ANTIOXIDANT HETEROCYCLIC NITROGENOUS AROMATIC CONTAINING OIL COMPOSITIONS

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Filed: Aug. 19, 1974

Appl. No.: 498,356

U.S. Cl. ................. 252/32.7 E; 252/33; 252/50; 252/401

Int. Cl. 5 C10M 1/48; C10M 3/42; C10M 1/32; C10M 3/26

Field of Search......... 252/32.7 E, 33, 33.4, 50, 252/401

References Cited

UNITED STATES PATENTS

3,788,992 1/1974 Sullivan ........................................... 252/50

3,793,200 2/1974 Billings ........................................... 252/32.7 E

3,846,312 11/1974 Cross et al. ..................................... 252/50

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ABSTRACT

Lubricating oil compositions containing antioxidant mixtures of heterocyclic nitrogenous aromatic compounds derived from uintaite which function to prevent the oxidative thickening of lubricant oils at high temperatures.

15 Claims, No Drawings
ANTIOXIDANT HETEROCYCLIC NITROGENOUS AROMATIC CONTAINING OIL COMPOSITIONS

BACKGROUND OF INVENTION

There exists a constant demand for improved lubricating oil compositions at significantly reduced cost. This demand has had specific impact in the search for antioxidants capable of controlling the thickening tendencies of lubricants and specifically crankcase engine oils at elevated temperatures.

The utilization, as effective antioxidants, of compositions recovered in the course of mining natural occurring, asphaltite type materials well-known and employed commercially for other applications would render the cost of recovering the latter materials less expensive while providing antioxidants of substantially unparalleled economy.

Thus, the discovery of a motor oil composition containing an effective, valuable and inexpensive antioxidant lubricant additive produced with comparative ease would represent a significant advance in the relevant art. This is particularly true where the recovered compositions require only minimal and inexpensive treatment to provide antioxidants of substantially uniform effectiveness.

SUMMARY OF INVENTION

It is accordingly an object of this invention to provide improved lubricating oil compositions.

It is a further object of this invention to provide lubricant oil compositions containing an antioxidant suitable for reducing the thickening of engine oils and particularly crankcase engine oils at high temperatures.

It is an additional object in accordance with this invention to produce the antioxidant additive from naturally occurring asphaltites requiring minimal processing prior to utilization as antioxidants.

Thus, it has now been discovered that the thickening propensity of crankcase engine oils under high temperature operating conditions, for example, crankcase bulk oil temperatures of 300°F, is significantly reduced by incorporation therein of the expensive by-products derived from the mining of the naturally occurring resin, uintaite, in a mineral oil base of lubricating viscosity. The foregoing by-products are composed substantially of heterocyclic amines, including alkyl substituted and unsubstituted quinolines, pyrroles, indoles and pyridines, it is believed.

DETAILED DESCRIPTION OF THE INVENTION

Specifically, the invention relates to hydrocarbon mineral oil formulations containing an antioxidant capable of controlling the thickening tendencies of said formulations, particularly under high temperature operating conditions, said antioxidant prepared by treatment of uintaite, a natural resin of the asphaltite type, found particularly in the Uinta Basin of Utah.

More specifically, the antioxidants employed in the practice of the invention are derived from uintaite by the following processes:

Uintaite is subjected to cracking temperatures within the range of 885° to 910°F, and most desirably about 900°F, to yield a fraction boiling in the range of about 204° to about 343°C. [400° to 650°F] and frequently referred to as the "diesel cut" which, when treated with a non-oxidizing, strong mineral acid, for example, concentrated sulfuric acid, hydrochloric acid, phosphoric acid or trichloro-acetic acid, yields an acid fraction which is readily separated from an accompanying acid-insoluble organic phase. This latter extractive step is accomplished most desirably at or about ambient temperature, particularly where concentrated sulfuric acid is employed, to avoid hydrolysis to which the acid phase is thereafter subjected in a separate step preferably at a temperature within the range of 50° to 100°C. If hydrochloric acid is employed in the extraction step, no water is added in the hydrolysis step. If anhydrous acid is used, the acid is diluted to an approximately 50% solution in water prior to addition to the diesel cut. Hydrolysis results in the formation of a further acid-insoluble organic phase and aqueous fraction. The latter fraction is neutralized with a base, illustratively, ammonia or sodium hydroxide, to yield an organic fraction and a water-containing phase. This organic fraction is a concentrated mixture of weak nitrogenous organic bases having a molecular weight of 140 to 200. This organic phase is substantially water-soluble and reactive with sulfuric acid, and is referred to hereinafter as "the broad unrefined fraction".

