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COMPLETE SPECIFICATION

Lubricating Oil Compositions

We, NAAMLOOZE VENNOOTSCHAP DE BATAAFSCHE PETROLEUM MAATSCHAPPIJ, a company organised under the laws of the Netherlands, of 30, Carel van Bylandtlaan, The Hague, The Netherlands, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to improved lubricating oil compositions particularly effective as turbine oils.

The essential requirements of a good turbine oil are that it be resistant to emulsification and oxidation and that it inhibit corrosion or rusting of metal parts exposed thereto. Lubricating oils which are normally regarded as effective corrosion and rust inhibiting compositions have been observed to be ineffective in this respect when used as turbine oils, apparently due to their inability to resist emulsification in the presence of water.

It is an object of this invention to produce an improved turbine oil which is resistant to emulsification in the presence of water and to oxidation, and which inhibits the rusting and corrosion of metals.

It has now been found that excellent lubricating oil compositions meeting these requirements can be prepared by the addition to a lubricating oil of minor proportions of

(a) an oil soluble aliphatic acid containing more than one —CXXH group (each X representing an oxygen or sulphur atom) or an amide or a partial ester of such an acid,

(b) an oil-soluble compound which contains a —YH group (Y representing an oxygen, sulphur, selenium or tellurium atom) attached to an aromatic ring but which does not contain a —CZZH group (each Z representing an oxygen, sulphur, selenium or tellurium atom), and

(c) a compound containing an aromatic ring and a —CZZH group but free from nitrile, nitro, nitroso and hydroxy groups.

Accordingly, the present invention provides lubricating oil compositions comprising a major proportion of a lubricating oil and minor proportions of an oil-soluble aliphatic acid containing more than one —CXXH group (each X representing an oxygen or sulphur atom) or an amide or a partial ester thereof, an oil-soluble compound which contains a —YH group (Y representing an oxygen, sulphur, selenium or tellurium atom) attached to an aromatic ring but which does not contain a —CZZH group (each Z representing an oxygen, sulphur, selenium or tellurium atom), and a compound containing an aromatic ring and a —CZZH group but free from nitrile, nitro, nitroso and hydroxy groups.

For the purpose of brevity, additive (a) will further be referred to as an "oil-soluble aliphatic polycarboxylic acid or derivative thereof," additive (b) as an "oil-soluble phenolic compound," and additive (c) as an aromatic acid.

Additive (a).

The oil-soluble aliphatic polycarboxylic acid or derivative thereof preferably contains one or more alkyl or alkenyl groups having from 3 to 36, and still more preferably, from 8 to 18, carbon atoms. Acids of this type include the aliphatic dicarboxylic acids substituted by such alkyl or alkenyl groups. Examples of suitable acids are malonic, succinic, glutaric, adipic, pimelic, sebacic, azelaic, tartaric, citric, maleic and citraconic acids substituted by alkyl or alkenyl groups of the above-mentioned type. Preferred acids are succinic acid substituted by an alkenyl group having 16 carbon atoms, succinic acid substituted

[*Price 3s. 0d.*]

by an alkenyl group having 18 carbon atoms, succinic acid substituted by an alkenyl group having 36 carbon atoms, tartaric acid substituted by an alkyl group having 10 to 18 carbon atoms and malonic acid substituted by an alkyl group having 10 to 18 carbon atoms. Examples of amides and partial esters, which can be used, are the mono-amides of alkyl substituted succinic acids, the mono-oleyl esters of alkenyl substituted succinic acids, the mono-octyl esters of alkyl substituted sebacic acids the mono-butyl esters of alkyl substituted tartaric acids, the mono-isopropyl ester of citric acid, the mono-2-ethylhexyl esters of citric acid, the mono-ester of phenol substituted by an alkyl group derived from paraffin wax and an alkenyl substituted succinic acid, the mono-ethyl ester of decenyl succinic acid, the mono-decyl ester of isobutenyl succinic acid, the mono-dicyclohexyl-amides of alkenyl substituted succinic acids, the mono-2-ethylhexylamide of succinic acid substituted by an alkenyl group having 16 carbon atoms, and the mono-amide of succinic acid substituted by an alkenyl group having 18 carbon atoms. Further examples of suitable additives of this class are alkenyl thio succinic acids and alkenyl thio tartaric acids. Mixtures of the above mentioned compounds can be used, if desired.

Additive (b).

