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3,438,898

NON-ASH FORMING ADDITIVE FOR LUBRICANTS

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10 Claims

ABSTRACT OF THE DISCLOSURE

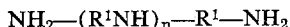
A non-ash forming additive suitable for use in lubricating oil compositions is obtained by reacting certain amides with organic sulfonic acids to form oil-soluble salts. These salts are particularly useful in lubricating compositions as rust inhibitors and dispersants.

Conventional rust inhibitors contain metals and consequently form ash deposits in the engine when added to motor oil or when added to oil which is mixed with gasoline in two-stroke engines form deposits which foul spark plugs. These deposits therefore contribute to preignition and overall lower engine performance and engine operating efficiency.

It has now been discovered in accordance with the present invention that a non-ash forming additive, useful as a rust inhibitor and dispersant in lubricating oil, can be obtained by reacting (1) an amide and (2) an organic sulfonic acid to form an oil-soluble salt.

Suitable amides for use in preparing the additive of the present invention include amides of fatty acids and polyalkylene polyamines. Fatty acids useful in preparing the amides are aliphatic fatty acids of the general formula RCOOH wherein R is a C_4 to C_{30} aliphatic radical, neo acids having from 8–22 carbon atoms, dimerized or trimerized fatty acids or mixtures thereof. Aliphatic fatty acids include the saturated fatty acids, such as, lauric, caproic, caprylic, myristic, palmitic, stearic, arachidic acids, as well as the corresponding iso-fatty acids, such as iso-stearic, iso-caprylic acids and the branched-chain fatty acids such as α,α -dimethylcaproic acid and other neo acids. Examples of suitable unsaturated fatty acids are oleic, linoleic, linolenic and eleostearic acids. Representative dimer and trimer fatty acids are the dimerized linoleic, linolenic, 8,12-eicosadiene-1,20-dioic acid, etc. Mixtures of acids may also be used, such as mixtures of iso-fatty acids and straight-chained fatty acids or a mixture of monobasic, dimerized and trimerized fatty acids, e.g., the acid designated by the tradename Empol 1014. Prefrom 12 to 30 carbon atoms, i.e., where R is a C_{12} to C_{30} fatty acids include the saturated fatty acids having alkyl radical, such as, lauric, stearic, iso-stearic and palmitic acids; particularly preferred is iso-stearic acid. Other preferred acids are those which are available commercially and are a mixture of, for example, C_{10-14} acids or a mixture of straight-chain acid and iso acid.

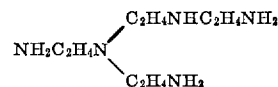
Polyamines useful in preparing the amide include those which are predominantly of the general formula



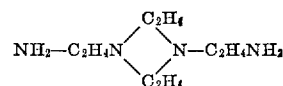
wherein R^1 is a C_{2-4} alkylene radical, and n is zero or an integer from 1 to 8 or higher. The amide therefore may contain $n+2$ amide groups, but generally contains only one or two such groups.

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Particularly preferred polyalkylene polyamines of the above formula are those wherein R^1 is either ethylene or propylene, for example, diethylene triamine, triethylene tetramine, tetraethylene pentamine, pentaethylene hexamine, dipropylene triamine, tripropylene tetramine, tetrapropyl pentamine, and the like. The polyamines may contain from 10–30% by weight of branched and cyclic structures such as:



and



which also form amides with fatty acids. Accordingly, the invention is intended to include amides formed from these structures.

The polyalkylene polyamine may be amidized with the fatty acid according to art recognized methods, for example, one to four moles of fatty acid are reacted with one mole of polyalkylene polyamine at the proper elevated temperature. Assuming one mole of amine is amidized, the amide will contain 1 amide group per mole of acid reacted therewith. Preferably, the amide is a diamide.

Other suitable amides for use in preparing the additive of the present invention include reaction products prepared by the condensation of an amide of the type just described with from one to four moles each of an aldehyde and a C_{6-18} alkylphenol. A specific example of an amide of this type is the condensation product of one mole of the diisostearamide of tetraethylene pentamine with 1.5 moles each of formaldehyde and dodecylphenol. Other suitable phenols which may be used to form the condensation product include laurylphenol, decylphenol, octylphenol, octadecylphenol; other suitable aldehydes include paraformaldehyde, benzaldehyde, furfural, acetaldehyde, etc., or mixtures thereof.