Particularly useful in that they assure uniform properties within even narrower and more preferred parameters than the initial broad unrefined fraction are those fractions of the foregoing product which when desalted, dried and distilled by conventional techniques are recovered above and below 580°F. The desalting step is accomplished using an inert organic solvent, desirably dioxane, ether or benzene followed by filtration; water is then azetrope out or, alternatively, a conventional drying agent added, and the solvent sequentially flashed off.

The exact composition of the broad unrefined fraction, the narrower fraction recovered below 580°F, referred to hereinafter as the "distillate", and that fraction recovered above 580°F, referred to hereinafter as the "high temperature residue", is not fully known. Generally, they are represented, although it is not intended that characterization be relied upon, as containing heterocyclic nitrogenous compounds, the heterocyclic ring structures of which are selected from five and six member rings and mixtures thereof containing one nitrogen atom and four and five carbon atoms respectively; the foregoing either unsubstituted; or substituted with an unsubstituted fused benzene ring, one or more alkyl moieties, a fused alkyl-substituted benzene ring, or one or more alkyl moieties and said substituted or unsubstituted fused benzene ring. The fusion, where it occurs, is normally in the 2,3-position of the heterocyclic ring. The foregoing heterocyclic compounds are thus predominantly quinolines, pyrroles, indoles, pyridines, and possibly acridines and condensation products or heterocyclic polymers thereof in which the foregoing compounds are unsubstituted and substituted; predominantly alkyl substituted, it is believed. Presumably, the broad unrefined fraction, distillate and high temperature residue contain many of the nitrogenous compounds which are believed to occur in uintaite such as the 3-ethylpyridine, 2,3,5-trimethylpyridine, pyridine, condensation products formed in the coking step to form the broad unrefined fraction, pyrrole, 2-methylpyrrole, possibly 1-methylpyrrole, and other lower alkyl-substituted pyrroles and condensation products therefrom, described by J. M. Sugiho and D. P. Sorensen, Journal of the American Society, vol. 77, pages 963 to 966 (Feb. 20, 1963).
The organic phase designated as the broad unrefined fraction used in the practice of this invention and recovered as described above, prior to desalting, drying or distillation, has, typically, physical properties recited in Table I:

| TABLE I |
|------------------|------------------|
| **Specific gravity at 77°F.** | 1.0171 |
| **at 60°F.** | 1.0226 |
| **API gravity** | 6.9 |

<table>
<thead>
<tr>
<th>Distillation (ASTM D-158)</th>
<th>Vol. %</th>
<th>°F at 760 mm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Start</td>
<td>400</td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>450</td>
<td></td>
</tr>
<tr>
<td>50</td>
<td>533</td>
<td></td>
</tr>
<tr>
<td>90</td>
<td>648</td>
<td></td>
</tr>
<tr>
<td>End point</td>
<td>656</td>
<td></td>
</tr>
<tr>
<td>Recovery</td>
<td>93%</td>
<td></td>
</tr>
</tbody>
</table>

Pensky-Martens flash point, °F. | 225 |
Pour Point, °F. | 0 |
Viscosity, centipoises at 77°F. | 32 |
Average molecular weight | 185 |
Total nitrogen, % by weight | 7.8 |
Basic nitrogen, % by weight | 6.2 |
Tertiary amine nitrogen, % by weight | 5.9 |
Carbon, % by weight | 82.8 |
Hydrogen, % by weight | 9.1 |
Sulfur, % by weight | 0.3 |
Oxygen, % by weight | 0.4 |

This fraction, constituting one of the desired additive products of the invention, will normally retain a residue of mineral acid salts remaining from the fractionation steps discussed hereinabove and used in securing the product, for example, sodium sulfate.

