

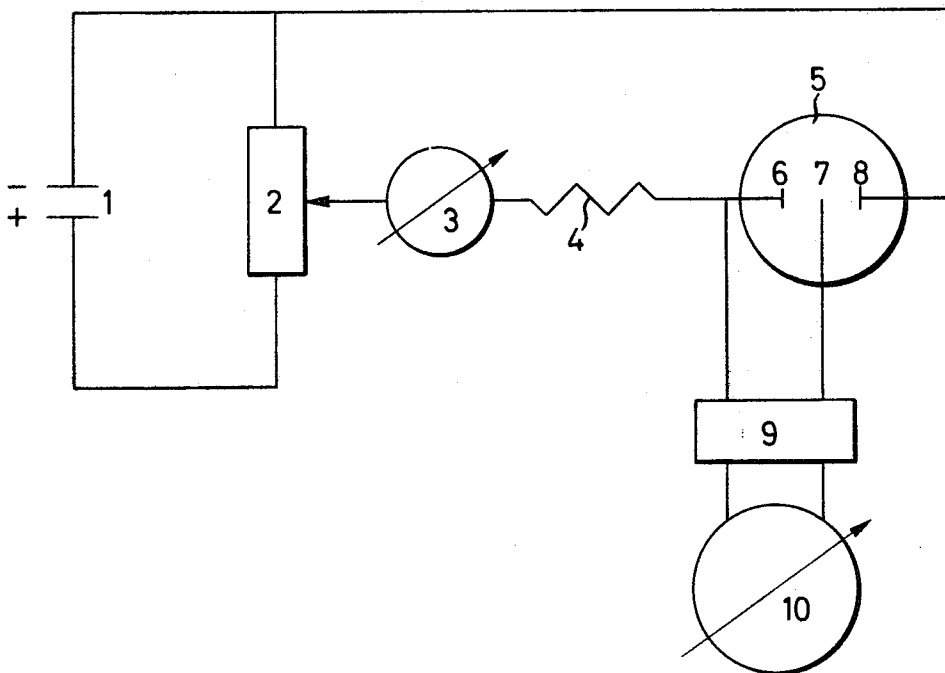
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CORROSION INHIBITED FUEL OILS

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INVENTORS

ADOLF MAY
HEINZ LIEBSCHER
HEINZ MÜLLER
ENGELBERT KREMPLE

BY *Curtis, Morris & Safford*
ATTORNEYS

1

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CORROSION INHIBITED FUEL OILS

Adolf May, Hofheim, Taunus, Heinz Liebscher, Schwalbach, Taunus, and Heinz Müller and Engelbert Krempel, Burgkirchen (Alz), Germany, assignors to Farbwerke Hoechst Aktiengesellschaft vormals Meister Lucius & Bruning, Frankfurt am Main, Germany, a corporation of Germany

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Claims priority, application Germany, Oct. 7, 1966, F 50,385

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U.S. Cl. 44—66

4 Claims

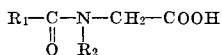
ABSTRACT OF THE DISCLOSURE

Corrosion inhibiting additives for fuel oils containing oil- and water-soluble salts or non-stoichiometric mixture of

- (a) primary, secondary or tertiary aliphatic amines containing 3 to 8 carbon atoms, and
- (b) mixtures of 20 to 80 parts by weight of carboxylic acids of the general formula



in which R represents a straight chain or branched alkyl radical containing 3 to 14 carbon atoms, and 80 to 20 parts by weight of amido-carboxylic acids of the formula



in which R₁ represents a saturated or unsaturated alkyl radical containing 11 to 17 carbon atoms, and R₂ represents the methyl or ethyl group.

This application is a continuation-in-part application of our copending patent application Ser. No. 672,463, filed Oct. 3, 1967, and now abandoned and relates to liquid fuel oils, in particular to oily hydrocarbons such, for example, as bunker oil, fuel oil, diesel oil, and the like, which contain organic compounds as corrosion inhibitors for preventing corrosion damages on storage vessels and transportation means caused by the presence of water.

During the transportation and storage of liquid fuels, in particular of oily hydrocarbons, the unavoidable presence of varying amounts of water leads to very disagreeable corrosions of the surface of the metals which come into contact with the liquid fuels. Such corrosions not only damage the containers but they also cause contamination of the fuels.