The organic sulfonic acids are either petroleum sulfonic acids or synthetic sulfonic acids and are of the general formula $\text{R}^2(\text{SO}_3\text{H})_n$, wherein R^2 is an organic radical, i.e., aliphatic, cycloaliphatic, or aromatic radical and n is an integer. As used herein the term "petroleum sulfonic acid" is intended to include all sulfonic acids which are derived directly from petroleum products, such as lubricating oils. Accordingly, R^2 may represent a hydrocarbon radical derived from petroleum base stock, e.g., a mineral lubricating oil base stock. Lubricating oils which may be used to obtain suitable petroleum sulfonic acids include a naphthenic base, paraffin base, and mixed base lubricating oils, and lubricating oils derived from coal products and synthetic oils, e.g., alkylene polymers such as polyethylene, polypropylene and polybutylene. Particularly preferred, are the neutral lubricating oils having a molecular weight from 250 to 1000 or higher, and a viscosity of 60 to 2000 SSU at 100°F ., and bright stock. Bright stock is a viscous product refined by solvent extraction, hydrotreated, and then dewaxed. The term "synthetic sulfonic acid" includes all organic sulfonic acids which are not petroleum sulfonic acids.

The petroleum sulfonic acids are conveniently prepared by sulfonation of the lubricating oil or other petroleum products with a sulfonating agent, such as sulfur trioxide, chlorosulfonic acid, or oleum (fuming sulfuric). Fuming sulfuric is preferred. Although the petroleum sulfonic acids are referred to as being derived from hydrocarbons, the acids could contain substituent groups attached to the hydrocarbon radical, such as nitrogen, sulfur, oxygen or chlorine, that may be present in the petroleum product, or the acids could be formed from synthetic lubricants which contain elements other than carbon and hydrogen, such as polymers of alkylene oxide.

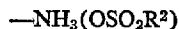
Synthetic sulfonic acids which may be used to prepare the salts of the present invention can be of the cyclic or aliphatic type, such as those described in U.S. Patent No. 3,250,710 and Canadian Patent No. 733,142. Thus, the acids may be of the general formula $R_a^3-T(SO_3H)_b$ or $R^4(SO_3H)_b$, wherein a and b are integers of at least one; R^3 and R^4 are aliphatic radicals such as alkyl, alkenyl, alkoxy, alkoxyalkyl, carboalkoxyalkyl, etc.; T is a cyclic nucleus such as benzene, naphthalene, anthracene, phenanthrene, diphenylene oxide, thianthrene, phenothioxine, diphenylene sulfide, phenothiazine, diphenyl oxide, diphenyl sulfide, diphenylamine, cyclohexene, decahydronaphthalene, cyclopentane, etc.; R^3-T and R^4 contain at least about 15 carbon atoms. Specific examples of R^4 are saturated and unsaturated paraffin wax, and polyolefins, including polymerized C_2 , C_3 , C_4 , C_5 , C_6 , etc. R^3 , R^4 and T in the above formulas can also contain other organic or inorganic substituents in addition to those given above such as, hydroxy, mercapto, halogen, nitroso, nitro, amino, sulfides, disulfides, etc.

Specific examples of oil-soluble synthetic sulfonic acids include mono- and poly-wax substituted sulfonic and poly-sulfonic acids of, e.g., naphthalene phenol, diphenyl ether, naphthalene disulfide, diphenylamine, thiophene, alpha-chloronaphthalene, etc.; other substituted sulfonic acids such as cetyl chlorobenzene sulfonic acids, cetylphenol mono-sulfide sulfonic acids, cetoxy caprylbenzene sulfonic acids, dicetyl thianthrene disulfide acids, dilauryl betanaphthyl sulfonic acids, dicapryl nitronaphthalene sulfonic acids, and alkaryl sulfonic acids such as dodecyl benzene "bottoms" sulfonic acids (i.e., those acids derived from benzene which have been alkylated with propylene tetramers or isobutene trimers to introduce 1, 2, 3, or more branched-chain C_{12} substituents on the benzene ring. Dodecyl benzene "bottoms," principally mixtures of mono- and di-dodecyl benzenes, are available as by-products from the manufacture of household detergents) and mono- and poly-tridecyl benzenes; aliphatic sulfonic acids such as paraffin wax sulfonic acid, unsaturated paraffin wax sulfonic acids, hydroxy-substituted paraffin wax sulfonic acids, hexapropylene sulfonic acids, tetraamylene sulfonic acids, polyisobutene sulfonic acids, chloro-substituted paraffin wax sulfonic acids, nitro-paraffin wax sulfonic acids, etc.; cycloaliphatic sulfonic acids such as petroleum naphthene sulfonic acids, cetyl cyclopentyl sulfonic acids, lauryl cyclohexyl sulfonic acids, bis(diisobutyl)cyclohexyl sulfonic acids, mono- and or poly-wax substituted cyclohexyl sulfonic acids, etc.