The desalted, dried distillate of the foregoing initial fraction boiling below 580°F. [304°C.] is a deep red oil with a characteristic odor, eighty volume percent of which forms water-soluble salts with 50% sulfuric acid.

This distillate is characterized by the physical properties recited in the following Table II:

| TABLE II |
|------------------|------------------|
| **Specific gravity at 77°F.** | 0.973 |
| **at 60°F.** | 0.979 |
| **API gravity** | 13.0 |

<table>
<thead>
<tr>
<th>Distillation (ASTM D-158)</th>
<th>Vol. %</th>
<th>°F at 760 mm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Start</td>
<td>361</td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>448</td>
<td></td>
</tr>
<tr>
<td>30</td>
<td>492</td>
<td></td>
</tr>
<tr>
<td>50</td>
<td>514</td>
<td></td>
</tr>
<tr>
<td>70</td>
<td>532</td>
<td></td>
</tr>
<tr>
<td>90</td>
<td>550</td>
<td></td>
</tr>
<tr>
<td>End point</td>
<td>579</td>
<td></td>
</tr>
<tr>
<td>Recovery</td>
<td>158</td>
<td></td>
</tr>
</tbody>
</table>

Pensky-Martens flash point, °F. | below 40 |
Pour point, °F. | 15 |
Viscosity, centipoises at 77°F. | 15 |
Average molecular weight | 185 |
Water, % by weight | 0.52 |
Total nitrogen, % by weight | 6.88 |
Basic nitrogen, % by weight | 4.66 |
Sulfur, % by weight | 0.289 |

The residue of heterocyclic compounds boiling above 580°F. (304°C.) and remaining after removal of the distillate characterized in Table II is composed predominantly, it is believed, of highly alkylated quinolines and indoles in addition to heterocyclic polymers formed from reactive pyridines, quinolines, indoles and pyroles, as noted above; that is, those of the foregoing compounds having a reactive hydrogen in the alpha position. This residue is characterized by the following physical properties:

| TABLE III |
|------------------|------------------|
| **Specific gravity at 77°F.** | 1.059 |
| **at 60°F.** | 1.064 |
| **API gravity** | 1.4 |

<table>
<thead>
<tr>
<th>Distillation (ASTM D-158)</th>
<th>Vol. %</th>
<th>°F at 760 mm</th>
</tr>
</thead>
<tbody>
<tr>
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<tr>
<td>10</td>
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<tr>
<td>50</td>
<td>659</td>
<td></td>
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<tr>
<td>70</td>
<td>692</td>
<td></td>
</tr>
<tr>
<td>90</td>
<td>888</td>
<td></td>
</tr>
<tr>
<td>End point</td>
<td>Cracked</td>
<td></td>
</tr>
</tbody>
</table>

Pensky-Martens flash point, °F. | 360 |
Pour point, °F. | 480 |
Viscosity, centistokes at 140°F. | 492 |
Average molecular weight | 280 |
Water, % by weight | 0.34 |
Total nitrogen, % by weight | 6.94 |
Basic nitrogen, % by weight | 3.32 |
Tertiary amine nitrogen, % by weight | 3.31 |
Sulfur, % by weight | 0.68 |


The foregoing fractions have been produced sporadically by the American Gilsonite Company, Salt Lake City, Utah; the broad unrefined fraction bearing the trade designation GN-103; the distillate being referred to as GN-200; and the high temperature residue being termed GN-201.

