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3,198,747

ACID RESISTANT COATING FOR METALLIC SURFACES

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This invention relates to corrosion-inhibiting compositions and, more particularly, to compositions and a method for treating surfaces subjected to corrosive environments in order to remove residual corrosion products and form a protective film on the surface.

It is often desirable to treat metallic surfaces, as well as non-metallic surfaces, that are subject to corrosive environments, such as the corrosive action of inorganic acids, in order to remove the residual corrosion products as well as to protect the surfaces from further corrosion. There are many examples of situations where materials are subject to corrosive substances, as in chemical plants manufacturing or utilizing inorganic acids. A very common example of such a situation is encountered in automobiles, buses, trucks, etc., utilizing conventional wet-cell storage batteries. The wet-cell batteries which contain an aqueous sulphuric acid solution are provided with vent holes in the battery caps through which acidic vapors and liquid escape and attack the metallic parts of the battery, and metallic components adjacent to the battery, to form sulfate corrosion products. The sulfate corrosion is of three types, namely, ferric or ferrous sulfate from the terminal bolts and the steel frame assembly which holds the battery in place, copper sulfate from the battery cable, and lead sulfate from the lead-alloy terminal posts and cable clamps. Accumulations of the corrosion products on and around the terminal connections permit current leakage, reduce the effectiveness of the contact between the battery terminal and cable clamp, cause failure of the hold-down frame assembly, and are otherwise deleterious.

Heretofore, numerous methods and compositions have been proposed for cleaning corroded surfaces and/or protecting surfaces against damage caused by corrosive substances. In the case of wet-cell storage batteries, a moderate degree of success in reducing corrosion of the terminals, clamps, etc., and in minimizing the deleterious effects of deposits and corrosion products, has been gained by periodic wire-brushing and scraping of the corroded elements followed by an application of a protective film of grease or petrolatum. However, these procedures are not entirely satisfactory since wire-brushing and scraping are not completely effective in removing the free acid as well as the deposits. Compositions which do not chemically react with the acidic materials are incapable of displacing the acidic materials, and it is difficult to apply the grease or petrolatum uniformly to completely cover the surfaces.

It is therefore one of the principal objects of this invention to provide a composition and method for removing residual corrosion products from a surface. Another object of this invention is to provide a composition and method to protect surfaces subject to corrosive environments. A further object of this invention is to provide a composition for forming an acid-resistant film on surfaces. A still further object of this invention is to provide a composition and method for treating surfaces corroded by acidic substances in order to remove residual corrosion products and form an acid-resistant coating. Still another object of this invention is to provide a composition adapted to remove sulfuric acid and sulfate corrosion products from a metallic surface and protect the surface with an acid-resistant coating. Still

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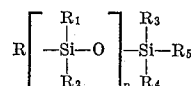
another object of this invention is to provide a composition for treating metallic battery parts and metallic surfaces subject to acidic vapors and liquid escaping from the battery. These and further objects of this invention will become apparent as the description herein proceeds.

This invention is based on the discovery that the dual function of removing residual corrosion products from a surface and protecting the surface with a corrosion-resistant coating can be obtained by treatment with a composition comprising water, a water-soluble base which reacts with mineral acids to form neutral salts, and an organo-silicon polymer which forms a protective coating on the surface. Preferably, the composition also contains minor amounts of a wetting agent and a pH-indicating chemical. Although the percentage composition of our invention is not critical and may be varied through quite broad limits, the various components should be present in amounts to effect the overall purpose of the composition without the necessity for using an excessive amount, and thereby makes its use impractical. It is preferred that the components are present in the following ranges:

Component:	Percent by weight
Water	60 to 90
Base (present in excess of basicity of wetting agent content)	2.5 to 24
Organo-silicon polymer	2.5 to 24
Wetting agent	0.5 to 6
pH Indicator	0.0004 to 0.16

