

[54] **OIL-SOLUBLE RUST PREVENTIVE COMPOSITION**  
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[58] Field of Search .....44/66, 70, 72; 252/33, 50, 252/51.5 A, 56 D, 56 R, 390, 396

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[57] **ABSTRACT**

An oil-soluble rust preventive composition consists essentially of (A) a polycarboxylic acid having seven to 44 carbon atoms and 2 or 3 carboxyl groups or a partial ester of said acid with analiphatic alcohol having one to 18 carbon atoms and (B) an aliphatic tertiary amine having three hydrocarbon groups, each of which has at least one to 20 carbon atoms and at least one of which has six to 20 carbon atoms. The weight ratio of (A) to (B) is in the range of 95:5 to 5:95. The composition, when added to hydrocarbon oil, provides improved rust preventive characteristics and improved demulsibility, particularly when the oil contains a dispersant of the metal salt type.

**5 Claims, No Drawings**

## OIL-SOLUBLE RUST PREVENTIVE COMPOSITION

### BACKGROUND OF THE INVENTION

#### 1. Field of the Invention

This invention relates to an oil-soluble rust preventive composition and, more particularly, it relates to a binary rust preventive composition suitable for use in hydrocarbon oils such as fuel oils or lubricant oils.

#### 2. Description of the Prior Art

It is important to prevent rusting when a fuel oil or lubricating oil is used in contact with a metallic surface in the presence of a small amount of water.

Frequently, rust preventives are employed together with sludge-dispersants or detergent-dispersants. Conventionally known rust preventives, for instance, higher aliphatic amines, carboxylates such as sodium alkylmercapto acetate, sulfonates such as petroleum calcium sulfonate, phosphates such as zinc dithiophosphonate and partial esters of polyhydric alcohols such as sorbitane monooleate have, however, poor demulsibility against dispersants used in combination therewith, particularly dispersants of the metal salt type, such as metal sulfonates.

The object of the present invention is to provide a composition which exhibits an excellent rust preventive property, when added to hydrocarbon oils.

Another object of this invention is to provide an oil-soluble rust preventive composition having a good demulsibility.

### SUMMARY OF THE INVENTION

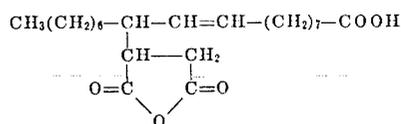
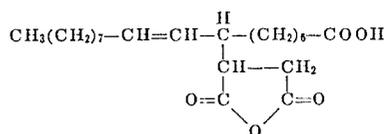
These objects of this invention can be accomplished by employing compositions containing (1) polycarboxylic acids or their partial esters and (2) aliphatic tertiary amines, such as described below.

The polycarboxylic acids to be used in the composition according to the present invention include alkenyl succinic acids, such as polyisobutenyl succinic acids having a polyisobutenyl group of 1-8 polymerization degree (four to 32 carbon atoms in the alkenyl group) and polyisopropenyl succinic acids having a polyisopropenyl group of 1-10 polymerization degree (three to 30 carbon atoms in the alkenyl group), unsaturated fatty acid-maleic anhydride addition products having 16-22 carbon atoms (which are also called maleated fatty acids), and, in general compounds with 7-44 carbon atoms possessing two or three carboxyl groups in a molecule such as dimerized fatty acids. Further, the aliphatic alcohols to be used for the partial esterification of these polycarboxylic acids are those which possess one-18 carbon atoms.

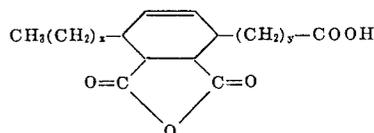
The above-described dimerized fatty acids are dimers of poly-unsaturated fatty acids having six-22 carbon atoms, for instance, dimers of dienoic acids such as sorbic acid (C<sub>6</sub>), palmitoleic acid (C<sub>16</sub>), linolic acid (C<sub>18</sub>) and eicosanoic acid (C<sub>20</sub>), and dimers of trienoic acids such as linoleic acid (C<sub>18</sub>) and eleostearic acid (C<sub>18</sub>).

