COATINGS FOR RENDERING CORRODIBLE METAL CORROSION RESISTANT

Eric W. Kjellmark, Jr., Wilmington, Del., assignor to E. I. du Pont de Nemours and Company, Wilmington, Del., a corporation of Delaware

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7 Claims

ABSTRACT OF THE DISCLOSURE

Corrodible metal such as in the form of wire is made corrosion resistant by having applied to it a coating of a corrosion inhibitor containing a reducing agent such as sodium nitrite, a dispersing agent, a hydrocarbon oil, and water, followed by a coating of a high molecular weight polymer having a low saturation moisture content, e.g., polyhexamethylene sebacamide.

This invention relates to the impartation of corrosion resistance to metals, especially wire, and more particularly, to the impartation of corrosion resistance to wire which is subjected to tensile fatigue under operating conditions in corrosion inducing environments.

Metal corrosion is a serious problem in many commercial operations where metal, the requisite material of construction because of its physical properties, is subjected to a corrosion inducing environment. Numerous expedients have been discovered and reported in the prior art in order to circumvent corrosion problems. In some cases special alloys which more effectively resist corrosion have been developed. In others it has been found possible to impart corrosion resistance to metals by applying a protective coating of a polymeric material which is resistant to the agents providing the corrosive attack on the metal. Such methods of inhibiting corrosion frequently are limited by either the high costs of the alloys or the polymer applied as a coating to the metal, or the difficulties encountered in achieving a satisfactory bond between the polymeric coating and the substrate metal.

It is an object of the present invention to impart corrosion resistance to metals which are susceptible to corrosion. Another object is to impart corrosion resistance to metals by an economically feasible process. Still another object of this invention is to provide corrosion resistant wire which, under in-use corrosion inducing conditions, is subjected to fatigue. Other objects will become apparent hereinafter.

The objects of this invention are achieved by means of an article comprised of a corrodible metal which has been coated first with a liquid corrosion inhibitor, and second, with a high molecular weight polymer. More particularly, the metal for which corrosion resistance is sought is coated with a liquid corrosion inhibitor whose thermal decomposition and active component boiling point temperatures are in excess of the melting temperature, and preferably the processing temperature, of the polymeric material used as a coating. Moreover, the high molecular weight polymer which is applied over the liquid corrosion inhibitor must exhibit a saturation moisture content at ambient conditions of less than 8 weight percent.

The metal for which corrosion resistance is sought may be any one of a wide variety of metals which are susceptible to corrosion under the operating conditions encountered, i.e. the corrosion inducing environment. Because of the effectiveness of the present invention in inhibiting corrosion, however, it has been found that considerable cost savings may be realized by utilizing relatively cheap metals whose chief deficiency is susceptibility to corrosion. An especially useful metal which is operable in the present invention, particularly when it is desirable to impart corrosion resistance to metal in the form of wire which will be subjected to tensile fatigue, is carbon steel.

Numerous commercially available liquid corrosion inhibitors are operable herein. As indicated hereinafore, prerequisites for the liquid inhibitor include thermal stability and active component boiling point temperatures preferably in excess of the temperature employed for the application of the polymeric coating or jacket. In most cases, because of the type of polymeric jacket normally employed, it has been found preferable to utilize corrosion inhibitors which are liquid and thermally stable at temperatures in excess of 200° C. Those employed in the preferable embodiments of this invention are liquid and thermally stable in the temperature range of at least about 250—350° C. In addition to the above prerequisites the liquid inhibitor must be substantially insoluble in the polymer used as the outer coating or jacket, and further, it must be amenable to effective coating techniques, i.e., it must be capable of being uniformly distributed over the entire surface of the substrate metal being protected.

Liquid corrosion inhibitors which have been found useful in the present invention contain a chemical reducing agent and a dispersing agent. Operable reducing agents include inorganic salts such as nitrates and the like, and especially sodium nitrite, as well as high molecular weight organic amines such as lauryl amine and the like. The dispersing agent may be selected from a wide variety of commercially available dispersing or emulsifying agents which include inorganic salts of sulfonated petroleum or sulfonated hydrocarbons, the aryl sulfonamides, and inorganic salts of high molecular weight fatty acids, i.e., aliphatic monocarboxylic acids, especially fatty acids having 12 to 20 carbon atoms. Generally incorporated therein along with the dispersing agent is an inactivating component, a liquid in which the agent itself is soluble, e.g., water. The particularly preferred liquid corrosion inhibitors are those which are comprised of at least three components, namely, the dispersing and reducing agents, and also a high molecular weight or viscous oil. Useful oils include not only the mineral oils or conventional hydrocarbon oils but high molecular weight oil-like materials often employed as plasticizers, for example, dibutyl phthalate. An especially preferred liquid corrosion inhibitor operable herein is comprised of a water soluble inorganic salt of a fatty acid, water, mineral oil and sodium nitrite.