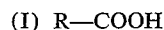
Oil-soluble organic compounds have hitherto been added to the fuels in order to prevent such corrosion. From U.S. Pats. 2,330,524, 2,433,243, 2,736,658 and 2,976,179 it is known to use mono- or polyamine salts of carboxylic acids as corrosion inhibitors. Furthermore, in U.S. Pat. 2,790,779 the use of amido-carboxylic acids or of their salts as corrosion inhibitors in liquid fuels has been proposed. However, these products do not satisfy the high requirements of the practice regarding corrosion inhibition. The oil- and water-soluble amine salts of the last-mentioned amido-carboxylic acids in addition have the disadvantage of forming in the liquid fuels, if low amounts of water are present, pasty emulsion flocks which cause serious troubles, for example, by clogging burners and filters in heating devices.

Now, we have found that a considerably better corrosion inhibition during storage and transportation of liquid fuel oils can be obtained while simultaneously prevent-

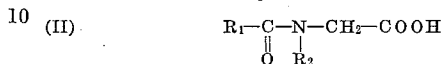
2

ing the formation of pasty emulsion flocks by adding to the liquid fuel oils, as corrosion inhibitors, salts or non-stoichiometrical mixtures of

- (a) primary, secondary or tertiary aliphatic amines containing 3 to 8 carbon atoms, and
- (b) mixtures of carboxylic acids of the Formula I



with amido-carboxylic acids of the Formula II



In the above general formulae, R represents a straight chain or branched alkyl radical containing about 3 to 14 carbon atoms, preferably 6 to 10 carbon atoms, R₁ represents a saturated or unsaturated aliphatic hydrocarbon radical containing 11 to 17 carbon atoms, and R₂ represents an alkyl radical containing 1 or 2 carbon atoms. The mixing ratio of both acid components should be in the range of 1:4 to 4:1 parts by weight.

As primary, secondary or tertiary aliphatic amines, there may be used especially alkyl- or alkenyl-amines containing 3 to 8 carbon atoms, as well as cycloalkyl-amines containing 5 to 7 carbon atoms in the ring. As preferred amines there may be mentioned, for example, isopropylamine, butylamine, hexylamine, triethylamine, iso-octylamine, allylamine, cyclohexylamine, N-methyl-cyclohexylamine and N,N-dimethyl-cyclohexylamine.

As acid components of the general Formula I, there may be used alkane-carboxylic acids containing 4 to 15 carbon atoms, suitably those containing 6 to 15 carbon atoms. There may be mentioned, for example, butyric acid, caprylic acid, caproic acid, capric acid, coconut oil fatty acid, as well as mixtures of fatty acids as those contained, for example in the coconut oil first run fatty acid or those contained in mixtures of fatty acids having unbranched and branched alkyl radicals of about 3 to 12 carbon atoms and obtained by the oxidation of paraffin hydrocarbons.

As suitable acid components of the Formula II, there may be mentioned, for example, N-oleyl-N-methyl-aminoacetic acid, N-lauroyl-N-methyl-aminoacetic acid, N-myristoyl-N-methyl-aminoacetic acid, N-cocosacyl-N-methyl-aminoacetic acid, N-stearoyl-N-methyl-aminoacetic acid, N-palmitoyl-N-methyl-aminoacetic acid and N-lauroyl-N-ethyl-aminoacetic acid.

The acids of the Formula I are used in admixture with the acids of the Formula II. In this mixture, the proportion of one of the two acid components must amount to at least 20% by weight. In particular, there are used mixtures of both acids at a ratio of 1:3 to 3:1.

In the corrosion inhibitors of the present invention, the amine component (a), on the one hand, and the two acid components (b), on the other hand, may be used in the stoichiometrical quantitative ratio required for the formation of neutral salts. However, there may also be used a small excess of the acid components or suitably, an excess of amine component. In general, about 0.9 to 2 gram-equivalents of amine component are used per one gram-equivalent of acid components. Preferably, mixtures of components (a) and (b) are used as corrosion inhibitors which contain an excess of amine, referred to the equivalent weights.