The additive (mono or polysulfonic acid salt) is conveniently prepared by reacting from 1 to 10 moles of sulfonic acid with 1 mole of amide at a temperature of from 0° to 100° C. and at atmospheric pressure under a blanket of nitrogen. Accordingly, the generic formula for the salts may be represented by the formula:



wherein R^2 is an organic radical selected from R^3 and R^4 and petroleum derivatives, A is an amide of a fatty acid and polyalkylene polyamine of the type described herein having x number of amino groups of the amide associated with x moles of R^2SO_2OH to form x number of



groups.

Lubricating oils to which the additive may be added include a wide variety of mineral lubricating oils, such as LVI, MVI and HVI mineral lubricating oils obtained from naphthenic, paraffinic and mixed base crudes. Particularly suitable are the lubricating oils which are used as base oil for SAE motor oils, e.g., SAE 10 to SAE 50 weight motor oils. In addition to mineral lubricating oil, the additive may be incorporated into synthetic lubricating oils such as polymerized olefins, esters and ethers, or the additive may be incorporated into a mixture of natural and synthetic oils.

The additive described herein can be used in oils in amounts of from 0.01% to 40% by weight, preferably 0.1% to 20%; more preferably 1% to 15%.

The following examples are given for purposes of illustrating the invention and are not intended to limit the invention in any way to the particular compounds, their method of preparation, or composition containing them, described therein.

EXAMPLE I

This example illustrates a method of obtaining the amide reactant of the additive.

2 moles of iso-stearic acid and 1 mole of tetraethylene pentamine were reacted in a reaction vessel at $170-210^\circ$ C. The resulting product was the di-isostearamide of tetraethylene pentamine designated for convenience as I(a).

Following the above procedure other amides were prepared and are listed below:

- I(b) isostearamide of tetraethylene pentamine
- I(c) dilauramide of tetraethylene pentamine
- I(d) stearamide of ethylene diamine
- I(e) dipalmitamide of diethylene triamine
- I(f) di-isostearamide of dipropylene triamine
- I(g) di-isostearamide of tetrapropylene pentamine
- I(h) the condensation product of 1 mole of I(a) with 1.5 moles each of formaldehyde and dodecylphenol.

EXAMPLE II

This example illustrates a method of preparing the petroleum sulfonic acid reactant of the additive.

A 3-liter, 3-necked, round-bottom flask equipped with stirrer, dropping funnel, thermometer and vent was charged with 1 kg. West Texas Ellenburger bright stock having the following properties:

Viscosity at:	
100° F., SSU	2812
210° F., SSU	116.1
Viscosity index	99
Sulfur, percent by wt.	0.07
Molecular weight	770
Total aromatics	40
Non-aromatics	28.1

The bright stock was stirred vigorously and 105% by wt. sulfuric acid (200 g., 20% by wt. oleum) was added dropwise during one hour; the temperature rose from 25° C. to 45° C. The mixture was stirred an additional 30 minutes and then 15 ml. of water was added with stirring. The mixture was diluted with a volume of hexane (1132 ml.) equal to the volume of bright stock charged and allowed to stand overnight. A small amount of spent acid (86 ml., 149 g.) separated which was dark brown, quite fluid and easily handled. The hexane layer was washed with a solution of 500 ml. water and 750 ml. methanol. The clear yellow lower layer which separated was discarded and the upper layer was shaken with 750 ml. absolute methanol. Two phases formed and separated completely within 2 hours. The top layer was discarded and the lower layer which contained petroleum sulfonic acid, was stripped of solvent. The residue was petroleum sulfonic acid, designated for convenience as II(a), having an average molecular weight of about 850 and an acid number of 5.0.