As indicated hereinabove the polymer employed for the outer coating or jacket must exhibit a saturation moisture content at ambient conditions, usually room temperature of about 25° C., of less than 8 weight percent. Useful polymers include polyolefins such as polyethylene, polypropylene and the like, and especially the polyolefins prepared from one or more a-olefins having 2—10 carbon atoms, some of the polyolefinic polymers, vinyl polymers, and the like. The selection of polymer will, of course, be dictated by considerations of the use to which the ultimate fabricated article will be put. Hence, for applications requiring flexibility the more rigid polymers, for example, polystyrene will be excluded. Toughness and abrasion resistance are other properties which usually influence the selection of the polymer. Particularly preferred in the present invention, especially when wire is the material being made corrosion resistant, is a polylamide formed from hexamethylenediamine and sebacic acid, normally referred to as a 610 nylon. With respect to the nylonos operable herein, it has been surprisingly noted that although 610 nylon is utilized in a preferred embodiment of this invention, a 6 nylon (from caprolactam) or a 66 nylon (from hexamethylene diamine and adipic acid) are ineffective.
Another unusual feature of the present invention is the fact that although liquid corrosion inhibitors are employed, bubble-free polymeric coatings can be achieved. Conventional equipment may be used as coating means for the application of both the liquid corrosion inhibitor and the polymer. For large articles, the liquid corrosion resistant dip coating and spray techniques often are useful. Continuous processes likewise may be utilized. When continuous lengths of wire are being made corrosion resistant, conventional wire coating extruders often may be used. Although the thickness of the polymeric coating, like the selection of the polymer itself, will be determined by the end-use conditions to which the article will be subjected, for most uses jacket thicknesses of 30 mils usually are adequate. When wire is being treated under the instant invention to impart corrosion resistance, for most uses the polymeric coating is adequate at thicknesses of 1 to 10 mils. The above-reported thicknesses of the polymeric coatings are not intended to reflect the thicknesses required to impart corrosion resistance, but the thicknesses required to meet all prerequisites of the in-use conditions to which the coated articles will be exposed. For importing corrosion resistance by the process of the instant invention only very thin polymeric coatings are required. Moreover, the thickness of the liquid corrosion inhibitor employed thereunder in the process of the present invention likewise need only be very thin. Generally, it has been found that only about 250 grams of combined active components in the liquid inhibitor is required per one square inch of metal surface being protected.

Evaluation of the operable coatings of the instant invention has been achieved by several means. As part of the initial screening process 1 mil samples of carbon steel foil were coated with a liquid corrosion inhibitor and then sandwiched between outer polymeric layers employing compression molding techniques. The samples were immersed in a 5 weight percent salt bath solution maintained at an elevated temperature, usually 50–75°C. Periodic removal of the samples from the salt bath was employed to examine the coupons or foils for evidence of corrosion. Table I depicts the results achieved in this coupon corrosion test. "Santiago" 8 is a mixture of diethyl ortho- and para-toluene sulfonamides and "Amino" 0 is high molecular weight amidazole having the formula