In the corrosion inhibitors of the present invention, care is to be taken by a suitable choice of the components that the products are soluble in oil as well as in water. In order to obtain oil- and water-solubility to the same extent, it is suitable, for example, if acid components are used which contain hydrocarbon radicals of about 14 or more carbon atoms, to employ as basic component, hydrophilic amines having a relatively short chain, for

example alkylamine. On the other hand, it is suitable, if acid components with shorter hydrocarbon radicals are used to employ preferably an amine which has more hydrophobic properties, for example N-methylcyclohexylamine.

The quantity of corrosion inhibitors of the present invention to be added to the liquid fuels may vary within certain limits, depending on the requirements. In general, the corrosion inhibitors are added in quantities of about 0.0001 to 0.5% by weight, referred to the liquid fuels; preferably, 0.001 to 0.05% by weight of corrosion inhibitors are used.

An important and surprising advantage in the use of the corrosion inhibitors of the present invention in liquid fuels, besides the excellent corrosion inhibiting action, is the fact that the risk of the aforementioned, disadvantageous formation of pasty emulsion flocks with small amounts of water is excluded or at least considerably reduced.

The excellent corrosion inhibiting action of the additives of the present invention, consisting of amines and mixtures of acids of the Formulae I and II, is shown in the following table listing the products as Examples 1-9. A comparison of these results with those obtained with the salts of the individual acid components listed under Nos. 10 and 11 and with that of the known corrosion inhibitors listed under Nos. 12 to 19, shows the superior action of the corrosion inhibitors of the present invention over the known corrosion inhibitors. As regards the products used for comparison, the number of the patent in which the respective product has been described is indicated in brackets. As No. 20, the corrosion of fuel oil alone was tested.

CORROSION INHIBITION IN FUEL OIL

No.	Additive dissolved in fuel oil EL	Quantity added (percent by weight)	Evaluation
1.....	Cyclohexylamine salt of a mixture of 75 parts by weight of N-myristoyl-N-methylamino acetic acid and 25 parts by weight of synthetic first run fatty acid. ¹	0.03 0.05	+ +
2.....	Mixture of 29.6 parts by weight of N-oleoyl-N-methylamino acetic acid +29.6 parts by weight isononanoic acid +40.8 parts by weight of cyclohexylamine, that are 1.5 gram-equivalents of amine per 1 gram-equivalent of acids.	0.03 0.05	+ +
3.....	Cyclohexylamine salt of a mixture of 25 parts by weight of N-cocosacyl-N-methylamino acetic acid and 75 parts by weight of a natural first run fatty acid. ²	0.03 0.05	- +
4.....	Mixture of 34.9 parts by weight of N-oleoyl-N-methylamino acetic acid +34.9 parts by weight of a synthetic first run fatty acid ¹ +30.2 parts by weight of butylamine, that are 1.2 gram-equivalents of amine per 1 gram-equivalent of acids.	0.03 0.05	+ +
5.....	Mixture of 22.5 parts by weight of N-lauroyl-N-methylamino acetic acid +22.5 parts by weight of synthetic first run fatty acid ¹ +55 parts by weight of N-methyl-cyclohexylamine, that are 2 gram-equivalent of amine per 1 gram-equivalent of acids.	0.03 0.05	+ +
6.....	N,N-dimethyl-cyclohexylamine salt of a mixture of 50 parts by weight N-oleoyl-N-methylamino acetic acid and 50 parts by weight of synthetic first run fatty acid. ²	0.03 0.05	- +
7.....	n-Hexylamine salt of a mixture of 50 parts by weight N-oleoyl-N-methylamino acetic acid and 50 parts by weight of synthetic first run fatty acid. ¹	0.03 0.05	- +
8.....	Triethylamine salt of a mixture of 50 parts by weight N-oleoyl-N-methylamino acetic acid and 50 parts by weight of synthetic first run fatty acid. ¹	0.03 0.05	- +
9.....	Allylamine salt of a mixture of 50 parts by weight N-palmitoyl-N-methylamino acetic acid and 50 parts by weight of synthetic first run fatty acid. ¹	0.03 0.05	+ +
10....	Butylamine salt of synthetic first run fatty acid. ¹	0.075 0.1	- +

