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LUBRICATING OILS CONTAINING EXTREME PRESSURE AGENTS

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This invention pertains to lubricating oil compositions having incorporated therein a combination of additives which synergistically (that is, through synergism effects) enhance the extreme pressure characteristics of lubricating oil compositions. In particular, this invention is directed to an improved lubricating oil composition useful especially for heavy duty service.

Because of greater pressures applied thereon than before, cams and valve lifters of internal combustion engines have shown greater than normal wear. Numerous attempts have been made to inhibit this wear by the use of known extreme pressure agents in lubricating oils. Since the majority of the lubricating oil compositions used in present-day lubrication of internal combustion engines have large amounts of detergents therein, it is necessary that extreme pressure agents incorporated in such oils be compatible with such detergents.

The usual extreme pressure agents which are added to lubricating oil compositions to enhance the extreme pressure characteristics thereof are of the sulfur- and chlorine-containing type. Known extreme pressure agents were added to the detergent-containing lubricating oil compositions in the belief that such agents would minimize cam and valve lifter wear. However, it was found that the usually effective extreme pressure agents did not promote the high load-bearing characteristics necessary for such high-detergent-level lubricating oils to overcome high cam wear and hydraulic valve lifter wear. For example, the detergent oils containing the usually effective extreme pressure agents (e.g., chlorinated aliphatic hydrocarbons) were no more effective than the oils without such agents therein. Thus, it was found that the known extreme pressure agents were inoperative to the lube oil compositions useful for crankcase lubrication.

Therefore, it is an object of this invention to describe detergent-containing lubricating oil compositions having incorporated therein a combination of additives, which combination effectively reduces wear of high load-bearing surfaces.

In accordance with this invention, it has been discovered that detergent-containing lubricating oil compositions capable of withstanding high load-bearing wear can be obtained by incorporating therein alkanolamides of naphthenic acids, and, in combination therewith, metal salts of dithiophosphoric acids. Thus, the lubricating oil compositions of this invention comprise a major proportion of an oil of lubricating viscosity, and, in addition to detergents, alkanolamides of naphthenic acids, and metal salts of dithiophosphoric acids.

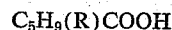
The invention resides in the discovery that the unique combination of amides of naphthenic acid and metal salts of dithiophosphoric acids provide outstanding effectiveness as extreme pressure additives for detergent-containing lubricating oil compositions. The combination of the metal salts of dithiophosphoric acids and alkanolamides of naphthenic acids of the present invention is remarkably effective in reducing the wear noted in cams and hydraulic valve lifters of internal combustion engines. Whereas, either the metal salts of dithiophosphoric acids or the

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alkanol naphthenamides are relatively ineffective in reducing valve lifter wear, the synergistic effect resulting from the combination of these additives is outstanding in reducing wear.

The amides of naphthenic acids which are used in combination herein with the dithiophosphates are hydroxyalkyl N,2-hydroxyalkyl, naphthenamides which are prepared by reacting naphthenic acids with alkanolamines. For purposes of simplification herein, the N,2-hydroxyalkyl, naphthenamides will be termed "alkanol naphthenamides."

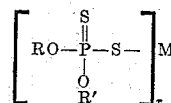
Naphthenic acids are complex mixtures of carboxylic acids which occur naturally in various petroleum oil compositions. These naphthenic acids have been defined as being of different types. However, the particular naphthenic acids with which we are concerned in this invention are those which are derivatives of cyclopentane and have the general formula:



wherein R is a hydrocarbon alkylene radical. These naphthenic acids have molecular weights which vary in the range of 200 to 500, and neutralization numbers (i.e., milligrams of KOH per gram of sample) which range from 300 to 100. It is preferred that the naphthenic acids are petroleum naphthenic acids having molecular weights of about 250 to 300.

The alkanolamines which are used herein in the reaction with the naphthenic acids are those having from 2 to 10 carbon atoms, which include ethanolamine, propanolamine, etc.

The metal salts of esters of dithiophosphoric acids which are used herein in combination with the alkanol naphthenamides are represented by the following formula:



wherein R and R' may be alkyl, aryl, alkaryl, aralkyl, or cyclic nonbenzenoid hydrocarbon radicals containing a total of from 7 to 70 carbon atoms, M is a metal of the Groups I, II, III, and IV of Mendeleeff's Periodic Table, and x is a number equal to the valence of the metal M. R and R' may or may not be identical. For particularly good results in the combination of this invention, it is preferred that the R radical is a hydrocarbon radical (more preferably an alkyl radical) containing from 1 to 25 carbon atoms, and that the R' radical is a hydrocarbon radical containing at least 6 carbon atoms, preferably from 6 to 25 carbon atoms.

