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CORROSION-INHIBITING COMPOSITION

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9 Claims

ABSTRACT OF THE DISCLOSURE

This invention relates to a corrosion-inhibiting composition comprising casein, an epoxidized oil and a hexavalent chromium compound, the proportions by weight being, for each part by weight casein, from about .1 to about .5 part by weight of epoxidized oil and from about .005 to about .3 part by weight hexavalent chromium compound (calculated as ammonium dichromate). The invention also comprises the method of inhibiting the corrosion of surfaces of articles composed of iron and steel by application thereof of the corrosion-inhibiting composition and drying thereof at room temperature.

BACKGROUND OF THE INVENTION

Corrosion of iron and alloys containing iron, by air or moisture, is well known. The surfaces of such metals may be protected from corrosion by application of a water-impermeable coating such as paint and by rendering the surfaces passive by treatment with oxidizing solutions, as for example by exposing iron to chromates. However, the passive stage is meta-stable and can be destroyed by any action that breaks the surface. Attempts which have been made heretofore to deposit chromate films resistant to breakage have been in the direction of using inordinately thick films in the hope that the passive surface would be healed by chromates in adjacent superimposed layers of the thick film. All such treatments have depended on a heat treatment to fix the coating on the surface. Coatings that have been applied and dried at ambient temperatures have failed to adhere uniformly and have not given sustained protection against rust. Solutions of ammonium dichromate in water, containing certain high polymers, are known to be effective rust-resistant coatings if the coating is baked, as for example at 100° C. for five minutes. Coatings which are not baked do not adhere well to the surface of the metal and consequently readily flake from the surface.

SUMMARY OF THE INVENTION

We have now found that articles of iron and iron-containing alloys can be protected against corrosion by application thereon of a composition which is dried at room temperature to a tough, corrosion-resistant coating that adheres well to the surfaces.

Briefly stated, the present invention comprises a corrosion-inhibiting composition comprising casein, an epoxidized oil, and a hexavalent chromium compound, and the method of inhibiting the corrosion of iron and iron-containing articles by applying the composition to such surfaces and drying the composition at room temperatures to form a durable corrosion-resistant coating on the surface of said article. It is required that the epoxidized oil always be present in an amount less than that of casein.

DETAILED DESCRIPTION OF THE INVENTION

The three essential ingredients of the composition are casein, a hexavalent chromium compound, and an epoxidized oil.

As to casein, commercially available casein whether from New Zealand, Argentina, or America can be used. Also utilizable are the casein hydrolysates.

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The preferred hexavalent chromium compound is ammonium dichromate, but alternative materials include sodium and potassium dichromate, sodium and potassium chromate, ammonium chromate, chromic oxide (Cr_2O_3) or any other salt or oxide of hexavalent chromium soluble at pH 8 or higher. However, chromic anhydride, CrO_3 , cannot be used in the dry powder form of the composition because its acidic nature would curd the casein immediately unless used with sufficient alkali.

For epoxidized oils, epoxidized soya bean or castor oils are preferred materials, but any epoxidized vegetable oil having oxirane content of at least 5% is suitable. Typical epoxidized vegetable oils are those marketed under the trade name Estynox, prepared by the action of peracetic acid on the double bonds in the molecules of the oil. By formation of epoxy bonds across the double bonds, oxirane rings are formed which are no longer auto-oxidizable in air. Commercial grades of epoxidized vegetable oils suitable for use in the practice of the instant invention include castor oil containing 5% of oxirane oxygen, epoxidized soy oil containing 7% of oxirane oxygen and, in general, vegetable oils such as safflower, cottonseed, and tung oils containing at least 5% oxirane oxygen.

The proportion by weight of epoxidized oil for each part by weight of casein may vary from .1 to .5; .2 being preferred, and as to the chromium compound .005 to .3, the hexavalent chromium compound being calculated as ammonium dichromate. The preferred ratio of ammonium dichromate to casein is .2:1.

The rust inhibition composition of the instant invention may be prepared as a dry or "wet" formulation. In the dry formulation an alkaline solvent for casein, such as ammonium carbonate, may be used in quantities up to 3% by weight of casein. Ammonium diborate can also be used as a source of ammonium alkali, or alkali in the dry base may be omitted entirely, relying upon the supply of basicity in the preparation of a solution of the dry composition by separate addition of ammonium hydroxide or other volatile base as above mentioned.

In preparing liquid composition, water is the preferred medium although other polar liquids can be used. As noted above, alkali must be included to solubilize the casein. The solids content can be varied widely; for most commercial purposes of solids content of from about 10 to about 20% is preferred.