CH₂CH₂CONCH₂CONH₂OH

Another test which was employed to evaluate the corrosion inhibiting coatings of the instant invention particularly for coatings applied to wire, was a dynamic corrosion fatigue test. The apparatus for conducting this test is described in "The Corrosion and Oxidation of Metals," U. R. Evans, St. Martin's Press, 1960, pp. 714–5. Under the conditions of operation of the wire 45–50 inches in length is bent into an arc in a vertical plane by means of four point loading. The stress in the wire is determined by the radius of curvature of the bend in accordance with the equation $S = Ey/r$ where $S$ is the stress in p.s.i., $y$ is the radius of the wire in inches, $E$ is the modulus of the wire and $r$ is the radius of curvature of the bend in inches. The coated or uncoated wires to be tested are immersed in a 5% brine bath at 75°C for one week to one month. After the preliminary soak the wire is evaluated dynamically in the aforesaid apparatus, with about 20 inches of the wire being immersed in the salt solution during the test. The wire is rotated at about 1500 r.p.m. until failure. If failure does not occur after 10,000,000 revolutions, the test is discontinued since such a wire life is well within commercially acceptable standards for most uses. Summarized in Table II are the results of dynamic corrosion fatigue evaluations on samples prepared by the examples provided herebelow. In order to more clearly delineate the present invention, some of the data appearing in Table II have been converted to graphical form by plotting the cycles to failure versus the stress level on the wire. It may be seen from the graph which is a part of this specification that bare wire which is subjected only to fatigue under a corrosion inducing environment exhibits a relatively short life (A, B). Further, it may be seen that wire which is treated by the process of the instant invention exhibits a use-life which is substantially better than the untreated wire (C, D); 610 nylon and polyethylene coated wires are shown for comparison (E, F). More preferred embodiments of this invention are shown as G and H, with I being a particularly preferred embodiment. These are seen to impart corrosion resistance which is about equal to or better than a control sample whose life is determined in the absence of the corrosion inducing environment, i.e., in air (J). A wire treated only with liquid corrosion inhibitor (K) is seen to be no better than the bare wire (A, B).

As the term is used hereinafter describes operable liquid corrosion inhibitors, "active component" refers to the chemical reducing agent and the dispersing agent, and

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Corrosion Inhibitor</th>
<th>Exposure</th>
<th>Time, Exposure (Days)</th>
<th>Results</th>
</tr>
</thead>
<tbody>
<tr>
<td>(a) 610 nylon, 1 mil</td>
<td>None</td>
<td>9% NaCl Solution at 75°C</td>
<td>1</td>
<td>Corrosion visible.</td>
</tr>
<tr>
<td>(b) 610 nylon, 1 mil</td>
<td>A</td>
<td>9% NaCl Solution at 75°C</td>
<td>75</td>
<td>No visible corrosion.</td>
</tr>
<tr>
<td>(c) Polyethylene, 3 mil</td>
<td>None</td>
<td>9% NaCl Solution at 50°C</td>
<td>75</td>
<td>No visible corrosion.</td>
</tr>
<tr>
<td>(d) Polyethylene, 3 mil</td>
<td>A</td>
<td>9% NaCl Solution at 75°C</td>
<td>75</td>
<td>No visible corrosion.</td>
</tr>
<tr>
<td>(e) Polyethylene, 3 mil</td>
<td>B</td>
<td>9% NaCl Solution at 75°C</td>
<td>75</td>
<td>No visible corrosion.</td>
</tr>
<tr>
<td>(f) Polyethylene, 3 mil</td>
<td>C</td>
<td>9% NaCl Solution at 75°C</td>
<td>75</td>
<td>No visible corrosion.</td>
</tr>
<tr>
<td>(g) Polyethylene, 3 mil</td>
<td>D</td>
<td>9% NaCl Solution at 75°C</td>
<td>75</td>
<td>No visible corrosion.</td>
</tr>
<tr>
<td>(h) Polyethylene, 3 mil</td>
<td>E</td>
<td>9% NaCl Solution at 75°C</td>
<td>75</td>
<td>No visible corrosion.</td>
</tr>
</tbody>
</table>

For example, A is a mixture of a high molecular weight hydrocarbon oil, water, inorganic salt of a fatty acid and sodium nitrite. 1 B = A with substantially all the water removed by distillation.
In the preferred inhibitors, also to the high molecular weight or viscous oil, but excludes inactive components, for example, water. The concentration of the inactive component can be varied widely to conform to the purpose for which it is employed. When water is utilized as the inactive component, amounts of water up to about 50 weight percent of the combined weights of the active components and the water do not adversely affect the present invention. In determining the maximum amount of inactive material which can be present, it must be kept in mind that in order to achieve corrosion resistance by the process of the present invention, the previously disclosed minimum level of active components eventually must be coated unto the metal surface prior to application of the polymeric jacket. By “liquid corrosion inhibitor,” as the term is used herein, is meant an inhibitor which is in a liquid form when applied, although each of the components of the inhibitor need not be a liquid at ordinary room temperature, for example, 20°-25° C.