When R and R' are identical and consist of the lower molecular weight hydrocarbon radicals (e.g., aliphatic radicals; i.e., butyl radicals), the metal salt normally does not have sufficient oil solubility to permit its use in lubricating oil compositions. However, when the R and R' radicals are different but still of low molecular weight (e.g., when R is a butyl radical, and R' is a hexyl radical), the metal salts of mixed esters of dithiophosphoric acids are of sufficient oil solubility to be effective in the particular combination of this invention.

Thus, in combination with the alkanol naphthenamides in accordance with this invention, it is preferred to use metal salts of mixed esters of dithiophosphoric acids wherein R is derived from an alcohol containing no more than 4 carbon atoms; for example, methyl, ethyl, propyl, isopropyl, butyl, secondary butyl, tertiary butyl, etc.; and wherein R' is derived from alcohols containing from 6 to 18 carbon atoms, including hexyl, methylisobutyl carbinol, methyl isopropyl carbinol, heptyl, isoheptyl, 2-ethylamyl octyl, isoctyl, 3-ethylhexyl, 2-propylamyl, decyl, undecyl, dodecyl, hexadecyl, octadecyl, etc.

Examples of R and R' when these are the same include the following radicals: octyl, decyl, dodecyl, tetradecyl, hexadecyl, octadecyl, hexylphenyl, decylphenyl, dodecylphenyl, hexadecylphenyl, octadecylphenyl, etc.

The esters of dithiophosphoric acids used in the preparation of the metal salts of dithiophosphoric acids include butylhexyl dithiophosphoric acid, methylhexyl dithiophosphoric acid, ethylhexyl dithiophosphoric acid, butylmethyl isobutyl carbinol dithiophosphoric acid, butylheptyl dithiophosphoric acid, butyldecyl dithiophosphoric acid, butylisoheptyl dithiophosphoric acid, butyloctadecyl dithiophosphoric acid, dioctyl dithiophosphoric acid, diheptyl dithiophosphoric acid, dihexadecyl dithiophosphoric acid, dioctadecyl dithiophosphoric acid, di-(decylphenyl) dithiophosphoric acid, etc.

Although the metals which are used in the formation of the dithiophosphates herein include the metals from Groups I, II, III, and IV of Mendeleeff's Periodic Table, it is preferred that the metals be divalent metals such as zinc and alkaline earth metals (i.e., calcium, barium, and strontium). Particularly beneficial results are obtained when the metal used is zinc. Where M is a divalent metal, "x" of the formula hereinabove then has the value "2."

The alkanol naphthenamides are used in lubricating oil compositions of the present invention in amounts from 0.1% to 5% or more, by weight, preferably from 0.2% to 2%, by weight.

The metal salts of dithiophosphoric acids are used in amounts from 0.05% to 10%, by weight, preferably from 0.25% to 5%, by weight.

The mol ratio of the alkanol naphthenamide to the metal dithiophosphates can vary from 0.05:1 to 10:1; however, because of the increased effectiveness obtained thereby, it is preferred that the mol ratio be from 0.05:1 to 2:1, that is, that the mol ratio has a value from 0.05 to 2.

The base oil which forms the major proportion of the lubricating oil of this invention may be any suitable lubricating oil, naphthenic base, paraffin base, and mixed base; other hydrocarbon lubricants, e.g., lubricating oils derived from coal products; and synthetic oils, e.g., alkylene polymers, such as polymers of propylene, butylene, and mixtures thereof, alkylene-oxide type polymers, dicarboxylic acid esters, liquid esters of acids of phosphorus, alkylbenzene, polymers of silicon, etc.

Synthetic oils of the alkylene oxide type polymers which may be used include those exemplified by the alkylene oxide polymers (propylene oxide polymers) and derivatives, including alkylene oxide polymers prepared by polymerizing the alkylene oxides, e.g., propylene oxide, in the presence of water or alcohol, e.g., ethyl alcohol; esters of ethylene oxide type polymers, e.g., acetylated ethylene oxide polymers prepared by acetylating ethylene oxide polymers containing hydroxyl groups; polyethers prepared from ethylene glycols, e.g., ethylene glycol; etc.