These products, which have been found frequently heretofore to possess properties lacking in uniformity in many of their areas of application, indicate satisfactorily uniform results when employed as antioxidants as provided herein.

The uintaite derivative antioxidants prepared according to the practice of the invention while particularly useful in crankcase motor oil formulations wherein they permit operation of equipment over wider temperature ranges than would otherwise be feasible have utility as well in lubricant formulations for gas turbine and hydraulic systems.

Concentrations in hydrocarbon lubricating oil of from about 0.01 to about 50% by weight of one of the foregoing uintaite derived mixtures, that is, the broad unrefined fraction, the distillate or the high temperature residue are contemplated. In the lubricating oil concentrates which are formulated for storage and/or transport and are subsequently blended into additional base oil to form finished motor oil formulations suitable for crankcase use, the content of the uintaite antioxidant normally ranges from about 10 to about 50 weight %.

Concentrations of these antioxidants in the finished motor oil composition are advantageously within the range of about 0.1 to about 10 weight %.

The nitrogenous antioxidant mixtures of the invention replace the significantly more expensive conventional amine antioxidants exemplified by the phenyl-naphthyl amines, phenothiazine and diphenylamine. Advantageous proportions of the heterocyclic nitrogenous compositions of the invention are within the range 0.1 to 5 % by weight and most desirably about 0.5 to 1.5 % by weight. The lubricant compositions of the invention are also fortified normally with conventional
additives such as anti-wear agents, dispersants corrosion inhibitors, antifoamants and other standard additives.

The hydrocarbon mineral oils employed in this invention can be paraffin base, naphthenic base, or mixed paraffin-naphthenic base distillate or residual oils. The lubricating oil base generally has been subjected to solvent refining to improve its lubricity and viscosity temperature relationship as well as solvent dewaxing to remove waxy components and to improve the pour of the oil. Generally, mineral lubricating oils have an SUS viscosity at 100°F between 50 and 1000 may be used in the formulation of the improved lubricants of this invention although the viscosity range will usually fall between 70 and 300 SUS at 100°F. A blend of base oils can be employed to provide a suitable base oil for either a single or multigrade motor oil.

An antiwear agent desirably incorporated in the lubricating oil compositions of the invention is zinc di-thiophosphate characterized by the formula:

\[
\begin{array}{c}
\text{RO} \\
\text{S} \\
\text{P} \\
\text{S} \\
\text{RO} \\
\end{array}
\]

\[
\text{Zn}
\]

in which R is a hydrocarbyl radical or a hydroxy-substituted hydrocarbyl radical having from 4 to 12 carbon atoms. The preferred zinc di-thiophosphates are those in which R represents an alkyl radical having from 4 to 8 carbon atoms. Examples of suitable compounds include zinc isobutyl 2-ethylhexyl di-thiophosphate, zinc di(2-ethylhexyl) di-thiophosphate, zinc isooctyl 2-ethylhexyl di-thiophosphate, zinc di(phenoxethyl) di-thiophosphate, zinc di(2,4 diethylphenoxethyl) di-thiophosphate and most desirably zinc isopropylmethyl iso-butyl carbinyl di-thiophosphate. In general, these compounds are employed in the oil composition in a concentration ranging from about 0.1 to 5.0% with the preferred concentration ranging from about 0.5 to 1.5%. These compounds can be prepared from the reaction of a suitable alcohol or mixture of alcohols with phosphorus pentasulfide. They are illustrated in U.S. Pat. Nos. 2,344,395 and 3,293,181.

Most desirable of the foregoing is zinc isopropyl methyl isobutyl carbinyl di-thiophosphate prepared by reaction of a methylisobutyl-carbinol and isopropanol with phosphorus pentoxide in a mole ratio respectively of about 2.7:2.3:1.0.