In the preparation of the liquid compositions for use in aerosol containers, it is preferred to use a mixture of ethyl alcohol and water as the medium, but other alcohols such as methanol or isopropanol may be used. The propellant may be any compressed gas known to those familiar with the art as effective for aerosol can pressurizing. The preferred propellant is a 1:1 mixture of Freon 11 and Freon 12. Alternatively, vinyl chloride, isobutane, or any suitable low cost propellant may be used.

While the casein, chromium compound and epoxidized oil constitute the three essential ingredients of this invention, formulations of both dry mix and solutions may contain other ingredients for various purposes; such as bactericidal, wetting and foam preventing functions.

For the purpose of emulsification of the epoxidized oil there may be included about 1% of oleic acid (by weight of casein) or its equivalent in other fatty acids which may include stearic acid, palmitic acid or other carboxy compounds with long hydrocarbon chains. The fatty acid combines with the ammonium ions supplied by the ammonium salts in the formulation or with the ammonium hydroxide added to the solution to form an emulsifier of the ammonium soap type. Any other alkaline solvent for casein may be substituted provided it volatilizes at room temperature. Thus volatile primary amines such as methylamine, also dimethyl amine or trimethyl amine or morpholine may be used.

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As bactericides there may be used, for example, phenyl mercuric acetate, sodium o-phenyl phenate (Dowicide A), sodium merthiolate, sodium ethyl mercuric thiosalicylate, 1-hydroxypyridine-2-thione or esters of p-hydroxybenzoic acid.

Among surfactants suitable as wetting agents nonionics are preferred, including dimethyl octyne diol, nonyl phenol, polyethylene glycol ether, isooctyl phenyl polyethoxy ethanol. Many other wetting agents are available which could be used and which would be known to those skilled in the art.

The product of the instant invention is useful not only as a permanent corrosion-preventive coating, but as a temporary coating to protect the metal from rust and other corrosive action while being stored pending use. The coating may also be used as illustrated in Example 15 as a primer coat over steel or iron objects to be painted later with surface paints.

As previously noted, the composition is applied to the surface of the metal to be protected and allowed to dry at room temperature, i.e., a temperature between about 65°-110° F.

The invention will be further described in connection with the following examples of the practice of it which are set forth for the purpose of illustration only and wherein proportions are in parts by weight unless specifically stated to the contrary.

Example 1

A solution was prepared of 100 grams casein in 300 ml. water containing 10 grams ammonium hydroxide by heating at 160° F. with stirring. To this was added an emulsion of 50 grams Estynox 130, a commercial epoxidized soya oil in 200 ml. water containing 20 grams sodium caseinate as emulsifying agent. There was then added 19.8 ml. of a 20% aqueous solution of ammonium dichromate. The solution was brushed on to cold-rolled steel plates which had been treated with phosphoric acid and rinsed according to Federal Test Method Standard No. 141—Method No. 2011 "Preparation of Steel Panels." The coatings were allowed to air-dry overnight. They were then placed in a closed cabinet holding a layer of free water on the floor. From time to time during the following months, the panels were removed to an area of approximately 40% ambient humidity for periods of 2 to 3 days, then returned to the wet cabinet, thus alternating the exposure between wet and dry.

Along with the panels treated with the solution of this initiator there were simultaneously tested an uncoated control panel and other control panels treated with a corresponding solution of casein and ammonium dichromate from which the epoxidized soya oil had been omitted. The uncoated control panel become very rusty after one month's exposure to the alternating wet and dry treatment; at the end of six months it was disintegrating. The coated control panels from which epoxidized oil had been omitted showed no evidence of corrosion in one month but soon thereafter isolated spots of rust began to appear. By contrast all the panels treated with the solution of this invention containing also the epoxidized oil showed absolutely no evidence of corrosion after 6 months.

Example 2

To 100 ml. of the first solution of Example 1, (containing 500 ml. water, 100 grams ammonium hydroxide, 50 grams Estynox 130, 20 grams sodium caseinate and 19.8 ml. of a 20% aqueous solution of ammonium dichromate) was added 1 ml. of Pluronic L64, a non-ionic surfactant of Wyandotte Chemicals Corp., said to be a condensate of ethylene oxide with a condensate of propylene oxide and propylene glycol, the molecular weight of said Pluronic L64 being about 2900. The wettability of the liquid to the surface of steel panels was thereby improved. When these were tested according to the procedure described in Example 1, they were found to be completely resistant to corrosion over a period of at least 6 months.