Synthetic oils of the dicarboxylic acid ester type include those which are prepared by esterifying dicarboxylic acids as adipic acid, azelaic acid, suberic acid, sebacic acid, alkenyl succinic acid, fumaric acid, maleic acid, etc., with alcohols such as butyl alcohol, hexyl alcohol, 2-ethylhexyl alcohol, dodecyl alcohol, etc. Examples of dibasic (dicarboxylic acid) acid ester synthetic oils include dibutyl adipate, dihexyl adipate, and di-2-ethylhexyl sebacate.

Synthetic oils derived from alkylbenzene include those which are prepared by alkylating benzene (e.g., dodecylbenzene, tetradecylbenzene, etc.).

Synthetic oils of the types of polymers of silicon include the liquid esters of silicon and the polysiloxanes, which include those exemplified by tetraethyl silicate, tetraisopropyl silicate, poly(methylphenyl) siloxane, and poly(siloxyl glycols), etc.

The above base oils may be used individually as such or in various combinations, wherever miscible, or wherever made so by the use of mutual solvents.

Detergents which form a part of the lubricating oil composition described herein include metal sulfonates (e.g., calcium petroleum sulfonates, calcium alkylbenzene sulfonates, etc.), and metal phenates (e.g., calcium alkylphenates).

As noted hereinabove, alkanol naphthenamides are prepared by reacting naphthenic acid with alkanolamines. It is preferred to use an excess of alkanolamine, and subsequently remove the unreacted alkanolamine by distillation. For example, 1 mol of naphthenic acid can be reacted with from 1.5 to 8 mols of alkanolamine, and after the reaction is complete, the excess alkanolamine can be removed by distillation.

The following examples illustrate the preparation of alkanol naphthenamides for use in combination with dithiophosphates according to the present invention.

EXAMPLE 1

Preparation of ethanol naphthenamide

A mixture of 100 grams of a naphthenic acid (0.4 mol) having an equivalent weight of 250, and 100 grams of ethanolamine (1.8 mols) was heated to 165° C., and the mixture was maintained at that temperature with constant agitation for 4 hours, during which time water was removed. Excess ethanolamine was then removed from the reaction mixture by distillation at a temperature of 170° C. and a pressure of 5 mm. of mercury. The resulting product had a hydroxyl number of 220.

EXAMPLE 2

Preparation of ethanol naphthenamide

A mixture of 100 grams of a petroleum naphthenic acid having an equivalent weight of 330, and 100 grams of ethanolamine was heated to 165° C.; and the mixture was maintained at that temperature with constant agitation for 4 hours, during which time water was removed. Excess ethanolamine was then removed from the reaction mixture by distillation at a temperature of 170° C., and a pressure of 5 mm. of mercury.

The following Table I presents Falex wear test data showing the effectiveness of the combination of alkanol naphthenamides and metal salts of dithiophosphoric acids in improving extreme pressure characteristics of lubricating oil compositions.

The base oil which was used as a reference oil was a solvent-refined SAE grade Mid-Continent oil containing 10 millimols per kilogram (based on the metal) of a calcium dodecylbenzene sulfonate, and 30 millimols per kilogram of a calcium dodecylphenate.

The Falex tests used are described in the "Journal of the Institute of Petroleum," vol. 32, April 1946. The load applied was 850 pounds.

The alkanol naphthenamide used was N,2-hydroxyethyl naphthenamide; and the dithiophosphate used was a zinc salt of a mixed diester of dithiophosphoric acid, wherein one ester group contained 4 carbon atoms, and the other ester group contained 6 carbon atoms.

TABLE I

Oil	Amount of Alkanol Naphthenamide used (percent by wt.)	Amount of Dithiophosphate used (percent by wt.)	Falex Wear, mgs.
Base Oil (reference).....			110
Base Oil.....		0.36	60
Reference Oil.....	1.0	0.36	37
Do.....	1.5	0.36	22
Do.....	2.0	0.36	16

¹ The naphthenic acid used herein was that described in Example 2, hereinabove.

² The naphthenic acid used was that described in Example 1, hereinabove.

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An actual hydraulic valve lifter wear test (known as the LS-5 Test Procedure) was run in a Chevrolet power glide engine using chilled cast iron hydraulic valve lifters. To accelerate lifter wear, the valve spring pressure was maintained at 240 p.s.i. with the valve fully open.

