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2,861,892

RUST PREVENTIVE COMPOSITION

Frederick J. Radd, D'Arcy A. Shock, and John D. Sudbury, Ponca City, Okla., assignors to Continental Oil Company, Ponca City, Okla., a corporation of Delaware

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This invention relates to coating compositions suitable for inhibiting or even preventing the rusting and corrosion of metal surfaces. More particularly, the present invention pertains to novel compositions of matter which on application to metal surfaces form protective films which serve as barriers to moisture, to corrosive fluids, and the like, thereby protecting said metal surface for relatively long periods of time. Still more specifically the invention has in view the employment of the improved protective agents in paints or coatings. Such coatings are especially useful when employed for the purpose of counteracting corrosion of metals and metal alloys, particularly steels and iron-containing metals. When these metals are exposed for long periods of time considerable losses are incurred as a result of the corrosive action of air and water. It is to be understood, however, that the present invention is not limited in its application to steel and iron-containing metals since the invention may also be used to protect other materials against corrosion.

Heretofore it has been proposed to eliminate corrosion by shielding or protecting materials from air and humidity or other corrosive agents by means of coating the surfaces of such materials with a compound containing a base or binding agent such as asphalt, tar, coal tar pitch, resin, artificial resin, lacquers, varnishes, rubber, and the like. These coating materials, however, are subject to cracking and pin-hole formation and, as a result, considerable corrosion will take place at the sites of the paint imperfections. Although the cracks may initially be as fine hair lines the corrosion undermines and loosens the remaining coating and exposes more and more surface of the material intended to be protected. In addition to the hair line cracks, the paint film may be ruptured by the development of blisters or pin holes. Under certain conditions the problem of corrosion is exceedingly serious because once started corrosion is accelerated. The presence of electrolytes and formation of corrosive decomposition products in oils and the like also greatly increase the rate of corrosion.

In addition to the conditions enumerated above, elevated temperatures greatly accelerate corrosion activity. Corrosion is also accelerated when moisture, salt spray, and other contaminants or acidic composition products or corrosive gases come in contact with hot metal bodies, particularly under conditions normally developed in machinery and in industrial equipment during operation. Under certain conditions corrosion of metallic surfaces can attain such an aggravated stage that the result is a stress concentration point and under such a condition cracking of the metal may be the ultimate result.

It is, therefore, a primary object of the present invention to provide coating compositions which when applied to metallic surfaces form coatings that protect the metal from corrosion even when the coating composition is ruptured by the initial presence or by the development of

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blisters, pin holes, or cracks. It is another object of our invention to provide paints which when applied to metals form coatings that protect the metals from corrosion for a long period of time. It is another object of the present invention to protect metal surfaces in contact with corrosive contaminants by coating said surfaces with a composition which has no detrimental effect upon the metal surface thus coated. Other objects and advantages of the invention will be apparent as the invention is more thoroughly described.

The foregoing objectives are in brief attained by the preparation of coating compositions comprising a major portion of paint and a minor quantity of a sulfonate as a corrosion inhibitor. The amount of sulfonate used in the coating composition varies according to the specific sulfonate used, being dependent upon both the anion and cation of the sulfonate. In general, however, good results are obtained when the amount used varies from about 0.002 to about 0.1 part of the sulfonate per 100 parts of the paint. Quantities in excess of 0.1 percent sulfonate impart no additional benefits and in many cases may be detrimental because such amounts cause the paint film to become water sensitive.

Before proceeding with specific examples illustrating our invention, it may be well to indicate in general the nature of the materials required in the process.