The above-described unsaturated fatty acid-maleic anhydride addition products can be prepared by mixing monoenoic acids such as oleic acid, dienoic acids such as linolic acid or trienoic acids such as linoleic acid with maleic anhydride with heating. This procedure is well known and is described, for example, in "Progress in the Chemistry of Fats and Other Lipids", Vol. 5,

page 201-209, by Holman et al (Pergamon Press, 1958). The addition product obtained from oleic acid is presumed to be a compound in which maleic anhydride is added at the  $\alpha$ -position of the double bond in oleic acid: that is,



When linolic acid or linoleic acid (preferably conjugated linolic acid or linoleic acid which has been previously conjugated) is used, the addition product obtained is a compound of the Diels-Alder type represented by the following formula, for instance, with linolic acid:



(x+y=12)

The tertiary fatty amines to be used in the present invention are fatty amines possessing three hydrocarbon groups, each having 1-20 carbon atoms, and at least one hydrocarbon group of which has 6-20 carbon atoms: for instance, there may be exemplified hexyldipentyl amine, octyldiisobutyl amine, decyldiisobutyl amine, dodecyldiethyl amine, octadecyldimethyl amine, octadecyldiisopropyl amine, ethyldihexyl amine, methyldioctyl amine, methylhexadecyloctadecyl amine, methyldioctadecyl amine, trioctyl amine, trihexyl amine, tridecyl amine, tridodecyl amine, tritetradecyl amine, trihexadecyl amine, and trioctadecyl amine. Triamines derived from fatty acids of coconut oil are also effective.

Some of the polycarboxylic acids or tertiary amines to be used in this invention have been already known as rust preventives when used separately, but the composition of the present invention is prepared by blending them to accomplish a synergistic rust preventive effect as well as to extend further the application fields in which rust preventives could be successfully used and to improve their demulsibility to dispersants of the metal salt type. The blending ratio of the polycarboxylic acid vs. tertiary amine should be in the range 95:5 to 5:95 by weight. Mixtures outside of this range cannot achieve the desired synergistic rust preventive effect and demulsibility to dispersants.

The rust preventive composition of this invention is usually used in an amount in the range of about 0.001 to 3 percent by weight, based on the weight of the hydrocarbon oil in which it is used.

The hydrocarbon oils in which the rust preventive composition is used include lubricating oils consisting of mixtures of paraffinic, olefinic, aromatic or naphthenic hydrocarbons having carbon numbers of 4 to 100, which have generally specific gravities (15/4°C)

of 0.75 to 1.05 and viscosities (100°F) of 3 to 20,000 cst, and fuel oils such as kerosene, diesel fuel oils, gas oils and heavy fuel oils.

As typical hydrocarbon oils, SAE No. 300 oil (commercially sold under the name of 500 neutral oil) and hydrotreated (hydrogen-treated) 100 neutral oil have following properties:

	SAE No. 300	Hydrotreated 100 neutral oil
Viscosity 100°F (cst) 210°F	106 11.3	22.2 4.2
Viscosity Index	100	99
Sp. Gr. (15/4°C)	0.876	0.862
$n_{D20}^{20}$	1.482	1.475
Flash Point	247°C	211°C
Mw	600	428
Paraffinic hydrocarbon (%)	72	70.4
Aromatic hydrocarbon (%)	3	2.7
Naphthenic hydrocarbon (%)	25	26.9

Also, representative dispersants to be used in combination with rust preventives include alkenyl succinimides, bisalkenyl succinimides, trisalkenyl succinimides, alkaline earth metal salts of alkyl benzene sulfonate, alkaline metal salts of sulfurized alkyl phenol and alkaline earth metal salts of alkyl sulfonate. The preferred alkaline earth metal salts are calcium and barium. These dispersants are usually used in the amount less than 15 percent by weight based on the hydrocarbon oil.

Further, oxidation and bearing corrosion inhibitor such as zinc or amine salts of dialkyl dithio phosphonate, bis-(di or tri alkyl phenols) phenols and alkyl mono- or polysulfides can be added in the amount of 0.1 to 5.0 percent by weight based on the base oil. Also, oilness improver such as fatty acids ( $C_{10}$  to  $C_{24}$ ), fatty acid esters (esters of fatty acid of  $C_{10}$  to  $C_{24}$  with alcohol of  $C_1$  to  $C_6$ ) and fatty amines of  $C_8$  to  $C_{18}$  can be used in the amount of 0.5 to 15 percent by weight based on the base oil.