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Example 3

To 100 ml. of the first solution of Example 1 was added 0.1 ml. of a 30% solution of phenylmercuric acetate for the purpose of protecting the solution and the coating on the metal from chance damage through bacterial growth. This solution was used to coat cold-rolled steel plates pre-treated with phosphoric acid as described in Example 1. The coated plates were tested as in Example 1 and found to be completely resistant to corrosion over a period of at least six months.

Example 4

Five solutions were prepared identical with the first solution of Example 1 excepting that the amount of ammonium hydroxide used to dissolve the casein was varied over a range so that the pH of the complete products varied over a range from 6.3 to 7.4. Phosphoric acid-treated steel panels were coated with the five respective products to give dried films calculated to be approximately 0.0005 inch thick. Upon exposure to moisture-saturated air for six weeks, all panels were free of rust. The products themselves, all of which had a solids content about 12.5%, remained fluid on storage.

Example 5

The procedure of Example 4 was repeated except that sufficiently less water was used in making the solutions of this invention so that the concentration of solids was increased to 17%. The treated panels were all free of rust after six weeks exposure to moisture-saturated air. However, the solutions of the products thickened to gels over the six week period.

Example 6

The procedure of Example 5 was modified to make a series of solutions at 17% total solids with sufficient ammonium hydroxide to bring the final pH respectively 8.0, 8.3 and 8.6. Treated panels were all free of rust after six weeks exposure to moisture-saturated air. The solution at pH 8.0 had begun to thicken at the end of six weeks, but the solutions at pH 8.3 and 8.6 were still fluid.

Example 7

The following ingredients were compounded by first dry-mixing the pulverulent materials, then slowly "oiling on" the liquid materials to give a final powdered product which does not "cake."

	Parts by weight
Casein	70.0
Ammonium dichromate	14.1
Epoxidized soya oil (Estynox 130)	14.0
Oleic acid	0.7
Pluronic L-64 (see description above)	0.08
NOPCO NDW defoaming agent	1.12

100.00

One pound of this dry base was cut to make one gallon of solution using the following procedure: Two quarts of water were charged to a mixer and one pound of the dry base gradually stirred in. There was then added 2.5 ounces (75 ml.) of 28% aqueous ammonium hydroxide. Stirring was continued until solution was complete. Then another 2 quarts of water was added.

Example 8

Using the mixing procedure of Example 7, the following ingredients were compounded into a non-caking powdered product.

Casein	67.5
Sodium dichromate	16.2
Ammonium carbonate	1.9
Estynox 130 (epoxidized soya oil)	13.6
Oleic acid	0.7
Isooctylphenyl polyethoxy ethanol (Triton X-100, non-ionic surfactant)	0.1

100.0

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One pound of this dry base was cut to make one gallon of aqueous solution using the procedure of Example 7.

Example 9

Using the mixing procedure of Example 7, the following ingredients were compounded into a non-caking powdered product:

Casein -----	67.7
Potassium dichromate -----	15.9
Ammonium dichromate -----	1.9
Estynox 130 (epoxidized soya oil) -----	13.7
Oleic acid -----	0.7
Dimethyl octyldiol (Surfynol 82 non-ionic surfactant) -----	0.1
	100.0

One pound of this dry base was cut to make one gallon of aqueous solution using the procedure of Example 7.

Example 10

Using the mixing procedure of Example 7, the following ingredients were compounded into a non-caking powdered product.

Casein -----	69.2
Ammonium dichromate -----	14.0
Ammonium diborate -----	2.0
"Castung," Baker Castor Oil Co. (epoxidizer castor oil) -----	14.0
Oleic acid -----	0.7
Nonylphenyl polyethylene glycol ether (Tergitol NPX, non-ionic surfactant) -----	0.1
	100.0

One pound of this dry base was cut to make one gallon of aqueous solution using the procedure of Example 7.

Example 11

A solution was prepared of one pound of the dry base of Example 7 in one gallon of a mixture of equal volumes of water and denatured ethyl alcohol. Sufficient ammonium hydroxide was used to reach pH 8.7. The solution was filtered and loaded into an aerosol can with compressed gas propellant compound of equal weights of Freon 11 and Freon 12. The pressurized aerosol container was equipped with suitable valves for convenient application of protective films. This can was used as in Example 12 only a few days after it was filled. However, stability of both can and product was good, as demonstrated by performance after one year when the can still functioned and the product was still sprayable to give a rust-proof coating.

