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CORROSION INHIBITING COATING COMPOSITION AND SUBSTRATES COATED THEREWITH

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This invention relates to coating compositions adapted for application to rusted or corroded metal and to a method for arresting the rusting of metal underneath a corrosion-inhibiting protective film.

Prevention of corrosion, particularly the prevention of rusting of iron and steel, is a problem of serious concern and numerous means have been employed to reduce corrosion and thereby minimize maintenance costs. Where the metal is corroded, the metal substrate is usually prepared for painting by removing most or substantially all of the corrosion products by means such as wire brushing, scraping, sanding, sand-blasting, or shot-blasting. Unless the corrosion products are substantially removed, corrosion continues underneath the protective coatings and leads to early failure of conventional protective coatings. Complete removal of rust or corrosion scale from structural metals is a costly and time-consuming operation. Hence, elimination of this step or minimizing the effort of preparing the corroded metal for painting is highly desirable in the art of metal protection and maintenance.

It is an object of this invention to provide a corrosion-inhibiting composition which obviates the need for complete removal of rust or corrosion deposits prior to application of the protective coating. Another object is to provide a corrosion-inhibiting coating composition which is durable and serviceable regardless of whether it is applied over a corroded and weathered coated metal substrate or over uncorroded uncoated metal. A further object is to provide a protective coating composition which, when applied to a corroded metal substrate, retards further corrosion beneath the applied protective coating. Still another object is to provide a method of arresting or retarding the corrosion of metals having corrosion already initiated on the surface thereof.

These objects and other important objects disclosed hereinafter are accomplished by applying to a metal substrate, subject to corrosion, a corrosion-inhibiting durable protective coating composition, capable of air-drying to a tack-free film comprising a drying oil vehicle, a pigment composition containing zinc oxide and barium soaps of saponified wool wax.

In a particularly preferred embodiment of the invention, the corrosion-inhibiting protective paint composition comprises a mixture of a predominating proportion of raw linseed oil and a minor proportion of linseed oil modified glyceryl phthalate resin, a pigment composition containing zinc oxide, and barium soaps of saponified wool wax.

The significant advantage of the compositions of this invention resides in their application over pre-rusted metal. While iron oxide is the principal product of the corrosion of iron and steel, the rust contains water-soluble sulfate salts which collect therein and accelerate the corrosion. Unless these soluble sulfate salts are eliminated or inhibited in their activity, corrosion will continue beneath the protective coating and cause premature failure of the coating. Sulfates are recognized as most detrimental to the corrosion of iron. This recognition is based

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on the fact that high concentrations of sulfate ion are found in the rust where corrosion is profuse, such as produced in industrial areas. In such areas a high content of sulfate contamination is supplied to the atmosphere by the burning of fuel and as by-products of various chemical operations and petroleum refining.

The superior performance of the compositions of this invention applied over a rusted metal surface or an un-rusted metal surface subject to rusting is attributed to the scavenging or elimination of the corrosive sulfate ion. The barium soaps of wool wax react with the sulfate ion to form the insoluble and non-reactive barium sulfate. Zinc oxide is incorporated in the compositions of this invention to counteract the acids released from the barium soap and/or any other acids that might be present.

In order that one skilled in the art may better understand the invention, the following examples are given by way of illustration and not by way of limitation. All parts and percentages are expressed on a weight basis unless otherwise designated.

Example 1

	Parts by weight
Raw linseed oil-----	29.3
Alkyd resin solution—83% resin content in high solvency petroleum hydrocarbon-----	8.9
Lead naphthenate drier solution—16% lead-----	2.6
Manganese naphthenate drier solution—3% manganese-----	0.7
Hydrocarbon solvent—mineral spirits-----	4.2
Barium lanolate (barium soaps of saponified wool wax)-----	2.7
Zinc oxide-----	8.0
Talc-----	40.5
Lamp black-----	2.6
10% solution of creosol in a mixture of mineral spirits and high solvency petroleum hydrocarbon-----	0.5
	100.0

The alkyd resin is a 64% linseed oil modified glyceryl-phthalate resin with 1.7% excess glycerine and an acid number of about 4.

The barium soaps represent the soap residue resulting from saponification of wool wax with barium oxide or barium hydroxide; the unsaponifiable components of the wool wax, such as cholesterol, being separated therefrom. These mixed barium soaps are referred to in the claims as barium lanolate.

