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CORROSION-INHIBITING COMPOSITION CONTAINING CETYL DIMETHYL AMINE PETROLEUM SULFONATES AND METHOD

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This invention relates to corrosion-inhibiting compositions and methods. In one aspect this invention relates to corrosion-inhibiting petroleum or mineral oil compositions. In another aspect the invention relates to a method for inhibiting corrosion of metals in contact with petroleum oils. In another aspect the invention relates to a petroleum liquid composition containing up to 0.03 weight percent (300 p. p. m.) of cetyl dimethylamine petroleum sulfonate.

An object of the present invention is to provide petroleum or mineral oil compositions and fuels which protect metals with which they come in contact against rusting and corrosion. Another object is to provide improved fuels containing an effective corrosion inhibitor which does not adversely affect the desirable properties of the oil or fuel itself. Still another object is to provide a method for inhibiting corrosion of metals, especially ferrous metals in contact with petroleum liquids. Other aspects and objects, as well as advantages of the invention, will become apparent hereinafter.

The invention is concerned with methods and compositions for preventing or retarding corrosion of metals, particularly ferrous metals, especially in the presence of water dissolved or entrained in or settled from such petroleum oils or liquids, including crude oil, lubricating oils, gasolines, kerosene and jet fuels. The method is particularly valuable as applied to prevent corrosion in pipe lines.

Corrosion frequently occurs in pipe lines, storage tanks, etc., and in automotive and similar equipment because of traces of moisture inevitably present in the fuel or lubricant. Gasoline and kerosene, for example, as they leave the refinery are usually free of occluded moisture but they can contain as much as 0.005 to 0.01 percent dissolved moisture. Part of this dissolved moisture separates when the oil is chilled in a storage tank, for instance, and settles as a separate liquid phase beneath the main body of the oil.

Water may also enter oil or fuel handling systems along with air through partially filled tanks provided with breather devices. As such a tank cools, for example at night, the contents contract and air laden with moisture enters. This moisture condenses on the walls of the tank, settles to the bottom and dried air is expelled when the contents of the tank again warm up as from the heat of the sun the next day. As will be readily appreciated, repetition of this cycle eventually leaves appreciable amounts of water at the bottom of the tank.

Although several methods have been proposed for preventing corrosion in product handling systems, each of these has rather obvious shortcomings. One method for example, involves drying of the product, such as gasoline, by absorption on dehydrated alumina before the product is pumped into pipe lines. Another method involves the introduction into the product of costly chemicals such as hydrogen or mercapto benzothiazole which react with dissolved oxygen and thereby arrest corrosion. Still another method involves the introduction of water soluble

corrosion inhibitors such as sodium nitrite or chromates. Each of these methods is disadvantageous as affording only temporary protection. Sodium nitrite applied to inhibit corrosion in pipe lines is frequently decomposed by the action of oxidizing agents present in some crude oils. Hydrogen is quickly lost from vented storage tanks while water-soluble inhibitors are lost when they settle to the bottom of storage tanks and are drawn off. Completely water-soluble inhibitors are further deficient in many instances in not affording protection in the oil phase.

According to the invention there is provided a composition comprising a petroleum liquid or mineral oil containing up to 0.03 weight percent of cetyl dimethylamine petroleum sulfonate. The amounts of my inhibitor employed are from as little as 0.001 or less to as much as 0.03 weight percent, amounts in the range from 0.002 to 0.01 usually being preferred.

Further, according to this invention there is provided a method for preventing or inhibiting corrosion of ferrous metals or non-ferrous metals which comprises contacting such metals with a petroleum liquid or mineral oil containing up to 0.03 weight percent of cetyl dimethylamine petroleum sulfonate.

Cetyl dimethylamine petroleum sulfonate employed in the practice of this invention is difficult to decompose and provides a high degree of protection not only in the oil phase but also in the aqueous phase when a separate aqueous phase is present. Moreover, my corrosion inhibitor is effective in extremely small proportions and over a wide range of temperatures.