The oil-soluble phenolic compound can be an oil-soluble alkyl phenol or naphthol or a sulphur, selenium or tellurium analogue thereof. Such compounds can be prepared by alkylate phenols by any known suitable means or they may be natural products, such as can be obtained from petroleum hydrocarbons or coal tars. For the alkylation of phenolic materials alkenes and their mixtures containing from 4 to 20 carbon atoms in the molecule are suitable alkylating materials. Mixtures of alkenes derived from paraffin waxes by cracking or from higher fatty alcohols by dehydration, are valuable and easily accessible starting materials. More than one alkyl group may be present in the phenol as in the case of compounds made by the di- or tri-alkylation of phenols with alkenes or alkyl halides or alcohols or ethers, or of compounds made by the mono-alkylation of, for example, a cresol, a xylol, or carvacrol. Substituents other than the —YH and alkyl groups may be present in the oil-soluble phenolic compound provided they do not increase substantially the water-solubility of the compound. Thus halogen atoms and alkoxy, alkylamino and nitro groups may be present. Moreover, di- or polyhydric phenols such as catechol resorcinol, pyrogallol and the dihydroxy naphthalenes may be alkylated to produce water-insoluble and oil-soluble phenolic compounds useful for the purpose of this invention. Specific compounds which can be used in the compositions of this invention are 2,4-dimethyl-6-tertiary butylphenol, 2,4,6-trimethylphenol, 2,4-dimethyl-6 - tertiary octylphenol, 2,4-dioctyl-6-methylphenol, 2-ethyl-4-octylphenol, 2,4 - dimethyl-6-tertiary butyl naphthol, 2,4 - dioctyl naphthol, 2,4-dimethyl-6-tertiary butyl thiophenol, 2,4-dimethyl-6-tertiary butyl selenophenol, 2-ethyl-4-octyl thiophenol, 2,4-dioctyl-6-methyl thionaphthol, 2,4-dimethyl-6-tertiary octyl tellurophenol, C_{14} alkylated cardanol, C_{14} alkylated thiocardanol, dodecyl phenol, bis-(beta-naphthylamino methyl)-p - tert - amylphenol, o-nitroso m-cresol, p-octyl aminophenol, dibutyl resorcinol, 2,6-ditertiary butyl-4-methylphenol, 2,4-ditertiary butyl-6-methylphenol, 2,4-di-sec-butyl-6-tertiary-butylphenol 2,4 - di-n-butyl-6-tertiary - octylphenol, 2,6-ditertiary-butyl-4-benzyl-phenol, 2,6 - ditertiary-amyl-4-methylphenol, 2,4-ditertiary-amyl-6-methylphenol, 2,4,6 - tritertiary-butylphenol, 2,6-ditertiary - butyl-4-methylthiophenol, 2,4-ditertiary-butyl-6-methylthiophenol, 2,4-dimethyl-6-tertiary-butylthiophenol, 2,4-dimethyl - 6-tertiary-octylthiophenol, 2,6-ditertiary-amyl-4-methylthiophenol, 2,4,6 - tritertiary-amythiophenol, 2,2' - methylene bis(4-methyl-6 - tertiary - butylphenol), 2,2'-methylene bis(4,6-ditertiary - butylphenol), 2,2'-methylene bis(4,6-ditertiary-octylphenol), 2,2'-methylene bis(4-methyl-6 - tertiary - amylphenol), 2,2'-methylene bis(4-methyl-6-tertiary-octylphenol), 2,2'-methylene bis (4-methyl-6-tertiary-butyl-thiophenol), 2,2'-methylene bis(4 - octyl - 6-tertiary - butylthiophenol), 2,2'-methylene bis (4,6-ditertiary-butylthiophenol), 2,2' - methylene bis(4,6-ditertiary-amylthiophenol), 2,2'-methylene bis(4-methyl-6-tertiary-amylthiophenol), 2,2'-methylene bis (4-methyl-6-tertiary-octylthiophenol), 1,1-bis(2 - hydroxy-3 - tertiary - butyl - 5-methylphenyl)isobutane, bis(2-hydroxy-3-tertiary-butyl-5 - methylphenyl)phenylmethane, 2,2-bis(2-hydroxy-3 - tertiary-butyl-5-methylphenyl)propane, and 2,2-bis(2 - hydroxy - 3 - tertiary - butyl - 5-methylphenyl)butane. Mixtures of these compounds may be used, if desired.

Additive (c).

The aromatic acids are used in conjunction with the above two classes of additives in order to render the compositions resistant to emulsification. As stated above the additive (c) should contain an aromatic ring and a —CZZH group. It may contain more than one —CZZH group, but compounds containing only one or two —CZZH groups are preferred. The —CZZH groups may be attached to the aromatic ring either directly or through a side chain. The aromatic ring may also be substituted by side chains not bearing a —CZZH group. Any side chains attached to the aromatic ring, as well as the aromatic ring itself, may be substituted by non-hydrocarbon substituents other than nitrile, nitro, nitroso and hydroxy groups.