Dispersants which may be included in the compositions of the invention are the monohydrocarbonyl thio-phosphonates characterized by the formula:

\[
\begin{array}{c}
\text{R}^1 \\
\text{R}^2 \\
\text{R}^3 \\
\end{array}
\]

wherein R^1 is a hydrocarbyl radical having at least 12 carbon atoms and R^2 and R^3 are selected from the group consisting of hydrogen and monovalent aliphatic hydrocarbyl radicals containing 1 to 6 carbon atoms, and X is predominantly, or normally, sulfur.

Mono-hydroxalkyl hydrocarbonyl thio-phosphonates can be prepared by reacting an alkylene oxide, such as ethylene oxide, alkylene carbonates, such as ethylene carbonate or propylene carbonate, with a hydrocarbonyl thio-phosphonic acid. The reaction of alkylene carbonate with hydrocarbonyl thio-phosphonic acid is usually effected in the presence of an alkaline catalyst, such as potassium carbonate.

The hydrocarbonyl thio-phosphonic acid employed in preparing the mono-hydroxyalkyl thiophosphate may be represented by the general formula:

\[
\begin{array}{c}
\text{R}^1 \\
\text{P} \\
\text{O} \\
\text{H} \\
\text{H} \\
\text{H} \\
\end{array}
\]

wherein R^1 is a hydrocarbonyl radical which may be aromatic aliphatic or cycloaliphatic in nature and which usually contains 12 or more carbon atoms and X is sulfur or a mixture comprising a major proportion of sulfur and a minor proportion of oxygen. The R^1 radical in this formula is advantageously a polyolefin radical such as polyisobutylene or polypropylene having an average molecular weight between about 250 and 50,000 since such materials are the preferred materials for reaction with P_S_X. The preferred hydrocarbyl radical is a polybutene radical having a molecular weight between 500 and 5,000.

The hydrocarbonyl thio-phosphonic acids of the above formula are conventionally prepared by the reaction of P_S_X with a hydrocarbonyl, the reaction mixture consisting of about 5 and 40 weight % P_S_X at an elevated temperature of between about 100° and 320°C in a non-oxidizing atmosphere, for example, under a blanket of nitrogen followed by hydrolysis of the resulting product by contact with steam at a temperature between about 100° and 260°C. Steam treatment of the P_S_X hydrocarbon reaction product results in its hydrolysis to form inorganic phosphorus acids and a hydrocarbonyl thio-phosphonic acid of the structure shown above.

The inorganic phosphorus acids are removed from the hydrolyzed reaction product prior to reaction with alkylene oxide or alkylene carbonate to form the mono-hydroxyalkyl hydrocarbonyl thio-phosphonates. Removal of the inorganic phosphorus acids from the hydrolyzed product can be effected by the procedures disclosed in U.S. Pat. Nos. 2,951,835 and 2,897,512 wherein removal is effected by contact with synthetic hydroxy alkaline earth metal silicates and synthetic hydroxy alkali metal silicates respectively. Inorganic phosphorus acid can also be removed by extraction with anhydrous methanol as disclosed in U.S. Pat No. 3,135,719.

An alkylene oxide is reacted with the hydrocarbonyl thio-phosphonic acid in about an equimolar basis in the absence of catalyst to form the mono-hydroxyalkyl thio-phosphonate additives of this invention. The preparation of this component is fully described in U.S. Patent No. 3,272,744 and this disclosure is incorporated in the present application.

The preferred thiophosphonates for use herein are mono(β-hydroxyethyl) alkene thiophosphonates, and most desirably mono(β-hydroxyethyl) polybutene thiophosphonate having an average molecular weight of about 1100. A phosphonate such as the foregoing is normally present in the lubricating oil in an amount of about 0.5 to 5.0 weight %.
Another suitable additive for lubricant composition of the invention is a calcium carbonate overbased calcium sulfonate component containing from about 5 moles to 30 moles of dispersed calcium carbonate per mole of calcium sulfonate and having a Total Base Number from about 100 to 500. The preferred overbased calcium sulfonate will have from about 10 to 20 moles of dispersed calcium carbonate per mole of calcium sulfonate. These overbased substances provide a high level of alkalinity in the lubricating oil composition useful in combating deleterious action of corrosive substances as well as providing dispersancy. They are advantageously present in amounts of between about 0.25 and 5 wt. %.