The following examples are given to illustrate but not limit the invention.

Example I

Employing conventional techniques, a commercially available 60 mil carbon steel wire is coated with a liquid corrosion inhibitor comprised of a high molecular weight hydrocarbon oil, a salt of a fatty acid, sodium nitrite and water. A second sample of wire is coated with a commercially available polyamide known as a 610 nylon and having a relative viscosity of about 32. The thickness of the coating is 10 mils. Still another sample of carbon steel wire is coated first with the liquid corrosion inhibitor and then with a 10 mil jacket of the 610 nylon. The four specimens were evaluated in the corrosion fatigue test described below. As a control, a fifth sample of car-

<table>
<thead>
<tr>
<th>Sample</th>
<th>Stress Level (X10^-7)</th>
<th>Number of Samples and Cycles to Failure (X10^5)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bare Wire in Air (Control)</td>
<td>2.4-10</td>
<td>2.1-4</td>
</tr>
<tr>
<td>Bare Wire in Salt Bath, 1 Week Soak</td>
<td>1.8-10</td>
<td>1.8-10</td>
</tr>
<tr>
<td>Bare Wire +10 mils 610 nylon, 1 Week Soak</td>
<td>1-80</td>
<td>1-80</td>
</tr>
<tr>
<td>Bare Wire - Al 1 Week Soak</td>
<td>1-80</td>
<td>1-80</td>
</tr>
<tr>
<td>Bare Wire - Al 10 mils 610 nylon, 1 Week Soak</td>
<td>1-80</td>
<td>1-80</td>
</tr>
<tr>
<td>Bare Wire in Air (Control)</td>
<td>1.8-10</td>
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<tr>
<td>Bare Wire in Air (Control)</td>
<td>1.8-10</td>
<td>1.8-10</td>
</tr>
</tbody>
</table>

A = Mixture of high molecular weight hydrocarbon oil, water, inorganic salt of a fatty acid and sodium nitrite (contains ca.
20 wt. percent water and 6-10 wt. percent sodium nitrite.)
bon steel wire was evaluated to determine its fatigue endur-
ance in the absence of the corrosive environment (in air).
The data from the evaluation are shown in Table II. The bare wire which had been soaked in brine solu-
tion, as well as the wire which had been coated with the liquid corrosion inhibitor, exhibited poor fatigue performance and showed signs of corrosion. The polyamide coated wire likewise appeared corroded and exhibited a fatigue performance only somewhat superior to the uncoated wire. The sample which had been processed according to the present invention showed no signs of corrosion and exhibited excellent fatigue performance, the latter being about equivalent to that observed for the uncoated wire which had not been subjected to the brine treatment.

**Example II**

Example I was repeated using another sample of commercially available carbon steel wire. The results were substantially the same as those realized in Example I.

**Example III**

A commercially available 60 mil carbon steel wire was processed as in Example I except that the 610 nylon was replaced with a commercially available high density polyethylene. As in Example I all, except the bare wire tested in air and the wire treated according to the process of the present invention, exhibited corrosion. The sample coated solely with polyethylene was somewhat superior in fatigue performance when compared to the bare wire which had been soaked in brine. The specimen which had been coated with liquid corrosion inhibitor and polyethylene exhibited excellent fatigue performance, although not quite as good as the untreared wire or the wire prepared in Example I and containing both liquid corrosion inhibitor and 610 nylon. The fatigue data arc shown in Table II.

**Example IV**

Example I is repeated except that another commercially available liquid corrosion inhibitor is employed, namely, an alkylammonium organic phosphate as an 80% active solution in kerosene. From the data shown in Table II it may be seen that the dual coating is intermediate in ef-
cfectiveness between the inventive products prepared in Examples I and III. In this example, just as in the others, the wires, except for the dual coated wires, showed signs of corrosion upon being subjected to the corrosive environ-
ment.

**Example V**

Example I was repeated except that the samples being evaluated were exposed to the brine solution for one month instead of one week. The samples treated by the process of this invention still exhibited no sign of corro-
sion and the fatigue performance was about equivalent to that realized in Example I.

**Example VI**

Example I was repeated except that castor oil was sub-
stituted for the liquor corrosion inhibitor. All samples which has been exposed to the corrosive environment were corroded and the fatigue performance was poor. The sample containing the dual coating of castor oil and 610 polyamide, as seen from Table II, exhibited fatigue endurance only slightly superior to the uncoated brine soaked wire.