Preferred acids are the aromatic carboxylic acids. Examples of suitable acids are benzoic acid, phthalic acid, toluic acid, xylic acid, phenyl substituted fatty acids (e.g. phenyl acetic acid to phenyl stearic acid), cinnamic acid, benzoyl propionic acid, phenyl laevulinic acid, phenyl alkyl succinic acids, benzyl alkyl succinic acids, phenyl akyl glutaric acid, o-vinyl benzoic acid, phenyl angelic acid, naphthoic acid, naphthyl stearic acid, anthranilic acid, mercapto phenyl, tolyl, xylyl, xenyl, naphthyl or anthracyl fatty acids, e.g., phenyl mercapto acetic or phenyl mercapto stearic acid, ethyl mercapto phenyl acetic acid, and the alkyl mercapto benzene-4-carboxylic acids.

The lubricating oil in the compositions of this invention can be any natural or synthetic lubricating oil. Thus it may be a hydrocarbon oil obtained from a paraffinic, naphthenic, Mid-continent or Coastal stock and/or mixtures thereof and preferably base stocks which have been highly refined. The viscosity of these oils may vary over a wide range such as from 50 SUS at 100° F. to 100 SUS at 210° F. Synthetic lubricating oils which may be used include olefin polymers, silicone fluids and organic phosphates. Mixtures of synthetic and natural oils also can be used.

The proportions in which the additives are generally used are given in the following table:

	General Range	Preferred Range
Oil-soluble aliphatic polycarboxylic acid or derivative thereof	0.01 to 0.2% by weight	0.01 to 0.05% by weight
Oil-soluble phenolic compound	0.01 to 1.0% by weight	0.1 to 0.8% by weight
Aromatic acid	0.001 to 0.1% by weight	0.001 to 0.01% by weight
Lubricating oil	Balance	Balance

Preferred compositions contain the additives of this invention in a total amount of 1% or less, and still more preferably in a total amount of less than 0.9%, the oil-soluble phenolic compound being present in the predominant amount of about 0.5%, the oil-soluble polycarboxylic acid or derivative thereof in an amount of from 0.01 to 0.2%, and the aromatic acid in the least amount of about 0.01% or less, all percentages based on the whole composition.

The compositions of this invention are illustrated by the following examples:

COMPOSITION A.

	% wt.
Succinic acid substituted by an alkenyl group having 18 carbon atoms	0.025%
2,6-ditert-butyl-4-methyl phenol	0.5%
Benzoic acid	0.003%
Mineral lubricating oil	Balance

COMPOSITION B.

Succinic acid substituted by an alkenyl group having 18 carbon atoms	0.025%
2,6-ditert-butyl-4-methyl phenol	0.5%
Cinnamic acid	0.003%
Mineral lubricating oil	Balance

COMPOSITION C.

	% weight
Succinic acid substituted by an alkenyl group having 18 carbon atoms	0.025%
2,6-ditert-butyl-4-methyl phenol	0.5%
Anthranilic acid	0.003%
Mineral lubricating oil	Balance

COMPOSITION D.

Monoester of oleyl alcohol and succinic acid substituted by an alkenyl group having 18 carbon atoms	0.03%
2,6-ditert-butyl-4-methyl phenol	0.5%
Toluic acid	0.01%
Mineral lubricating oil	Balance

COMPOSITION E.

Monoamide of succinic acid substituted by an alkenyl group having 18 carbon atoms	0.04%
2,4,6-tritert-amyl phenol	0.6%
Benzoic acid	0.01%
Mineral lubricating oil	Balance

The succinic acid substituted by an alkenyl group having 18 carbon atoms referred to in Compositions A, B, C, D and E above and in Compositions X and Y below, was made by hydrolysing the reaction product of maleic anhydride and an olefin containing 18 carbon atoms obtained by cracking paraffin wax.