In general, an overbased calcium sulfonate is prepared by reacting a calcium sulfonate (derived from the reaction of a natural or synthetic sulfonic acid having a molecular weight ranging from about 350 to 600 with hydrated lime) with carbon dioxide at an elevated temperature, 135°C-160°F., for an extended time period of several hours and under total reflux conditions. Thereafter the reaction mixture is filtered to recover an approximately 45 percent oil solution of calcium carbonate overbased calcium sulfonate prescribed above. The preparation of this component is fully described in U.S. Pat. No. 3,537,996 and the disclosure of this reference is incorporated herein.

An effective dispersant and viscosity index improving component also contemplated for use in the lubricant oils provided herein is a basic amine-containing addition-type copolymer formed of a plurality of polymerizable ethylenically unsaturated compounds, at least one of which is amino-free and contains from 8 to about 18 carbon atoms in an aliphatic hydrocarbon chain, preferably predominantly straight chain in nature, and one of which as it exists in the polymer contains a basic amino nitrogen in the side chain, in an amount by weight of said polymer of 0.5 to 3.5 %.

It is essential that at least one of the monomeric components employed in making the polymer should introduce an oil-solubilizing or oleophilic structure to insure that the polymer is soluble to the extent of at least 0.1% by weight in napthenic or paraffinic lubricating oils. In addition, the presence of basic amino groups, either primary, secondary or tertiary is necessary to impart the unique sludge dispersing properties which characterize these polymers. The proportion of basic amino nitrogen is best expressed in weight percent based on the total copolymer and should be within the range of 0.05 to 3.5 weight % as described above. Elaborating on the description provided hereinabove, introduction of the basic amino nitrogen structure can be accomplished by the use of at least one monomeric component containing the amino group or by use of a monomer containing a group which is reactive, when present in the polymer, toward ammonia, or primary or secondary non-aromatic amines. These monomers can also contain oleophilic structures that will assist in contributing to the requisite oil solubility. In addition, some of the polymers coming within the scope of this invention can, without sacrificing either oil solubility or dispersing properties, include certain proportions of monomers that do not themselves yield oil soluble polymers.

Most preferred of these methacrylate-containing polymers is the copolymer of butyl, lauryl, stearyl and dimethylaminoethyl methacrylate wherein the butyl, lauryl, stearyl and dimethylamino monomers are incorporated in a weight ratio respectively of 21:53:22:4. It should be understood, additionally, that lauryl methacrylate monomer charged to the polymerization reaction frequently contains about 25 to 28% by weight of myristyl methacrylate and the stearyl methacrylate monomer includes, by weight, about 32 to 44% of cetyl methacrylate and possibly up to 16% by weight of lower hydrocarbyl-containing methacrylates.

Copolymers useful in the practice of the invention can be prepared by conventional bulk, solution, or dispersion polymerization methods involving known initiators, including oxygen-yielding compounds, such as benzoyl peroxide, and azo compounds, such as alpha, alpha’-azo-disobutynitrile. The polymerization processes usually are carried out in an inert atmosphere, e.g. nitrogen or carbon dioxide, at temperatures ranging from 30° to 150°C., depending on the catalyst used and generally at temperatures between 50°C. and 70°C. when alpha, alpha’-azo-disobutynitrile is used as catalyst. It is important to carry the copolymerization substantially to completeness so that no unpolymerized monomers remain and the proportions of each component in the final product are essentially those of the original monomer mixture. The method of preparing these polymers is described in detail in U.S. Pat. No. 2,737,496 and this disclosure is incorporated herein.

The above described methacrylate copolymer is employed in the lubricating oil in a concentration ranging from about 0.5 to 5% with the preferred concentration ranging from about 1 to 4%.