**Example VII**

Example VI was repeated with di-n-butyl phthalate being used in place of the castor oil. As seen from the data in Table II the results were essentially the same as those realized in Example VI.

Although, as indicated above, the instant invention is useful for imparting corrosion resistance to metals which are employed in corrosive environments, a particularly useful application of this invention is found in the opera-
tion of oil wells. Continuous lengths of carbon steel wire which have been treated by the process described herein are useful in the formation of sucker rods, which application enhances the economic feasibility of pumping oil from the base of a well to the surface. Sucker rods which are fabricated by stranding together a plurality of wires which have been treated by the process of the instant invention exhibit a longer use-life than many ma-
terials currently employed for such applications. More-
over, the present invention permits the use of wire made from certain metals, for example, carbon steel, which have superior tensile properties but inferior resistance to corrosion. Wire fabricated from such metals may be de-
signcd to smaller diameters while maintaining minimum specifications as to requisite physical properties. Still fur-
ther, sucker rods prepared by employing wire which has been treated by the process of this invention may be made in continuous lengths, thus precluding the neces-
sity for mechanically coupling together a plurality of short lengths of rod as is the current practice. Other ad-
vantages, for example, in handling, storing, shipping, in-
stallation and retrieval of flexible continuous sucker rod, produced as indicated above, are provided. Finally, the use of continuous lengths of sucker rod prepared from wire which has been treated according to the present in-
vention facilitates the withdrawal of oil from wells which arc of much greater depth than conventional producing wells.

What is claimed is:

1. An article comprised of a corrodible metal substrale having a first coating of a liquid corrosion inhibitor con-
sisting essentially of a chemical reducing agent which is an inorganic salt or a high molecular weight organic
amine, a dispersing agent and a hydrocarbon oil, and a second coating of a high molecular weight polymer hav-
ing a saturation moisture content of less than 8 weight
percent at about 25° C., said corrosion inhibitor being substantially insoluble in said polymer and having ther-
al decomposition and active component boiling point
temperatures in excess of the melting temperature of said polymer.

2. The article of claim 1 wherein the liquid corrosion inhibitor contains as an inactive component, water, the chemical reducing agent is sodium nitrite, the dispersing agent is a water soluble salt of an aliphatic monocar-
boxylic acid, the hydrocarbon oil is mineral oil, the polymer is a polyhexamethylene sebacamide.

3. The article of claim 1 wherein the liquid corrosion inhibitor contains as an inactive component, water, the chemical reducing agent is sodium nitrite, the dispersing agent is a water soluble salt of an aliphatic monocar-
boxylic acid, the hydrocarbon oil is mineral oil, and the poly-
mer is a polyolefin formed from an α-olefin having 2–10
carbon atoms.

4. An article comprised of a corrodible wire having a first coating of a liquid corrosion inhibitor consisting es-
sentially of a chemical reducing agent which is an inor-
ganic nitrite, a dispersing agent and a hydrocarbon oil and a second coating of a high molecular weight polymer
having a saturation moisture content of less than 8 weight
percent at about 25° C., said corrosion inhibitor being substantially insoluble in said polymer and having ther-
al decomposition and active component boiling point
temperatures in excess of the melting temperature of said polymer.

5. The article of claim 4 wherein the liquid corrosion inhibitor contains as an inactive component, water, the chemical reducing agent is sodium nitrite, the dispersing agent is a water soluble salt of an aliphatic monocar-
boxylic acid, the hydrocarbon oil is mineral oil, and the polymer is a polyhexamethylene sebacamide.

6. The article of claim 4 wherein the liquid corrosion inhibitor contains as an inactive component, water, the chemical reducing agent is sodium nitrite, the dispersing agent is a water soluble salt of an aliphatic monocarboxylic acid, the hydrocarbon oil is mineral oil, and the polymer is a polyolefin formed from an α-olefin having 2–10 carbon atoms.

7. A sucker rod comprised of a plurality of strands of a carbon steel wire, each having a first coating of a liquid corrosion inhibitor consisting essentially of sodium nitrite, water, a water soluble salt of an aliphatic monocarboxylic acid and mineral oil, and a second coating of a high molecular weight polyhexamethylene sebacamide.

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