of high density polyethylene and acrylic acid.

4. The article according to claim 1 wherein the copolymer contains from about 6 to about 12 percent by weight of an ethylenically unsaturated carboxylic acid comonomer.

5. The article according to claim 1 wherein the polymer coating contains a solid filler.

6. The article according to claim 5 wherein the solid filler is calcium silicate.

7. A method of producing a corrosion-resistant ferrous metal surface comprising the steps of coating the surface of an iron phosphate-treated ferrous metal with a composition consisting essentially of a copolymer of at least about 75 percent by weight of an olefin and not more than about 25 percent by weight of an ethylenically unsaturated carboxylic acid having 3 to 8 carbon atoms per molecule, inclusive.

8. A method according to claim 7 wherein the polymer is a graft copolymer of high density polyethylene and acrylic acid.

9. A method according to claim 8 wherein a thin sheet of the copolymer is pressed against the phosphate-treated ferrous metal surface at a temperature of between about 130° and about 220° C. and at a pressure of between about 10 and about 400 p.s.i.

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