The zinc oxide was a French process type pigment substantially free of sulfate ions.

The lamp black pigment used mainly to tint the coating composition to a dark gray color was substantially free of water-soluble salts.

The above rust-inhibiting paint composition was applied to pre-rusted hot rolled steel panels by brushing, applying an amount of paint corresponding to that which will provide a dry film thickness of about 2.5 mils. The rust was not completely removed from the corroded panels before coating except that loose surface scale was eliminated by light wire brushing.

The coated panels were exposed to the weather and examined periodically to determine the corrosion-inhibiting protection afforded by the coating composition of Example 1 in comparison with several control protective compositions.

While the compositions are generally identified as corrosion-resisting primers with the implication that topcoats are to be superimposed, the exposure tests were conducted with the compositions as the sole coating without topcoats.

In comparative exposure tests, results showed the composition of Example 1 to be consistently better than costly

red lead-linseed oil metal primer, with respect to corrosion resistance.

In another series of tests, pre-rusted steel panels coated with the composition of Example 1 and exposed in a non-industrial area at a 45° angle for 24 months remained in substantially perfect condition while controls of red lead-linseed oil primer and zinc chromate-linseed oil primer showed failure by rusting.

In a practical test, corroded metal floor grating subject to heavy foot traffic in an industrial area was painted with the composition of Example 1 and a zinc chromate primer as a control. When examined after 30 months' service, the zinc chromate primer showed blistering and extended rusting under the blisters. The coating of Example 1 showed no failure due to rusting except where the protective coating was ruptured by abrasion; which type of failure was similarly present in the control.

Example 2

A degreased steel test panel was brush-coated with the following primer:

	Parts by wt.
Raw linseed oil	24.4
83% solution linseed oil modified alkyd resin in high solvency petroleum hydrocarbon	7.5
Manganese naphthenate drier solution (3% mn) ..	.5
10% solution creosol in a mixture of mineral spirits and high solvency petroleum hydrocarbon	.4
Mineral spirits	3.4
Lead naphthenate drier solution (16% Pb)	2.2
Zinc oxide	6.8
Iron oxide	52.5
Barium lanolate	2.3

100.0

Sufficient of the above composition was applied in one coat to deposit a dry film thickness of about 2 mils. After drying, one-half of the primed surface was topcoated with a conventional linseed oil modified alkyd resin paint. The primed and topcoated panel was heat aged overnight at 130° F.

As a control a second panel was prepared differing only from that described above in that the barium lanolate was omitted from the primer.

In an accelerated test for corrosion resistance the two panels were placed in a humidity cabinet (100% relative humidity and 110° F.) overnight and then examined for blistering. The amount of blistering has been found to be in direct proportion to the corrosion resistance, which is a reliable accelerated test for corrosion resistance. The control panel without barium lanolate showed considerable blistering over the entire coated surface, including the topcoated and non-topcoated area, whereas the panel with the barium lanolate showed essentially no blistering.

Since traces of sulfate ion can bring about failure of painted metal surfaces, an improvement with respect to preventing or inhibiting rusting can be realized with traces of barium lanolate in the primer composition. In order to assure complete protection where the sulfate ion is highly concentrated a practical amount of barium lanolate to incorporate in the primer composition has been found to be about 2.7%, based on the total weight of the primer composition. Amounts greater than about 5%, based on total weight of primer, are unnecessary to accomplish the objects of this invention.

The barium soaps of saponified wool wax contain the barium soap of hexacosanoic acid as the major component. While the mixture of barium soaps derived from saponification of wool wax with barium oxide or hydroxide are preferably used alone as the corrosion inhibitor in the practice of this invention, the mixture of barium soaps may include other barium soaps in minor proportion. For example, barium soaps of higher fatty acids

may be substituted in part for the barium soaps of wool wax in the composition of Example 1 providing the latter are in predominating proportion. By higher fatty acids is meant monocarboxylic acids obtainable from vegetable oils.