In order to illustrate the effectiveness of the compositions of the present invention in resisting emulsification and in inhibiting corrosion and rust, Compositions A, B and C were tested by the "Navy Emulsion Test," Method 320.1 of Federal Specification VV—L—791; the Salt Water Rust Test (ASTM—D—665—50T) and the Turbine Oil Stability Test (ASTM D—943—47T), and compared with Compositions X, Y and Z which are turbine oils outside the scope of the invention. The following results were obtained:

Composition	I Navy Emulsion Test * (F.S.320.1 VV—L—791)	II Rust Test ** (ASTM D—665—50T)	III Turbine Oil Stability Test *** (ASTM D—943—47T)
Composition A	Excellent	Excellent	Excellent
Composition B	,,	,,	—
Composition C	,,	,,	—
Composition X(a)	Poor	—	—
Composition Y(b)	,,	—	Poor
Composition Z(c)	—	Poor	—

* Excellent—complete demulsification in less than 15—30 minutes in both distilled and synthetic sea water.
Fair—at least 1 to 3 ml. of emulsion remains around 30 minutes.
Poor—at least 5 to 80 ml. of emulsion remains after 30 minutes.

** Excellent—no rust after 48 hours.
Fair—some rust noted after 48 hours.
Poor—rust noted in less than 24 hours.

*** Excellent—over 1,000 hours.
Fair—less than 600 hours.
Poor—less than 200 hours.

(a) Composition X comprised a mineral lubricating oil having incorporated therein about 0.3% each of succinic acid substituted by an alkenyl group having 18 carbon atoms, and 2,6-ditert-butyl-4-methyl phenol.

(b) Composition Y comprised a mineral lubricating oil having incorporated therein about 0.3% succinic acid substituted by an alkenyl group having 18 carbon atoms.

(c) Composition Z comprised a mineral lubricating oil having incorporated therein about 1% of 2,6-ditert-butyl-4-methyl phenol.

From the above test results it is clear that compositions of this invention are excellent rust inhibitors and are resistant to emulsification.

Other additives such as oiliness agents, extreme pressure agents, anti-clogging agents and the like, can be added to

compositions of this invention in minor proportions, such as from 0.001% to 5% by weight.

In addition to being excellent turbine oils, compositions of this invention can be utilized as hydraulic oils cutting fluids, drawing and rolling oils and the like.

What we claim is:—

1. A lubricating oil composition comprising a major proportion of a lubricating oil and minor proportions of an oil-soluble aliphatic acid containing more than one —CXXH group (each X representing an oxygen or sulphur atom) or an amide or a partial ester thereof, an oil-soluble compound which contains a —YH group (Y representing an oxygen, suphur, selenium or tellurium atom) attached to an aromatic ring but which does not contain a —CZZH group (each Z representing an oxygen, sulphur, selenium or tellurium atom), and a compound containing an aromatic ring and a —CZZH group, but free from nitrile, nitro, nitroso and hydroxy groups.

2. A lubricating oil composition as claimed in claim 1, wherein the oil-soluble aliphatic acid containing more than one —CXXH group is an aliphatic dicarboxylic acid substituted by an alkyl or alkenyl group having from 3 to 36 carbon atoms.

3. A lubricating oil composition as claimed in claim 2, wherein the oil soluble aliphatic acid containing more than one —CXXH group is succinic acid substituted by an alkenyl group having 18 carbon atoms.

4. A lubricating oil composition as claimed in any one of the preceding claims, wherein the oil-soluble aliphatic acid containing more than one —CXXH group or amide or partial ester thereof, is present in an amount of 0.01 to 0.2% by weight. based on the whole composition.

5. A lubricating oil composition as claimed in any one of the preceding claims, wherein the oil-soluble aliphatic acid containing more than one —CXXH group or amide or partial ester thereof, is present in an amount of 0.01 to 0.05% by weight, based on the whole composition.

6. A lubricating oil composition as claimed in any one of the preceding claims, wherein the oil-soluble compound which contains a —YH group attached to an aromatic ring is an alkyl phenol.

7. A lubricating oil composition as claimed in claim 6, wherein the alkyl phenol is 2,6-di-tert - butyl-4 - methyl phenol.

8. A lubricating oil composition as claimed in claim 6, wherein the alkyl phenol is 2,2¹-methylene-bis-(4-methyl-6-tert-butyl phenol).

9. A lubricating oil composition as claimed in any one of the preceding claims, wherein the oil-soluble compound which contains a —YH group attached to an aromatic ring, is present in an amount of 0.01 to 1.0% by weight, based on the whole composition.

10. A lubricating oil composition as claimed in any one of the preceding claims, wherein the oil-soluble compound which contains a —YH group attached to an aromatic ring, is present in an amount of 0.1 to 0.8% by weight, based on the whole composition.

11. A lubricating oil composition as claimed in any one of the preceding claims, wherein the compound containing an aromatic ring and a —CZZH group is an aromatic carboxylic acid.