The invention will be further explained hereinbelow by the following nonlimiting examples.

#### EXAMPLE 1

A sample oil was prepared by dissolving 0.2 percent by weight of a mixture of maleated oleic acid (A) and trioctyl amine (B) as a testing rust preventive in a hydrogen-treated 100-neutral base oil, and the rust preventive and demulsibility properties of the sample oil were examined.

##### 1. Rust Preventive Property

An iron test piece, the surface of which had been cleaned, (JIS G-3310, the dimensions of which were 40 × 50 × 1 mm) was immersed in a sample oil, then the oil was drained off. The test piece was hung in a closed plastic container with 2N hydrochloric acid at the bottom thereof. After allowing the test piece to stand at 25°C for 24 hours in the HCl-H<sub>2</sub>O vapor, it was taken out. Then the oil was washed off with benzine gently so as not to disturb the surface condition of the test piece. After coating the surface of the test piece with clear lacquer, the sample was rated in comparison with the color with the standard color chart. The chart comprises 10 grades from 1 to 10, 10 being the best and 0 the poorest. Table 1 shows the formulations of the sample oils and the rust ratings.

TABLE 1

No. of samples	Formulation (% by wt.)			Rust Rating
	A	B	Base oil	
1	0.2	-	99.8	8.5
2	-	0.2	99.8	8.4
3	0.060	0.14	99.8	9.4
4	0.140	0.06	99.8	9.6
5	-	-	100.0	7.1

The samples Nos. 3 and 4 are compositions according to the present invention, and a synergistic effect is obviously recognized, as compared with those of Nos. 1 and 2.

##### 2. Demulsibility

Following the testing method for demulsibility of turbine oil, according to JIS K-2520, the demulsibility of the sample oils Nos. 3, 4 and 5 in Table 1 was examined. The results are shown in Table 2.

TABLE 2

No. of sample	Sample oil-water ratio (c.c.)		
	72-8	64-16	40-40
3	72-8-0 (5)*	64-16-0 (5)	40-40-0 (5)
4	72-8-0 (20)	64-16-0 (15)	40-40-0 (10)
5	72-8-0 (20)	64-16-0 (15)	40-40-0 (10)

\*The numerals in these columns represent ratios of oil-water-emulsion and (time (min.)) required for separating.

Similarly, 0.2 percent and 0.4 percent by weight of calcium alkylbenzene sulfonate, a typical detergent-dispersant for lubricant oils, were dissolved respectively in the above-described base oil and the demulsibility was examined on the composition having the oil-water ratio of 40-40. The results are shown in Table 3.

TABLE 3

No. of sample	Added amount of calcium alkyl benzene sulfonate (%)	
5	0.2	0.4
6	2-40-38 (60)	2-37-41 (60)

The demulsibility was also tested on the compositions which consisted of a base oil containing 4.0 percent by weight of calcium alkylbenzene sulfonate and 0.2 percent by weight of rust preventive compositions identical to the samples Nos. 3 and 4, respectively. The results are shown in Table 4.

TABLE 4

No. of Sample	Added amount (% by weight)	Demulsibility
7	A 0.06 B 0.14	40-40-0 (20)
8	A 0.14 B 0.06	40-40-0 (35)

As shown in Tables 2 to 4, the composition of this invention does not improve the demulsibility of a base oil

greatly when it is used alone, but when it is added into oil which also contains a metal salt type dispersant, a remarkable improvement of demulsibility is achieved as compared with an oil which contains only a metal salt type dispersant.

EXAMPLE 2

The rust preventive property and the demulsibility were examined for the following various rust preventive compositions.