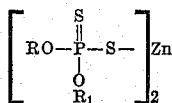
The reference oil used in the LS-5 test was a solvent refined paraffin base 10 SAE California oil containing 6 millimols per kilogram of a calcium dodecyl-benzene sulfonate, 14 millimols per kilogram of a calcium dodecyl phenate, 5 millimols per kilogram of a zinc di(dodecyl-phenyl) dithiophosphate, and 0.2% of a diparaffin thioether.

When the test engine was lubricated with the reference oil, 12 pitted hydraulic valve lifters were obtained. On the other hand, when 0.5%, by weight, of N,2-hydroxyethyl, naphthenamide was added to the reference oil, the number of pitted lifters was reduced to 7.

In addition to the additives noted hereinabove, the lubricating oil composition may contain grease thickening agents, oxidation inhibitors, etc.

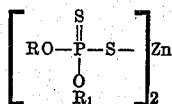
I claim:

1. A lubricating oil composition comprising a major proportion of an oil of lubricating viscosity having incorporated therein a detergent selected from the group consisting of metal sulfonates and metal phenates, from 0.2% to 2%, by weight, of an alkanol naphthenamide containing from 2 to 10 carbon atoms in the alkanol radical and wherein the naphthenic acid radical is derived from petroleum naphthenic acids having molecular weights from 200 to 500 and having neutralization numbers from 100 to 300, and from 0.25% to 5%, by weight, of a metal salt of a dithiophosphoric acid of the formula:



wherein R and R₁ are selected from the group consisting of alkyl and alkaryl radicals containing a total of 6 to 25 carbon atoms, and wherein the mol ratio of said alkanol naphthenamide to said metal salt of dithiophosphoric acid is from 0.05:1 to 2:1.

2. A lubricating oil composition comprising a major proportion of an oil of lubricating viscosity having incorporated therein a detergent selected from the group consisting of alkaline earth metal sulfonates and alkaline earth metal phenates, from 0.2% to 2%, by weight, of an alkanol naphenamide containing from 2 to 10 carbon atoms in the alkanol radical and wherein the naphthenic acid radical is derived from petroleum naphthenic acids having molecular weights from 200 to 500 and having neutralization numbers from 100 to 300, and from 0.25% to 5%, by weight, of a metal salt of a dithiophosphoric acid of the formula:

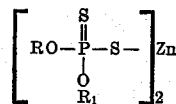


wherein R and R₁ are selected from the group consisting

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of alkyl and alkaryl radicals containing a total of 6 to 25 carbon atoms, and wherein the mol ratio of said alkanol naphthenamide to said metal salt of dithiophosphoric acid is from 0.05:1 to 2:1.

3. A lubricating oil composition comprising a major proportion of an oil of lubricating viscosity having incorporated therein a detergent selected from the group consisting of alkaline earth metal sulfonates and alkaline earth metal phenates, from 0.2% to 2%, by weight, of an alkanol naphthenamide containing from 2 to 10 carbon atoms in the alkanol radical and wherein the naphthenic acid radical is derived from petroleum naphthenic acids having molecular weights from 200 to 500 and having neutralization numbers from 100 to 300, and from 0.25% to 5%, by weight, of a metal salt of a dithiophosphoric acid of the formula:



wherein R and R₁ are alkyl radicals containing a total of 6 to 25 carbon atoms, and wherein the mol ratio of said alkanol naphthenamide to said metal salt of dithiophosphoric acid is from 0.05:1 to 2:1.

4. A lubricating oil composition comprising a major proportion of a mineral lubricating oil having incorporated therein a detergent selected from the group consisting of alkaline earth metal sulfonates and alkaline earth metal phenates, from 0.2% to 2%, by weight, of an alkanol naphthenamide containing from 2 to 10 carbon atoms in the alkanol radical and wherein the naphthenic acid radical is derived from petroleum naphthenic acids having molecular weights from 200 to 500 and having neutralization numbers from 100 to 300, and from 0.25% to 5%, by weight, of a zinc salt of a mixed disester of dithiophosphoric acid, wherein one ester group contains 4 carbon atoms and the other ester group contains 6 carbon atoms, and wherein the mol ratio of said alkanol naphthenamide to said zinc salt is from 0.05:1 to 2:1.

5. The lubricating oil composition of claim 4 wherein said alkaline earth metal sulfonate is calcium dodecyl sulfonate.

6. The lubricating oil composition of claim 4 wherein said alkaline earth metal sulfonate is calcium dodecyl sulfonate and said alkaline earth metal phenate is calcium dodecyl phenate.

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