A suitable anti-foaming agent is a dimethyl silicone polymer having a kinematic viscosity at 25°C. of about 100 centistokes and above. A very satisfactory anti-foaming agent for this purpose is prepared by diluting 10 grams of a dimethyl silicone polymer (1000 centistokes at 25°C.) with kerosene to provide a solution of 100 cubic centimeters. From 0.005 to 0.025% by weight of this concentration is generally employed to provide from 50 to 200 parts per million of the silicone polymer based on the lubricating oil composition.

An example of a crankcase lubricant composition for use herein will comprise a base oil blend such as the foregoing in an amount of at least 77 to about 99 weight % (e.g. 99.05 weight %) and preferably about 89 % (e.g. 89.46 weight %) and will contain from about 0.5 to 8 weight % (e.g. 5 weight %) of an oil concentrate containing about 35% by weight of a basic amino nitrogen-containing addition type of alkyl esters of methacrylic acid, that is, butyl, lauryl, stearyl and dimethyl amino-ethyl methacrylates in approximately 21:53:22:4 weight ratios (as described in U.S. Pat. No. 2,737,496); about 0.25 to 5.0 weight %, for example, 2 weight %, of an oil concentrate containing 50 weight % of a calcium carbonate overbased calcium sulfonate of a 300 TBN; about 0.1 to 5, and for example, about 2.5 weight % of an oil concentrate containing about 44% by weight of a naphthenic lubricating oil of an SUS viscosity of about 100 at 100°F. mono(β-hydroxyethyl) alkene thio-phosphonate and from about 0.50 to 5 weight %, illustratively 0.54 weight %, as indicated above, of a heterocyclic nitrogenous-containing mixture of the invention.

The formulations so described are supplied by standard procedures to the crankcase of the engine. When the engine is in operation the oil will attain elevated temperatures and, in accordance with the invention, the viscosity increases in the oil, which would occur in the absence of the inactive derivatives of the invention,
will be found to be significantly alleviated by their presence. Thus, it has been found that at 100°F. from approximately 700% to 100% reduction in viscosity increase is realized by use of the compositions of the invention at a concentration of one weight percent in the lubricant blend. The present invention is further illustrated by the following example:

**EXAMPLE**

This example illustrates, in comparative test procedure, the oxidative-thickening resistant properties imparted to typical crankcase engine lubricating oils under high temperature operating conditions by the practice of this invention.

The mixture of the invention, the high temperature residue, distillate and broad unrefined fraction derived from sump antifreeze were incorporated individually to lubricant oil compositions incorporating, as well, the full complement of additives shown in Table IV, and tested, as also shown in Table IV, in a sequence of Runs for terminal viscosity, percentage increases in viscosity and the period required before break, if any. The additives of the invention were incorporated in like amounts in each of Runs 1, 2 and 3 in a test oil formulation designated "Composition A" and the test results secured using identical test procedures. A control Run 4, made for purposes of comparison and the results of which also appear in Table IV, was undertaken under identical conditions, excluding the additives of the invention.

The test procedure employed in all four runs was one which correlates the results of field trials with the thickening properties of motor oils and is designed to simulate extreme service conditions in a road test. In this test procedure, a 1969 Ford 289-CID V-8 engine was installed on a dynamometer test stand instrumented to control engine operating conditions. The engine was modified by replacing the filter housing with a blank plate and by enclosing the engine oil pan with 1-inch thick Fiberglas insulation about the outside. The test stand included an intake air temperature control to maintain a prescribed carburetor inlet air temperature. The automotive radiator was submerged in a water tank with means to control the engine jacket temperature.

After a 3½ hour break-in, the engine was operated at the following test conditions:

- Oil charge, quarts: 4.0
- Duration, hours: 40
- Load, BHP: 105±2
- Speed, revolutions per minute: 3200±10
- Air-fuel ratio: about 15:1
- Exhaust back pressure, inches mercury: 230±2
- Intake air: 15±2
- Oil gallery: about 3.0
- Spark Advance, °BTC: 32

Approximately 5 gallons of test oil are required for each run. About 600 gallons of gasoline is used in each run as fuel.