Other petroleum sulfonic acids are prepared according to the foregoing procedure using different lubricating oils in place of bright stock which are listed below:

II(b)—Prepared from a neutral oil having a viscosity of 1250 SSU at 100° F. and 82.5 SSU at 210° F.; a flash COC of 480 and a VI (viscosity index) of 55.

II(c)—Prepared from a neutral oil having a viscosity of 1080 SSU at 100° F. and 71.2 SSU at 210° F.; a flash COC of 440; and a VI of 25.

II(d)—Prepared from a neutral oil having a viscosity of 106 SSU at 100° F. and 38.2 SSU at 210° F.; and a flash COC of 325° F.

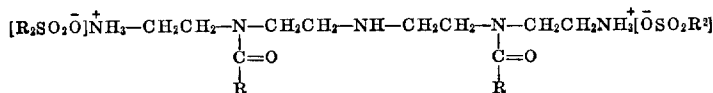
II(e)—Prepared from a neutral oil having a viscosity of 557 SSU at 100° F. and 55.8 SSU at 210° F.; a flash COC of 415; and a VI of 25.

II(f)—Prepared from a neutral oil having a viscosity of 265 SSU at 100° F. and 50 SSU at 210° F.; a flash COC of 430; and a VI of 93.

EXAMPLE III

This example illustrates the preparation of the additive of the present invention.

A mixture of (1 mole) di-isostearamide of tetraethylene pentamine I(a) was reacted at ambient temperature with (2 moles) petroleum sulfonic acid II(a) to form the di-salt designated for convenience as III(a). It contained 0.44% by wt. basic nitrogen and 1.19% by wt. total nitrogen. Although the structure of the salt is not known with absolute certainty, it is believed to have the following structure:



wherein R contains 8-22 carbon atoms, preferably derived from an isostearyl radical and R² is a hydrocarbon radical corresponding to the hydrocarbon make-up of the bright stock of Example I. Of course, the amide and salt groups in the above formula could be attached or associated with nitrogen atoms of the polyamine other than those shown; the particular nitrogen atoms in the above formula were merely chosen for purposes of illustrating the structure.

Other salts of the invention are prepared according to the procedure of Example III and are given below:

III(b)—The di-salt of di-isostearamide of tetraethylene pentamine and the petroleum sulfonic acid defined in Example II as II(b).

III(c)—The di-salt of isostearamide of tetraethylene pentamine and the petroleum sulfonic acid defined in Example II as II(a).

III(d)—The di-salt of stearamide of ethylene diamine and the petroleum sulfonic acid as defined in Example II as II(e).

III(e)—The di-salt of di-isostearamide of tetrapropylene pentamine and the petroleum sulfonic acid defined in Example II as II(d).

III(f)—The mono-salt of di-isostearamide of tetraethylene pentamine and the petroleum sulfonic acid defined in Example II as II(a).

III(g)—The di-salt of di-isostearamide of tetrapropylene and the petroleum sulfonic acid defined in Example II as II(a).

III(h)—The di-salt of amide condensation product defined in Example I as I(h) and the petroleum sulfonic acid defined in Example II as II(a).

III(i)—The mono-salt of amide condensation product defined in Example I as I(h) and the petroleum sulfonic acid defined in Example II as II(a).

III(j)—The di-salt of di-isostearamide of tetraethylene pentamine and sulfonic acids derived from dodecyl benzene "bottoms."

III(k)—The mono-salt of di-isostearamide of tetraethylene pentamine and sulfonic acids derived from dodecyl benzene "bottoms."

III(l)—The di-salt of the amide condensation product defined in Example I as I(h) and dodecyl benzene "bottoms."

Example IV

This example illustrates the formulation of lubricating oil compositions containing the additives of the type described in Example III.