While Example 1 shows the preferred use of linseed oil in the paint vehicle, other drying oils commonly used in the formulation of air-drying paints may be substituted for the linseed oil, wholly or in part on a pound for pound basis. Suitable drying oils include soybean oil, tung oil, chinawood oil, oiticica oil, perilla oil and dehydrated castor oil. Synthetic unsaturated hydrocarbon oils capable of air-drying to a tack-free film may also be used. Oil acids of the aforementioned vegetable drying oils may be substituted for the linseed oil acids as a modifier for the alkyd resin. The oil length of the alkyd resin may vary in the range of about 30 to 70% and the acid number of the resin is preferably no greater than about 10. Resins of higher acid number react with the zinc oxide of the pigment composition and are to be avoided. Glyceryl-phthalate type alkyd resin is preferred in the practice of this invention, but other polyhydric alcohols such as pentaerythritol, propylene glycol or ethylene glycol, may be used in place of part or all of the glycerine and other dicarboxylic acids, such as maleic, fumaric, sebacic, adipic, isophthalic or terephthalic acid may be used in place of phthalic anhydride in the preparation of the alkyd resin.

The vehicle composition of Example 1 has drying oil and alkyd resin in the ratio of 4 parts by weight of raw linseed oil for each part of alkyd resin. This ratio is not particularly critical and the alkyd resin may be eliminated entirely in which case the drying oil represents the entire film-forming vehicle.

The chemical constitution of the pigment composition is not critical except that it should include a sufficient concentration of reactive zinc oxide to serve as an acid acceptor to neutralize any acidity which may develop during aging of the coating and/or resulting from the reaction of barium lanolate with sulfate ions. The pigment composition should preferably be substantially free of sulfates and water-soluble salts.

The optimum amount of total pigment and filler in the compositions of this invention correspond to about 30% of the volume of the non-volatile components and the preferred range is 20% to 35% of the volume of the non-volatile components. Useful compositions can be prepared where the pigment and filler represents about 50% of the volume of the non-volatile components of the composition. The minimum amount of pigment is an amount of zinc oxide which will react with the acids that are present or formed in the composition. Example 1 includes the preferred amount of reactive zinc oxide at a concentration of about 16% based on the weight of the pigment composition. A minimum concentration of about 2% by weight based on the pigment composition is required to provide adequate alkalinity as an acid acceptor. There is no critical upper limit for the zinc oxide content, since it may represent the entire pigment composition.

The balance of the pigment composition may vary widely, economics generally guiding the choice of pigments. Use of a proponderance of extender pigment permits the coating composition to be formulated at low cost. Talc is a preferred economical extender, but other extenders such as asbestine, barytes, china clay or silica may be used in its place.

The inorganic tinting pigments are preferably used in admixture with zinc oxide and extender at a concentration only sufficient to provide the desired color of the product and opacity or hiding power.

The conventional metallic driers are included in the primer compositions to accelerate the drying and conventional oxidation inhibitors are used to prevent skinning

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of the paint without detrimental effect on corrosion-inhibiting activity.

Coating compositions of this invention provide an economical means of protecting structural iron and steel whereby longer service is obtained than with the use of costly red lead in oil and other conventional corrosion-inhibiting coatings. Also, less effort is required to prepare a surface for painting inasmuch as removal of practically all of the rust is unnecessary. The primer compositions of this invention make possible the use of pigments, which contain small amounts of sulfates, which would initiate corrosion except for the presence of barium lanolate.

It is apparent that many widely different embodiments of this invention may be made without departing from the spirit and scope thereof and, therefore, it is not intended to be limited except as indicated in the appended claims.

I claim:

1. A corrosion-inhibiting coating composition comprising a drying oil, pigment composition including at least 2% by weight of zinc oxide based on the total pigment content, said total pigment content representing about 20% to 50% of the volume of the non-volatile components of the composition, and a barium salt of wool fat fatty acids, said salt of wool fat fatty acids being present in an amount of about 2.3% to 5.0% based on the weight of the total composition.

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2. The composition of claim 1 in which the drying oil is linseed oil.

3. The composition of claim 1 in which the paint vehicle is comprised of raw linseed oil and a drying oil modified alkyd resin having an acid number less than about 10.

4. The composition of claim 3 wherein said alkyd resin is a linseed oil modified alkyd resin.

5. The composition of claim 3 wherein said alkyd resin is modified with an unsaturated fatty acid in an amount corresponding to 30 to 70% by weight of fatty acid glyceride based on the weight of said resin and further characterized by an acid number less than about 10.

6. The composition of claim 1 in which the barium salt is barium lanolate and is present in an amount of about 2.7%, based on the total weight of the composition.

7. The composition of claim 1 in which the total pigment content represents from 20% to 35% of the volume of the non-volatile components of the composition.

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