As the appropriate component to react with acidic substances to form neutral salts, either inorganic or organic bases can be used, but a strongly basic component is preferred. Non-limiting examples of bases which are suitable for use in compositions of this invention are inorganic bases such as ammonium, alkali and alkaline earth metal hydroxides, oxides, carbonates, etc., and organic bases such as amines, including alkylolamines. Specific examples of bases which can be used are ammonium hydroxide, sodium hydroxide, potassium hydroxide, calcium hydroxide, sodium carbonate, sodium bicarbonate, lithium hydroxide and oxide, ammonium carbonate, di-2-ethylhexylamine, octadecylamine, ethanolamine, dipropanolamine, triethanolamine, pyridine, quinoline, and piperidine. Although some bases are effective for the purpose of this invention, it may not be desirable to utilize them from an aesthetic consideration. For example, sodium carbonate is effective in neutralizing battery acid and removing residual deposits, but compositions containing sodium carbonate leave undesirable amounts of the sodium carbonate after the water has evaporated, contributing to a poor appearance. The amount of the base included in the composition will vary, depending upon the strength and molecular weight of the base used, but in general will be in the range of about 2.5 to 24 percent by weight of the total composition.

The film-forming silicone component of our composition is of the following general structure:



in which R, R₁, R₂, R₃, R₄, and R₅ represent alkyl, alkaryl, or aralkyl radicals and n has a value of about 0–2000, as discussed on pages 336 to 352 of "Polymers and Resins," by B. Golding, published by D. Van Nostrand Company, Inc., in 1959. These compounds and methods for preparing them are described in U. S. Patents 2,352,974, 2,258,222, 2,258,219, and 2,371,068. Illustrative of such compounds are polymers of dimethyl silicone, diethyl silicone, ethyl methyl silicone, diphenyl silicone, phenyl tolyl

silicone, methyl phenyl silicone, and ethyl phenyl silicone. The amount of the silicone added to the composition will vary inversely proportional to the viscosity of the silicone used, with amounts varying from about 2.5 to 24 percent by weight of the composition being preferred. If the silicone separates from the composition upon prolonged standing, it can be readily re-introduced into the mixture with mild shaking.

Preferably incorporated in the composition is one of the well-known wetting and penetrating agents, which enhance penetration of the acidic substances and corrosion products by the solution on the surface being treated, to aid the neutralization action of the base, as well as to allow the film-forming agent to come into direct contact with the surface. Any suitable water-soluble wetting agent compatible with the other components of our invention may be used, such as soaps formed by the combination of a base such as ammonium, alkali metal and alkaline earth metal hydroxides, amines, including primary, secondary and tertiary alkyolamines, etc., and a soap-forming acid such as saturated or unsaturated fatty acids, tall oil acids, naphthenic acids, sulfonic acids derived by the treatment of lubricating oils with sulfuric acid, and acids produced by the oxidation of paraffin wax or other petroleum fractions. Examples of soaps useful as wetting agents in the composition of our invention are ammonium linoleate, ammonium oleate, ammonium palmitate, sodium caproate, potassium stearate, sodium myristate, magnesium palmitate, calcium stearate, strontium caprylate, barium palmitate, di-2-ethylhexylatimonium stearate, propanolammonium caprylate, n,n-di-methylethanolammonium oleate, triethanolammonium linoleate, sodium naphthenate, and potassium tallate. Other wetting agents which may be used include sodium petroleum sulfonate, lithium diwaxbenzenesulfonate, calcium diwaxnaphthalenesulfonate, monoethylphenol, sodium monosulfonate, sulfonated castor oil, and sulfonated cetyl alcohol.

The base used in preparing the wetting agent may be different from the base which is added to the composition to react with the acidic substances. In preparing the composition, the base and the wetting agent may be added directly, or the base and the soap-forming acid may be combined in the course of formulation of the composition with the resultant wetting agent being formed in situ. It will be evident that the amount of base required will be greater if the wetting agent is formed in situ than if the wetting agent is added directly to the composition. The wetting agent need be present in the composition in only a very small amount, preferably in the range of about 0.5 to 6.0 percent by weight of the composition, to achieve the desired result.

A small amount of pH indicator, such as phenolphthalein, is preferably added to the composition to indicate when neutralization of residual acidic substances is accomplished. The use of phenolphthalein in an alcohol, such as ethanol, presents a red-dyed appearance to the composition, and the presence of red fluid on the surface being treated indicates neutralization of residual acidic substances. The red color will fade away upon evaporation of the alcohol, leaving a colorless glaze, and the color will not return with future applications of water. Examples of other pH indicators which may be used include thymol blue and thymolphthalein. The pH indicator need be added to the composition in only a small proportion. For reasons of economy, it is preferred to employ the minimum concentration of indicator which is compatible with the desired results, usually in the range from about 0.0004 to 0.16 percent by weight of the composition.