Suitable sulfonates for use in this process are those prepared by the neutralization of sulfonic acids. Specific sulfonic acids used in the neutralization process may be selected from a large list as, for example, those produced in the sulfonation of the petroleum fractions obtained in the refining of petroleum by fractionation, extraction, or other refining processes. Other sulfonic acids which may be used are those obtained by sulfonating hydrocarbons, which hydrocarbons are produced by the alkylation of mono- and poly-nuclear hydrocarbons such as benzene, toluene, xylenes, diphenylmethane, alkyl diphenylmethane, naphthalene, biphenyl, alkyl diphenyl, and alkyl naphthalene. The alkylation process may be carried out by using an alkylating agent containing from about 3 to 20 carbon atoms or more in the presence of a catalyst. Such an alkylation agent includes halo-paraffins, olefins as may be prepared by the dehydrohalogenation of halo-paraffins, and poly olefins. Poly olefins include polymers of ethylene, propylene, butylene, ethylene and propylene, alkyl sulfates, aliphatic alcohols and others. As is well known to those skilled in the art the sulfonation step may be carried out using a sulfonating agent such as sulfuric acid oleum sulfur trioxide and chloro sulfonic acid. Preferred sulfonic acids for use in our invention include those sulfonic acids prepared by the sulfonation of secondary cycle oil. A secondary cycle oil is a product known to the petroleum industry as that material which separates out as a raffinate at 120° F. from the furfural extract obtained in the production of pale oil and having a viscosity index of about 50 to 70. Other preferred sulfonic acids are those prepared by sulfonating the product obtained by the alkylation of benzene or toluene or xylenes with dodecylene or dodecylchloride and boiling within a range of from 140 to 230° C. at a pressure of 20 mm. mercury.

A preferred specific sulfonic acid is the acid prepared by sulfonating the detergent alkylate sometimes called polydodecylbenzene which consists of monoalkylbenzenes and dialkylbenzenes in the approximate mole ratio of 2:3. Typical physical properties of this alkylate are as follows:

Specific gravity at 38° C	0.8649
Average molecular weight	365
Percent sulfonatable	88

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I. B. P	° F	647
5	° F	682
50	° F	715
90	° F	760
95	° F	775
F. B. P	° F	779
Refractive index at 23° C		1.4900
Viscosity at:		
10° C	centipoises	2800
20° C	do	280
40° C	do	78
80° C	do	18
Aniline point	° C	69
Pour point	° F	-25

Magnesium, calcium, strontium, barium, copper, cobalt, and nickel sulfonates have been found suitable as corrosion inhibitors. In addition to the above-mentioned cations, ammonium and substituted ammonium cations as, for example, morpholine, alkylamines, alkanolamines, di-alkanolamines, etc., may also be used.

Secondary cycle oil and the detergent alkylate also known as polydodecylbenzene both of which are identified above were sulfonated by the procedure disclosed in the copending patent application of Luntz and Popovac, S. N. 396,822, filed December 8, 1953, now U. S. Patent No. 2,768,199, which application is assigned to the present assignee. After the two sulfonic acids were obtained, sulfonates of each were prepared in which the cations were calcium, cobalt, copper, sodium and ammonium. Specific sulfonates prepared were as follows:

Calcium secondary cycle oil sulfonate
Cobalt secondary cycle oil sulfonate
Copper secondary cycle oil sulfonate
Lithium secondary cycle oil sulfonate
Sodium secondary cycle oil sulfonate
Ammonium secondary cycle oil sulfonate

Calcium polydodecylbenzene sulfonate
Cobalt polydodecylbenzene sulfonate
Copper polydodecylbenzene sulfonate
Ammonium polydodecylbenzene sulfonate

In addition to the above-mentioned sulfonates, diethanol amine secondary cycle oil sulfonate and diethanol amine polydodecylbenzene sulfonate were also prepared.

In order to disclose more clearly the nature of the present invention and the advantages thereof, reference will hereinafter be made to certain specific embodiments which illustrate the flexibility of the herein described process. It should be clearly understood, however, that this is done solely by way of example and is not to be construed as a limitation upon the spirit and scope of the appended claims.

The foregoing sulfonates were subjected to test as rust inhibitors in each of the various coating compositions listed below. In these tests the inhibitor was added to the primer in a concentration of 0.1 percent by weight. The specimens were cut from 16 gauge AISI 1020 carbon steel to 2 3/4" x 5 1/2". Each specimen was sandblasted over its entire surface and then stored in a desiccator until ready for use. The primer containing the inhibitor was applied to the specimen by means of a brush using a different brush for each inhibitor. After the priming coat had dried the finish coat was applied by spraying and then a two inch cross was inscribed on the specimen cutting down to the bare metal. For comparison purposes a specimen coated with the primer without the addition thereto of an inhibitor was used as control. All tests including the control were run in duplicate. The coated samples were subjected to accelerated weathering test by placing them in an Atlas twin-arc weatherometer for a period of 20 hours per day, 5 days per week following the procedure described in ASTM method D-822-46T.