To demonstrate the water-resistance of our coating and to discover means of removing it, test panels were brush-coated to receive a coating thickness of 0.002 inch (0.045 mm.), allowed to air-dry in diffuse daylight and immediately immersed in water or in dilute alkali or dilute acid. The resistance of the coating to removal after one hour of immersion was as follows:

In cold water: film intact but soft
In hot water: film intact and hard
In dilute ammonia: film intact but soft
In dilute caustic soda: film completely removed
In dilute phosphoric acid: film completely removed.

Example 12

The solutions of Examples 7, 8, 9 and 10 and the pressurized solution of Example 11 were used to coat cold-rolled steel panels pretreated as in Example 1. Methods of application to respective panels included dipping, brushing and spraying. Some coated panels were allowed to dry 15 to 30 minutes in the air. Others were first air-

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dried for 2 to 3 minutes at room temperature, then forced-dried at 150-175° F. The thickness of the deposited films was in the range 0.0005 to 0.0010 inch. Exposure tests of both panels and castings were carried out over a two-year period, alternately in atmospheres of high and low humidity. The singly-coated objects were found to be protected from rusting over this period of time.

Example 13

Small grey iron "marker" castings about two pounds in weight obtained from Bennett-Ireland Co. were shot-blasted and immediately spray-coated with a one pound per gallon cut in water of the dry base of Example 7. After air-drying in diffuse daylight, the treated castings were stored away in a warm saturated atmosphere along with untreated castings. Inspection after one week showed no evidence of rusting on the treated pieces, whereas the untreated pieces were red with rust.

Example 14

As a demonstration of the effectiveness of our product in preventing the rusting of restored iron antiques, a sad iron of vintage about 1870 was cleaned from rust by mild sand blasting, then coated over most of its surface with the aerosol product of Example 11, leaving a small area untreated. After one year of shelf storage, the small untreated area shows red rust. The treated area shows no evidence of rust and has maintained its original restored appearance of lustrous dark gray under the transparent film of coating.

Example 15

The solution of Example 10 was applied to steel test panels. After a drying period for 1 hour at room temperature the panels were overcoated with a commercial white latex paint, thus employing the rust-preventive coating as a primer coat. The panels were exposed alternately to wet and dry atmospheres. Six weeks later inspecting showed excellent condition of the white surface paint. Thus, the product of this invention can serve as a primer under latex paint as well as prevent the metal surface from rusting prior to painting.

It will be understood that it is intended to cover all changes and modifications of the examples of the invention herein chosen for the purpose of illustration which do not constitute departures from the spirit and scope of the invention.

What is claimed is:

1. A corrosion inhibiting coating composition for iron and iron-containing alloy surfaces consisting essentially of casein as the major film-forming component, an epoxidized vegetable oil, and a hexavalent chromium compound, the proportions by weight being, for each part by weight casein, from about .1 to about .5 part epoxidized vegetable oil and from about .005 to about .3 part by weight hexavalent chromium compound calculated as ammonium dichromate.

2. The composition of claim 1, wherein the casein is casein, the epoxidized oil is epoxidized soya bean oil, and the chromium compound is ammonium dichromate.

3. The composition of claim 2, wherein the proportions by weight, for each part by weight casein, are 0.2 part epoxidized soya bean oil and 0.2 part ammonium dichromate.

4. The composition of claim 2, including an alkaline solvent for casein.

5. The method of inhibiting corrosion of a metal surface of iron or of an iron-containing alloy which comprises preparing a volatile alkaline solution of the composition of claim 1, applying the solution on the surface and allowing the composition to dry at room temperature to form a durable corrosion-resistant coating on said surface.

6. The method of inhibiting corrosion of a metal surface of iron or of an iron-containing alloy which comprises preparing a volatile alkaline solution of the composition of claim 2, applying the solution on the surface and allow-

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ing the composition to dry at room temperature to form a durable corrosion-resistant coating on said surface.

7. The method of inhibiting corrosion of a metal surface of iron or of an iron-containing alloy which comprises preparing a volatile alkaline solution of the composition of claim 3, applying the solution on the surface and allowing the composition to dry at room temperature to form a durable corrosion-resistant coating on said surface.

8. The method of inhibiting corrosion of a metal surface of iron or of an iron-containing alloy which comprises preparing a volatile alkaline solution of the composition of claim 4, applying the solution on the surface and allowing the composition to dry at room temperature to form a durable corrosion-resistant coating on said surface.

9. The method of inhibiting rusting of an iron-containing surface which comprises preparing an aerosol solution of the composition of claim 4 spraying the solution on the

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surface and allowing the composition to dry on said surface to a durable rust-resistant coating at room temperature.

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