1. Samples tested (Table 5)

a. Blended Composition

TABLE 5

No. of sample	Polycarboxylic acid or its partial ester 90% by wt.	Aliphatic tertiary amine 10% by wt.
1	Diisobutylene succinic acid	Hexyldipentyl amine
2	Diisobutylene succinic acid	Trioctyl amine
3	Tetraisopropylene succinic acid	Trihexyl amine
4	Isopropylene succinic acid	Octyldiisobutyl amine
5	Isobutylene succinic acid	Ethyldihexyl amine
6	Tetraisobutylene succinic acid	Methyldioctyl amine
7	Octaisopropylene succinic acid	Tridodecyl amine
8	Maleated oleic acid	Trioctadecyl amine
9	Maleated methyl oleate	Decyldiisopropyl amine
10	Dimer acid of C <sub>36</sub> (85% dimer acid) 70% by wt.	Octadecyldimethyl amine
11	Diisobutylene succinic acid	Methyldioctyl amine
12	Tetraisopropylene succinic acid	Octyldiisobutyl amine
13	Tetraisobutylene succinic acid	Tridodecyl amine
14	Maleated methyl oleate 50% by wt.	Trioctyl amine
15	Isopropylene succinic acid	Trihexyl amine
16	Isobutylene succinic acid	Octadecyldimethyl amine
17	Octaisopropylene succinic acid	Tridodecyl amine
18	Diisobutylene succinic acid	Ethyldihexyl amine
19	Maleated oleic acid	Trioctyl amine

30% by wt.

70% by wt.

20	Tetraisobutylene succinic acid	Trihexyl amine
21	Isopropylene succinic acid	Methyldioctyl amine
22	Maleated oleic acid	Octyldiisobutyl amine
23	Dimer acid of C <sub>36</sub> (85% dimer acid) 10% by wt.	hexyldipentyl amine
24	Diisobutylene succinic acid	90% by wt. hexyldipentyl amine
25	Diisobutylene succinic acid	Trioctyl amine
26	Tetraisopropylene succinic acid	Trihexyl amine
27	Isopropylene succinic acid	Octyldiisobutyl amine
28	Isobutylene succinic acid	Ethyldihexyl amine
29	Tetraisobutylene succinic acid	Methyldioctyl amine
30	Octaisopropylene succinic acid	Tridodecyl amine
31	Maleated oleic acid	Trioctadecyl amine
32	Maleated methyl oleate	Decyldiisopropyl amine
33	Dimer acid of C <sub>36</sub> (85% dimer acid)	Octadecyldimethyl amine

b. Single Composition

- 34 Diisobutylene succinic acid
- 35 Tetraisopropylene succinic acid
- 36 Maleated methyl oleate
- 37 Trioctyl amine
- 38 Ethyldihexyl amine
- 39 Tridodecyl amine
- 40 Calcium alkylbenzene sulfonate (which will be abbreviated as Ca-Sulfonate herein-after)

2. Testing Method

a. Rust Preventive Property

An iron test piece, the surface of which had been cleaned (JIS G-3310, the dimensions of which were 40 × 50 × 1 mm), was immersed in a sample oil, then the oil was drained off. The test piece was hung in a closed plastic testing box having 2N hydrochloric acid at the bottom thereof. Then it was allowed to stand at 25°C for 24 hours in the HCl-H<sub>2</sub>O vapor and taken out. The oil was washed off with benzine gently so as not to disturb the surface condition of the test piece. After coating the surface of the test piece with clear lacquer, the sample was rated comparing the color with the standard color chart, 10 being the best and 0 being the poorest.

The sample oil was prepared by dissolving 0.2 percent by weight of each of the above-described samples Nos. 1 to 40 in hydrogen-treated 100 neutral base oil. (The words of "base oil" hereinafter mean the said hydrogen-treated 100 neutral base oil unless otherwise specified).

b. Demulsibility

The test was performed according to "JIS K-2520, the testing method for demulsibility of turbine oil". In describing the data, the number of minutes required for separating was shown as to the samples which completely separated within 75 minutes, while the samples which still contained the emulsified part after 75 minutes past were described as "not separated".

The above-described samples Nos. 1 to 40 were employed and the tests were performed with the above-described base oil as well as with the same oil containing 4.0 percent by weight of calcium alkylbenzene sulfonate added thereto.