In conducting the test a 3 percent aqueous sodium chloride solution was sprayed intermittently on the samples for a period of 18 minutes out of every 2 hours. A blower provided mild circulation of air in the chamber. The different primers used were as follows:

Example 1

Alkyd resin red lead primer consisting of pigment, non volatile vehicle, and solvent and drier in the approximate ratio of 50, 20 and 30% respectively.

Example 2

Vinyl wash primer consisting of pigment, non volatile vehicle, and solvent in the approximate ratio of 12, 15 and 73% respectively.

Example 3

Red lead epon primer consisting of pigment, non volatile vehicle, and solvent in the approximate ratio of 70, 20 and 10% respectively.

Example 4

Aluminum primer consisting of pigment, non volatile vehicle, and solvent and drier in the approximate ratio of 12, 30, and 58% respectively.

Example 5

A lacquer base primer consisting of pigment, non volatile vehicle, and solvent in the approximate ratio of 1.0, 16, and 83% respectively.

Example 6

A zinc chromate primer consisting of pigment, non volatile vehicle, and solvent and drier in the approximate ratio of 19, 30, and 51% respectively.

Example 7

A bitumastic primer (cold dip) consisting of petroleum tar, rosin, gilsonite and solvent naphtha in the approximate ratio of 28, 1, 9, and 62% respectively.

Example 8

A bitumastic primer (cold dip) consisting of coal tar, benzene, and silica black in the approximate ratio of 42, 33, and 25% respectively.

As mentioned above each of the foregoing primers as a control and each containing 0.1 percent of the inhibitor were run in duplicate using an Atlas twin-arc weatherometer for an accelerated weathering test. All the inhibitors used did not show equal effectiveness as rust inhibitors in the various primers. In the table below the most effective rust inhibitors for each of the primers are listed.

TABLE

Primer	Most effective rust inhibitor
Example 1	Lithium polydodecylbenzene sulfonate.
Example 2	Cobalt polydodecylbenzene sulfonate.
Example 3	Calcium secondary cycle oil sulfonate.
Example 4	Calcium secondary cycle oil sulfonate.
Example 5	Copper secondary cycle oil sulfonate.
Example 6	Calcium polydodecylbenzene sulfonate.
Example 7	Sodium secondary cycle oil sulfonate.
Example 8	Diethanol amine secondary cycle oil sulfonate.
	Ammonium polydodecylbenzene sulfonate.
	Sodium secondary cycle oil sulfonate.
	Calcium secondary cycle oil sulfonate.
	Ammonium secondary cycle oil sulfonate.
	Cobalt secondary cycle oil sulfonate.
	Copper secondary cycle oil sulfonate.
	Copper polydodecylbenzene sulfonate.
	Ammonium polydodecylbenzene sulfonate.
	Lithium polydodecylbenzene sulfonate.
	Diethanol amine polydodecylbenzene sulfonate.
	Copper secondary cycle oil sulfonate.
	Calcium polydodecylbenzene sulfonate.
	Ammonium polydodecylbenzene sulfonate.
	Sodium secondary cycle oil sulfonate.

While particular embodiments of the invention have been described, it will be understood, of course, that the invention is not limited thereto since many modifications may be made, and it is, therefore, contemplated to

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cover by the appended claims any such modifications as fall within the true spirit and scope of the invention.

The invention having thus been described, what is claimed and desired to be secured by Letters Patent is:

1. A coating composition adapted for use as a corrosion inhibitor comprising a bitumastic primer (cold dip) consisting of petroleum tar, rosin, gilsonite, and solvent naphtha in the approximate ratio of 28, 1, 9, and 62 percent, respectively, and from 0.002 to 0.1 part of a sulfonate per 100 parts of said primer wherein the cation of said sulfonate is organic.

2. The composition of claim 1 wherein the sulfonate is derived from a sulfonated polydodecylbenzene.

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3. The composition of claim 1 wherein the cation of the sulfonate is calcium.

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