CORROSION INHIBITION IN FUEL OIL

No.	Additive dissolved in fuel oil EL	Quantity added (percent by weight)	Evaluation
11....	Cyclohexylamine salt of N-oleoyl-N-methylamino acetic acid.	0.05 0.075	- +
12....	Cyclohexylamine salt of an aliphatic carboxylic acid having a mean molecular weight of 170 and obtained by petroleum oxidation. (U.S. Patent No. 2,330,534, Claims 2 and 5.)	0.075 0.1	- +
13....	2-Ethylhexylamine salt of synthetic first run fatty acid. ¹ (U.S. Patent No. 2,330,524, Claims 4 and 5.)	0.1	-
14....	Coconut fat amine salt of oleic acid. (U.S. Patent No. 2,433,243, column 3, line 3.)	0.1	-
15....	Tallow fat propylene-diamine salt of oleic acid (dioleate). (U.S. Patent No. 2,736,658, Example 1.)	0.1	-
16....	Coconut fat-amine salt of N-stearoyl-N-methylamino acetic acid. (U.S. Patent No. 2,700,779.)	0.1	-
17....	Tallow fat-propylene diamine salt of sebacic acid. (U.S. Patent No. 2,939,842, col. 1, line 67 and col. 2, line 29.)	0.1	-
18....	Tallow fat-propylene-diamine salt of dilinolic acid. (U.S. Patent No. 2,939,842, col. 1, line 67 and col. 2, line 41— "Duomeen T" and "Empol 1022".)	0.1	-
19....	Triethylene-tetramine salt of oleic acid (Tetraoleate). (U.S. Patent No. 2,976,179, Example 1, Composition D.)	0.1	-
20....	No addition.....	-	-

¹ Mixture of acids obtained upon oxidation of paraffin and containing alkane-carboxylic acids with straight chain and branched alkyl chains, essentially consisting of the following carboxylic acids in the proportions indicated below:

Carboxylic acids with—	Proportion in percent by weight
4 carbon atoms.....	1
5 carbon atoms.....	6.1
6 carbon atoms.....	14.0
7 carbon atoms.....	22.6
8 carbon atoms.....	23.2
9 carbon atoms.....	17.1
10 carbon atoms.....	9.8
11 carbon atoms.....	4.5
12 carbon atoms.....	1.7

² Mixture of carboxylic acids originating from natural fats, essentially consisting of the following carboxylic acids in the proportions indicated below:

Carboxylic acids with—	Proportion in percent by weight
6 carbon atoms.....	2
8 carbon atoms.....	44
10 carbon atoms.....	35
12 carbon atoms.....	19

The not-inhibited fuel oil (Example 20) and the inhibited fuel oils (Examples 1 to 19) were tested electrochemically according to the galvanostatic principle (cf. the works by H. Kaesche, "Die Korrosion de Metalle," Springer-Verlag Berlin-Heidelberg-New York, 1966, pages 44 et seq., and by K. Risch "Verfahren zur Prüfung eines Inhibitors gegen Chlorid-Korrosion an unlegiertem Stahl" in the Journal "Werkstoffe und Korrosion" 19 (1968), H 9, pages 756 to 701) in the following manner:

(I) DESCRIPTION OF THE MEASUREMENT

A degreased and clean polished sample of steel St 1303 as the measuring electrode, a platinum electrode as the counter-electrode and an electrode of saturated calomel as the comparison electrode are introduced into an electrolyte-containing glass beaker in a measuring cell. The saturated calomel electrode has a potential with reference to the standard hydrogen electrode which is by 250 mv. positive. As can be seen from the diagram (FIG. 1), the counter-electrode and the measuring electrode are connected in a closed circuit and the potential between measuring and comparison electrode is recorded by means of a compensation recorder which is connected to the

5

measuring cell over an amplifier having an input impedance of more than 10^{12} ohms.

In the diagram, the indicated numerals means:

- (1) direct current source (anode battery, 50 v. output)
- (2) variable potentiometer ($10^4\Omega$)
- (3) amperemeter
- (4) resistor ($10^6\Omega$)
- (5) measuring cell
- (6) measuring electrode (sample of steel St 1303)
- (7) comparison electrode (saturated calomel electrode)
- (8) counter-electrode (platinum)
- (9) "Knick"-amplifier (input impedance $10^{12}\Omega$)
- (10) compensation recorder

In the first part of the measuring procedure, the rest potential is allowed to establish, i.e. the system is left staying without any influence from outside, only the building up of the potential between the measuring and the comparison electrode is followed. Thus, for allowing the rest potential to establish, the system is left standing for about 15 hours. In the second part of the measuring procedure, the measuring electrode is subjected to a current load: the voltage is increased over a potentiometer connected to a 50 v. battery until the measuring electrode is loaded with a current density of $20/\mu\text{A./cm.}^2$. This current density is maintained during the measurements. The course of the potential between measuring and comparison electrode is recorded versus time.