TABLE 6

No. of sample	Rust Ratings	Demulsibility H-treated 100 neutral base oil	The same oil containing Ca-sulfonate
1	9.7	16	40
2	9.7	18	39
3	9.4	20	44
4	9.6	18	40
5	9.2	13	34
6	9.8	20	41
7	9.5	15	35
8	9.0	21	42
9	9.4	17	37
10	9.3	19	39
11	9.6	17	33
12	9.2	20	43
13	9.2	13	32
14	9.5	16	30
15	9.4	16	36
16	8.8	9	23
17	9.4	12	28
18	9.4	11	32
19	9.3	14	31
20	9.4	12	28
21	9.2	15	29

22	9.5	9	19
23	9.1	11	21
24	9.3	7	15
25	8.6	9	20
26	9.0	6	18
27	9.2	10	25
28	9.4	11	23
29	9.5	12	26
30	8.8	12	30
31	9.1	15	33
32	8.6	7	29
33	8.5	11	34
34	9.4	13	Not separated
35	9.2	8	72
36	9.0	10	Not separated
37	8.5	8	28
38	8.6	4	22
39	8.3	4	20
40	8.0	Not separated	Not separated
Basic oil	7.1	6	Not separated

From the test results shown in Table 6, it is recognized that the tertiary amines (Nos. 37, 38 and 39) have the rust preventive property to some degree compared with the base oil when used alone, but, when they are compounded with polycarboxylic acids or their partially esterified ones, the rust preventive property is improved to a greater extent.

As to the demulsibility, the base oil containing only 0.2 percent by weight of Ca-sulfonate dissolved therein leaves a considerable emulsion layer even 75 minutes after the mixing, while the demulsibility is a little improved by adding carboxylic acid or its partial ester and it is greatly improved by adding further aliphatic tertiary amine.

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

1. An oil composition consisting essentially of a hydrocarbon lubricating oil or fuel oil containing from about 0.001 to 3 percent by weight of an oil-soluble rust preventive composition consisting essentially of

- A. material selected from the group consisting of (1) alkenyl succinic acids having three to 32 carbon atoms in the alkenyl substituent, (2) unsaturated monoenoic, dienoic or trienoic fatty acid-maleic anhydride addition products having 16 to 22 carbon atoms and their lower alkanol esters, (3) dimers of polyunsaturated dienoic and trienoic

- fatty acids having six to 22 carbon atoms, and  
 B. an aliphatic tertiary amine having three hydrocarbon groups, each of which has from one to 20 carbon atoms and at least one of which has six to 20 carbon atoms,

the weight ratio of (A) to (B) being in the range of 95:5 to 5:95 and

- C. an alkaline earth metal alkyl benzene sulfonate as a dispersant, and

10 the balance of the composition is a hydrocarbon lubricating or fuel oil, said dispersant being present in an amount less than about 15 percent by weight of said oil composition.

2. The oil composition according to claim 1, in which said material is the addition product of maleic anhydride and a monoenoic fatty carboxylic acid having 16 to 22 carbon atoms.

3. The oil composition according to claim 1, in which said material is diisobutylene succinic acid or tetraisopropylene succinic acid.

4. An oil soluble rust preventive composition having good demulsibility, consisting essentially of

- A. the addition product of maleic anhydride and a monoenoic fatty carboxylic acid having 16 to 22 carbon atoms, and

- B. an aliphatic tertiary amine having three hydrocarbon groups each of which has from one to 20 carbon atoms

and at least one of which has six to 20 carbon atoms, the weight ratio of (A) to (B) being in the range of 95:5 to 5:95.

5. An oil composition consisting essentially of a hydrocarbon lubricating oil or fuel oil containing from about 0.001 to 3 percent by weight of an oil-soluble rust preventive composition consisting essentially of

- A. the addition product of maleic anhydride and a monoenoic fatty carboxylic acid having 16 to 22 carbon atoms, and

- B. an aliphatic tertiary amine having three hydrocarbon groups, each of which has from one to 20 carbon atoms, and at least one of which has six to 20 carbon atoms,

the weight ratio of (A) to (B) being in the range of 95:5 to 5:95, and

the balance of the composition is a hydrocarbon lubricating oil or fuel oil.

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