Any oil soluble petroleum sulfonate can be used to prepare cetyl dimethylamine petroleum sulfonate employed in the invention. For example, mahogany acids are useful in preparing the cetyl dimethyl amine petroleum sulfonate. Mahogany acids are prepared by sulfonation of light neutral oils, having viscosities up to about 50 SUS at 210° F., and separation of the oil-soluble mahogany acids from the oil-insoluble green acids by a solvent such as alcohol. Another class of petroleum sulfonic acids suitable for the preparation of the cetyl dimethyl amine sulfonate consists of the sulfonic acids prepared by sulfonating a dewaxed, deasphalted, solvent-refined bright stock having a viscosity in the range of 80–700 SUS at 210° F.

Methods of making cetyl dimethyl amine petroleum sulfonate include: (1) the direct neutralization of petroleum sulfonic acids with cetyl dimethyl amine, or (2) a double decomposition reaction of a salt of cetyl dimethyl amine with a metal petroleum sulfonate such as sodium or calcium sulfonate. Where direct neutralization is employed, the reaction proceeds quite rapidly at atmospheric temperatures. In the case where metal sulfonates are used as the source of the sulfonate ion, the metal salt can be decomposed with a mineral acid such as hydrochloric or sulfuric acid and then neutralized with a basic nitrogen compound; or the metal sulfonate may be reacted with an amine salt as, for instance, cetyl dimethyl amine hydrochloride.

Example I

In a typical small scale preparation of cetyl dimethyl amine petroleum sulfonate, the petroleum sulfonic acid was neutralized with cetyl dimethyl amine by titration. A slight excess of cetyl dimethyl amine was added.

A polished mild SAE 1020 hot rolled steel strip ½ inch by 5 inches and 1/16 inch thick was placed in a 4 ounce oil sample bottle with the steel strip resting on the bottom of the bottle. Fifteen milliliters of distilled water, 100 milliliters of fuel, and the cetyl dimethyl amine petroleum sulfonate were placed in the bottle and a cork stopper inserted in the bottle. A small air space was

present above the liquid in the bottle. Air was bubbled through the contents of the bottle once a week. The corrosion tests were of 90 days' duration.

The tables compare the effectiveness of cetyl dimethyl amine petrolem sulfonate in the described tests with other amines and with other sulfonates.

TABLE I

[Premium gasoline was added to the water.]

Test No.	Material Tested	Additive Conc., p. p. m.	Corrosion Product, Grams	Corrosion Reduction, Percent Based on Control
1	Control	0	0.0833	None
2	Sulfonate C [1]	20	0.0233	72
3	do	40	0.0154	82
4	t-Octylamine	40	0.0710	15
5	Aniline Sulfonate	40	0.0492	41
6	t-Octylamine Sulfonate.	40	0.0976	−17

[1] Cetyl dimethyl amine petroleum sulfonate prepared as described from commercial oil-soluble petroleum sulfonate.

TABLE II

[Aviation gasoline 100/130 was added to the water.]

Test No.	Material Tested	Additive Conc., p. p. m.	Corrosion Product, Grams	Corrosion Reduction, Percent Based on Control
7	Control	0	0.2726	None
8	Sulfonate C [1]	40	0.0495	80
9	t-Octylamine	40	0.1394	42
10	n-butylamine sulfonate.	40	0.1490	39
11	aniline sulfonate	40	0.1478	39
12	t-octylamine sulfonate.	40	0.2170	11

[1] Cetyl dimethyl amine petroleum sulfonate prepared from commercial sulfonate.

TABLE III

[JP-4 jet fuel was added to the water.]

Test No.	Material Tested	Additive Conc., p. p. m.	Corrosion Product, Grams	Corrosion Reduction, Percent Based on Control
13	Control	0	0.0653\ 0.0690	None
14	do	0	0.0728/ average	
15	Sulfonate C [1]	40	0	100
16	do	20	0	100
17	t-octylamine	20	0.0504	27
18	do	40	0.0698	−1
19	n-butylamine sulfonate.	40	0.0614	11
20	Aniline sulfonate	40	0.0692	0
21	t-octylamine sulfonate.	40	0.0913	−32

[1] Cetyl dimethyl amine petroleum sulfonate prepared from commercia oil-soluble petroleum sulfonate.