Composition	Ingredients	Amount (wt. percent)
IV(a).....	III(a).....	7.88
	Mineral oil (SAE 30).....	Balance
IV(b).....	III(b).....	8.00
	Mineral oil (SAE 30).....	Balance
IV(c).....	III(a).....	7.5
	Zinc bis(octylphenyl)dithiophosphate.....	3.4
	Acryloid 150.....	0.5
	Mineral oil (SAE 30).....	Balance
IV(d).....	III(c).....	9.0
	Polyisobutylsuccinimide of tetraethylene pentamine.....	1.0
	Zinc bis(octylphenyl)dithiophosphate.....	3.0
	Acryloid 150.....	0.5
	Mineral oil (SAE 10w).....	Balance
IV(e).....	III(d).....	9.5
	Mineral oil (SAE 30).....	Balance
IV(f).....	III(e).....	5.0
	Mineral oil (SAE 10/20w).....	Balance
IV(g).....	III(f).....	8.5
	4,4'-methylene bis(3,6-di- <i>t</i> -butylphenol).....	5.0
	Acryloid 150.....	0.5
	Mineral oil (SAE 10w).....	Balance
IV(h).....	III(h).....	8.5
	Mineral oil (SAE 20).....	Balance
IV(i).....	III(i).....	9.0
	Mineral oil (SAE 30).....	Balance
IV(j).....	III(l).....	9.3
	Mineral oil (SAE 30).....	Balance

Example V

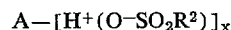
This example illustrates the effectiveness of the additive as a rust inhibitor in motor oil. Composition IV(a) was tested in a 1960 Oldsmobile engine of the type used in Sequence I of the AMA-MS Test described in ASTM Technical Publication 315, copyright 1962, under the heading "Reference Sequences I, II, III." The Oldsmobile engine, however, has been modified to induce heavy rusting conditions, e.g., increasing the blowby to about 1.5 cubic feet per minute. The test run consists of 30 cycles with each cycle consisting of ten minutes running time at 2500 r.p.m. under no load and twenty minutes down time. The oil-sump temperatures are 130°-175° F. at the beginning and the end of the running cycle, respectively. Composition IV(a) gave a 9.5 rust rating (10 rating is no rust). Thus, the additive of the present invention is an effective rust inhibitor and being non-ash forming it does not contribute to engine deposits.

The other additives of Example III when incorporated into motor oil will provide rust rating in the test comparable to that recorded for Composition IV(a).

The additive may be incorporated into a wide variety of lubricating compositions wherein rust protection is of importance and cleanliness may be a factor, such as gear oils and 2-stroke fuel/oil mixtures.

We claim as our invention:

1. A lubricating oil composition comprising a major amount of lubricating oil and from 0.1% to 20% of a compound of the formula:



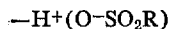
wherein A is selected from the group consisting of (1) the amide of a fatty acid of the formula RCOOH and a polyalkylene polyamine of the formula



and (2) the reaction product prepared by condensing the amide of (1) with a C₈ to C₁₈ alkylphenol and formaldehyde, wherein R is an aliphatic radical, R¹ is a C₂₋₄ alkylene radical, R² is an aliphatic, cycloaliphatic or aromatic radical, and wherein x is a number from 1 to 10 and cor-

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responds to the number of amino groups of the amide which are associated with x moles of RSO_2OH to form x number of



radicals.

2. A composition as defined in claim 1 wherein A is the amide (1), R^1 is ethylene and R^2 is a hydrocarbon radical derived from lubricating oil.

3. A composition as defined in claim 2 wherein x is 2.

4. A composition as defined in claim 2 wherein x is 1.

5. A composition as defined in claim 2 wherein R^2 is derived from a neutral mineral lubricating oil.

6. A composition as defined in claim 2 wherein R^2 is derived from bright stock.

7. A composition according to claim 1 wherein the compound is the disulfonic acid salt of di-isostearamide of tetraethylene pentamine and a sulfonic acid derived from mineral lubricating oil base stock.

8. A composition according to claim 1 wherein the compound is the mono-sulfonic acid salt of di-isosteara-

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mide of tetraethylene pentamine and a sulfonic acid derived from mineral lubricating oil base stock.

9. A composition as defined in claim 1 wherein A is the reaction product (2).

10. A composition as defined in claim 9 wherein the reaction product is prepared by condensing the di-isostearamide of tetraethylene pentamine with a C_8 to C_{18} alkylphenol and formaldehyde.

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