12. A lubricating composition as claimed in claim 11, wherein the aromatic carboxylic acid is benzoic acid.

13. A lubricating oil composition as claimed in claim 11, wherein the aromatic carboxylic acid is cinnamic acid.

14. A lubricating oil composition as claimed in claim 11, wherein the aromatic carboxylic acid is anthranilic acid.

15. A lubricating oil composition as claimed in any one of the preceding claims, wherein the compound containing an aromatic ring and a —CZZH group, is present in an amount of 0.001 to 0.01% by weight, based on the whole composition.

16. A lubricating oil composition as claimed in any one of the preceding claims, wherein the lubricating oil is a mineral lubricating oil.

17. A lubricating oil composition as claimed in any one of the preceding claims, containing additionally minor proportions of an oiliness agent, extreme pressure agent and/or anti - clogging agent.

18. Lubricating oil compositions substantially as hereinbefore described with reference to Compositions A to E.

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compositions of this invention in minor proportions, such as from 0.001% to 5% by weight.

In addition to being excellent turbine oils, compositions of this invention can be utilized as hydraulic oils cutting fluids, drawing and rolling oils and the like.

What we claim is:—

1. A lubricating oil composition comprising a major proportion of a lubricating oil and minor proportions of an oil-soluble aliphatic acid containing more than one —CXXH group (each X representing an oxygen or sulphur atom) or an amide or a partial ester thereof, an oil-soluble compound which contains a —YH group (Y representing an oxygen, suphur, selenium or tellurium atom) attached to an aromatic ring but which does not contain a —CZZH group (each Z representing an oxygen, sulphur, selenium or tellurium atom), and a compound containing an aromatic ring and a —CZZH group, but free from nitrile, nitro, nitroso and hydroxy groups.

2. A lubricating oil composition as claimed in claim 1, wherein the oil-soluble aliphatic acid containing more than one —CXXH group is an aliphatic dicarboxylic acid substituted by an alkyl or alkenyl group having from 3 to 36 carbon atoms.

3. A lubricating oil composition as claimed in claim 2, wherein the oil soluble aliphatic acid containing more than one —CXXH group is succinic acid substituted by an alkenyl group having 18 carbon atoms.

4. A lubricating oil composition as claimed in any one of the preceding claims, wherein the oil-soluble aliphatic acid containing more than one —CXXH group or amide or partial ester thereof, is present in an amount of 0.01 to 0.2% by weight, based on the whole composition.

5. A lubricating oil composition as claimed in any one of the preceding claims, wherein the oil-soluble aliphatic acid containing more than one —CXXH group or amide or partial ester thereof, is present in an amount of 0.01 to 0.05% by weight, based on the whole composition.

6. A lubricating oil composition as claimed in any one of the preceding claims, wherein the oil-soluble compound which contains a —YH group attached to an aromatic ring is an alkyl phenol.

7. A lubricating oil composition as claimed in claim 6, wherein the alkyl phenol is 2,6-di-tert - butyl-4 - methyl phenol.

8. A lubricating oil composition as claimed in claim 6, wherein the alkyl phenol is 2,2'-methylene-bis-(4-methyl-6-tert-butyl phenol).

9. A lubricating oil composition as claimed in any one of the preceding claims, wherein the oil-soluble compound which contains a —YH group attached to an aromatic ring, is present in an amount of 0.01 to 1.0% by weight, based on the whole composition.

10. A lubricating oil composition as claimed in any one of the preceding claims, wherein the oil-soluble compound which contains a —YH group attached to an aromatic ring, is present in an amount of 0.1 to 0.8% by weight, based on the whole composition.

11. A lubricating oil composition as claimed in any one of the preceding claims, wherein the compound containing an aromatic ring and a —CZZH group is an aromatic carboxylic acid.

12. A lubricating composition as claimed in claim 11, wherein the aromatic carboxylic acid is benzoic acid.

13. A lubricating oil composition as claimed in claim 11, wherein the aromatic carboxylic acid is cinnamic acid.

14. A lubricating oil composition as claimed in claim 11, wherein the aromatic carboxylic acid is anthranilic acid.

15. A lubricating oil composition as claimed in any one of the preceding claims, wherein the compound containing an aromatic ring and a —CZZH group, is present in an amount of 0.001 to 0.01% by weight, based on the whole composition.

16. A lubricating oil composition as claimed in any one of the preceding claims, wherein the lubricating oil is a mineral lubricating oil.

17. A lubricating oil composition as claimed in any one of the preceding claims, containing additionally minor proportions of an oiliness agent, extreme pressure agent and/or anti - clogging agent.

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