Cetyl dimethyl amine petroleum sulfonate prepared using an oil-soluble petroleum sulfonic acid, made by sulfonating a high molecular weight hydrocarbon fraction inhibited corrosion about the same as the cetyl dimethyl amine petroleum sulfonate prepared from commercial sulfonate. This sulfonate was prepared as follows:

A dewaxed, solvent refined, lubricating oil of 203 SUS at 210° F. and a viscosity index of 93 was sulfonated with 20 percent fuming sulfuric acid in a weight ratio of 1 to 0.4. The sulfonation was carried out at 130° F. for 65 minutes. This mixture was washed twice with equal volumes of a solution of 90 percent water and 10 percent isopropyl alcohol to remove the acid. Upon adding 90 percent isopropyl alcohol to the washed sulfonated oil, an emulsion formed. Cetyl dimethyl amine was added to this emulsion by titration. Upon neutralization, the oil layer separated out and was removed. The solvent was evaporated. The product was cetyl dimethyl amine petroleum sulfonate.

Cetyl dimethyl amine on a 90-day corrosion test when dissolved in oil did not show any corrosion inhibition.

Example II

In tests conducted in the same manner as in Example I, the following comparative results were obtained:

[Reduction in corrosion based on 10 lbs. inhibitor per 1000 bbl. of oil.]

Test No.	Inhibitor	Composition (Major Compound)	Percent Reduction in Corrosion		
			Avgas	Premium Gasoline	Jet Fuel
Control	None		0	0	0
22	Cetyl Dimethyl Amine Petroleum Sulfonate.		80	82	100
23	Santolene C [1]	(Dimerized Linoleic Acid).	55	45	8
24	RD119 [2]	Ammonium Mahoganate.		24	
25	RD155 [2]	Unknown	72	68	0
26	Kontol 77 [3]	Imidazoline Derivative.	69	57	19
27	Alrosperse 100 [4]	Unknown	51	62	81

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As will be evident to those skilled in the art, various modifications of this invention can be made or followed in the light of the foregoing disclosure and discussion without departing from the spirit or scope of the disclosure or from the scope of the claims.

I claim:

1. A corrosion-inhibiting composition comprising a petroleum liquid containing from 10 to 300 p. p. m. of cetyl dimethylamine petroleum sulfonate derived from an oil soluble petroleum sulfonate.

2. The composition of claim 1 wherein said cetyl dimethylamine petroleum sulfonate is present in an amount from 20–100 p. p. m.

3. A method for inhibiting corrosion of ferrous metals in contact with a petroleum liquid and in the presence of moisture which comprises providing from 10 to 300 p. p. m. in said petroleum liquid of cetyl dimethylamine petroleum sulfonate derived from an oil soluble petroleum sulfonate.

4. The method of claim 3 wherein said cetyl dimethylamine petroleum sulfonate is present in said composition in an amount from 20–100 p. p. m.

5. A composition according to claim 1 wherein said petroleum liquid is a crude oil.

6. A composition according to claim 1 wherein said petroleum liquid is a lubricating oil.

7. A composition according to claim 1 wherein said petroleum liquid is a gasoline.

8. A composition according to claim 1 wherein said petroleum liquid in kerosene.

9. A composition according to claim 1 wherein said petroleum liquid is jet fuel.

10. A method of claim 3 wherein said cetyl dimethyl amine petroleum sulfonate is prepared from mahogany acids, said mahogany acids being prepared by sulfonation of light neutral oils having viscosities up to 50 SUS at 210° F. and subsequent separation of the oil-soluble mahogany acids from the oil-insoluble mahogany acids by a solvent.

11. A method of claim 3 wherein said cetyl dimethyl amine petroleum sulfonate is prepared from sulfonic acids prepared by sulfonating a dewaxed, deasphalted, solvent refined bright stock, having a viscosity in the range of 80–700 SUS at 210° F.

12. The method of claim 3 wherein said cetyl dimethyl amine petroleum sulfonate is prepared from an oil-soluble petroleum sulfonate.

13. A method of inhibiting corrosion of ferrous metal pipelines in the presence of moisture which comprises providing in the petroleum liquid charged to said pipeline from 10 to 100 p. p. m. cetyl dimethylamine petroleum sulfonate derived from an oil soluble petroleum sulfonate.

14. A method according to claim 13 wherein said petroleum liquid is a gasoline.

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