(II) PREPARATION OF THE ELECTROLYTES

4 liters each of fuel oil, inhibited by the addition of 0.03 to 0.1% by weight of each of the additives to be tested together with 20 ml. of a 3% sodium chloride solution are stirred for 15 minutes by means of a laminar stirrer. The aqueous phase is allowed to settle and it is then withdrawn and introduced as electrolyte into the measuring cell.

(III) EVALUATION OF THE TESTS

The potential values which have established during the measurements are referred to the standard hydrogen electrode. The rest potential which establishes at the steel sample to be tested, is of between +100 and +400 mv. with well inhibited samples; with poorly inhibited or not inhibited steel samples, the rest potential is considerably lower.

If, in a test, a steel sample whose test potential has established, is loaded with current in the manner described above and if, under this current load, it takes a high and constant potential in the range of between 1000 and 1500 mv., then this steel sample is with security rendered sufficiently passive by the inhibitor and protected against corrosion, especially against pitting. Visual examination of the steel samples after the test will reveal that no corrosive attack has taken place.

If the steel sample under current load does not show a constant potential or shows a potential which is distinctly below 1000 mv., the steel sample can be considered as being incompletely or not at all rendered passive. Visual examination after the test will show strong surface corrosion and pitting.

In the above table, the inhibitor which at the quantity indicated provided the steel sample with a good passivity, was considered as positive (+) and the inhibitor which produced at the concentration used an incomplete or no passivity was designed as negative (-).

Where a tested corrosion inhibitor provided sufficient corrosion protection already at low quantities, the test

6

results of higher quantities were not listed. On the other hand, with products which did not provide sufficient corrosion protection, only the measurement with negative result for the highest amount in the tested range and, if this was the case, the measurement for the lowest quantity showing a positive result were listed in the table.

Furthermore, samples of fuel oil EL, to which the corrosion inhibitors indicated in the table had been added, were tested for their tendency to form emulsion flocks. For this purpose, 0.050% by weight of the inhibitor to be tested and, in addition, 0.4 ml. of water were added each time to 1 liter each of the fuel oil. The samples were then vigorously shaken twice for 5 minutes and examined visually for the presence of separated flocks.

With the corrosion inhibitors of the present invention (Examples 1 to 9), such separations did not occur and likewise not with the inhibitors Nos. 12 to 16 and 19. Emulsion flocks were observed upon addition of the inhibitors Nos. 11, 17 and 18.

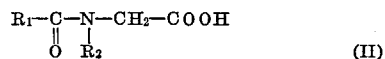
We claim:

1. Liquid fuel oils containing as corrosion inhibiting additives oil- and water-soluble salts of the following components (a) and (b) or non-stoichiometric mixtures of the following components (a) and (b), said components being:

- (a) primary, secondary or tertiary aliphatic amines containing 3 to 8 carbon atoms, and
- (b) mixtures of 20 to 80 parts by weight of carboxylic acids of the general Formula I



in which R represents a straight chain or branched alkyl radical containing 3 to 14 carbon atoms, and 80 to 20 parts by weight of amido-carboxylic acids of the Formula II



in which R₁ represents a saturated or unsaturated alkyl radical containing 11 to 17 carbon atoms, and R₂ represents the methyl or ethyl group, said non-stoichiometric mixtures having 0.9 to 2 gram-equivalents of the amine component per 1 gram-equivalent of the acid components.

2. Liquid fuel oils as claimed in claim 1, which contain 0.0001 to 0.5% by weight of the said additives.
3. Liquid fuel oils as claimed in claim 1, which contain 0.001 to 0.05% by weight of the said additives.
4. An improved corrosion inhibitor for fuel oils having the composition recited in claim 1.

References Cited

UNITED STATES PATENTS

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2,433,243	12/1947	Smith et al.	44-66
2,699,427	1/1955	Smith et al.	44-71 X
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PATRICK P. GARVIN, Primary Examiner

W. J. SHINE, Assistant Examiner

U.S. Cl. X.R.

44-71; 252-392