These compositions can be applied by spraying, as from aerosol bombs and rechargeable spray containers, or by other suitable means, such as by brushing the battery terminals, clamps, hold-down frames, and other surrounding parts to flush off the deposits and neutralize any residual acid. When used in an aerosol bomb any pro-

pellant which is not reactive with the various components, such as Freon, can be used. While any amount of deposit can be removed with copious quantities of our composition, the removal of loose salts by means of a brush is preferred from an economic point of view. This then permits the composition to remove salts still adhering to the metal and to neutralize the residual acids. The maximum protection against further corrosion and deposit formation is dependent upon a maximum removal of residual salts and acids by brushing and flushing.

The following examples are given to illustrate the compositions of our invention, but in no way limit it as to reagents or proportions.

EXAMPLE I

	Percent by weight
Triethanolamine	9.60
Oleic acid	1.92
Alcoholic phenolphthalein solution (1% phenolphthalein)	0.04
Dimethyl silicone polymer (sold under the proprietary name of Dow Corning Antifoam B and having an average molecular weight of 15,000)	9.60
Water	78.84

EXAMPLE II

Sodium carbonate	2.0
Alcoholic phenolphthalein solution (1% phenolphthalein)	0.1
Diethyl silicone polymer	5.0
Water	92.9

EXAMPLE III

Ammonium hydroxide (28.6% as NH ₃)	7.0
Alcoholic phenolphthalein solution (1% phenolphthalein)	0.1
Methyl phenyl silicone polymer	5.0
Water	87.9

EXAMPLE IV

Dipropylamine	4.1
Sodium oleate	0.97
Dimethyl silicone polymer	4.5
Alcoholic phenolphthalein solution (1% phenolphthalein)	0.02
Water	90.41

Any suitable method may be employed for preparing the composition of this invention. For example, the wetting agent can be added directly or formed in situ, as indicated above. The composition can be prepared with water as the major ingredient, as previously indicated, so that it can be used without any further dilution. Alternatively, the composition can be prepared as a concentrate containing little or no water, necessitating its dilution with water before it is used. The concentrate may be anhydrous or may contain a small amount of water, that is, up to about 25% by weight of the concentrate. The composition of the anhydrous concentrates may be varied through broad limits, but preferably will have the following ingredients in the following approximate proportions:

Anhydrous concentrate

Component:	Percent by weight
Base	25-60
Organo-silicon polymer	25-60
Wetting agent	5-15
pH Indicator	0.004-0.4

Following is an example of the composition of an anhydrous concentrate of this invention:

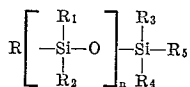
	Percent by weight
Triethanolamine	45.0
Sodium oleate	9.8
Dimethyl silicone polymer	45.0
Alcoholic phenolphthalein solution (1% phenolphthalein)	0.2

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Although our invention has been described in relation to specific embodiments, obvious modifications may be made by those skilled in the art without departing from the intended scope of this invention.

The embodiments of this invention in which an exclusive property or privilege is claimed are defined as follows:

1. A composition for treating bodies subject to attack by sulfuric acid, whereby sulfate corrosion products are formed, consisting of about 60-90% by weight of water, about 0.5-6.0% by weight of a water-soluble, organic wetting agent in the form of a water soluble soap adapted to enhance the penetration of said corrosion products by said composition, about 0.0004-0.16% by weight of a pH indicator having the property of changing in color when acidic material contacted with said composition is neutralized, about 2.5-24% by weight of a base, selected from the group consisting of ammonium, alkali metal and alkaline earth metal hydroxides, oxides and carbonates, and amines, capable of reacting with sulfuric acid to form salts, and about 2.5-24% by weight of an organo-silicon polymer of the formula



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wherein the R's are radicals selected from the group consisting of alkyl, alkaryl and aralkyl radicals and n has a value of about 0-2000.

2. A composition in accordance with claim 1 in which the wetting agent is a triethanolamine soap.

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