In this test the oils were runs, as indicated, for 40 hours of total and continuous testing time with samples being removed every four hours, and both viscosity and infrared nitro-oxidation patterns monitored.

The test lubricant oil, Composition A, incorporated a blend of mineral oils of lubricating viscosity having the following inspection tests:

- Gravity °API: 31.0
- Flash COC °F: 410
- Viscosity, SUS at: 60°F. (extrapolated) 7500
- 100°F. 160
- 210°F. 44

The lubricant oil included the components and weight percentages thereof recited in Table IV, as follows:

<table>
<thead>
<tr>
<th>TABLE IV</th>
</tr>
</thead>
<tbody>
<tr>
<td>Run No.</td>
</tr>
<tr>
<td>Composition</td>
</tr>
<tr>
<td>Composition A</td>
</tr>
<tr>
<td>Mono (2-hydroxy-ethyl) polystyrene (1,100 average mol wt.) dihydrogen phosphate</td>
</tr>
<tr>
<td>Basic amino nitrogen-containing addition type methacrylate copolymer</td>
</tr>
<tr>
<td>Zinc isopropyl methyl isobutyl carbonyl dihydrogen phosphate</td>
</tr>
<tr>
<td>Calcium carbonate overbased calcium sulfonate</td>
</tr>
<tr>
<td>Dimethyl Silicone Antifoamant</td>
</tr>
<tr>
<td>High Temperature Residue</td>
</tr>
<tr>
<td>Distillate</td>
</tr>
<tr>
<td>Broad Unrefined Fraction</td>
</tr>
<tr>
<td>Hours To Break</td>
</tr>
<tr>
<td>Viscosity</td>
</tr>
<tr>
<td>DIR° 5.8</td>
</tr>
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</table>
It will be evident from the foregoing Table IV that the composition of Run 4, from which the additives of the invention were excluded, manifested oxidative breaks as measured by viscosity and infra-red nitro-oxidation patterns at about 27 hours and 22 hours respectively. These breaks are significant in that thickening of the lubricant oil occurs characteristicly very rapidly after these breaks are found and often lead in commercial practice with many typical lubricant compositions to engine failure. It will be equally evident that these breaks did not occur under the rigorous test conditions employed where high temperature residue or broad unrefined fraction is incorporated in the lubricant composition; and occurs where distillate is incorporated (Run 2) only after the passage of a significantly greater period of time, i.e. 37 hours and 29 hours respectively, than is seen in the control of Run 4.

Thus, when additives of the type described are used, the times transpiring until an oxidation break occurs (as measured by either viscosity increase or infra-red nitro-oxidation patterns) are significantly increased, indicating clearly the superior performance of crankcase engine oils incorporating the nitrogenous compositions of the invention. This conclusion is reinforced by the comparison of terminal viscosities secured in each of the foregoing runs as recited in Table IV above.

The method of the invention involves operating an internal combustion reciprocating engine employing the lubricant oil compositions of the invention. It will be evident that the terms and expressions which have been employed are used as terms of description and not of limitation. There is no intention in the use of such terms and expressions of excluding equivalents of the features shown and described or portions thereof and it is recognized that various modifications are possible within the scope of the invention claimed.

We claim:

1. A lubricant oil composition resistant to oxidative thickening at elevated temperatures comprising a mineral lubricating oil containing from 0.01 to 50% by weight of a heterocyclic nitrogen-containing mixture derived from uintaite and distilled therefrom by a procedure that comprises subjecting uintaite to a cracking temperature within the range of about 885°F to about 910°F to yield a fraction boiling in the range of about 400°F to 650°F which is sequentially treated with a strong mineral acid to form an acid phase and an acid insoluble organic phase; hydrolyzing said acid phase to form an acid insoluble organic fraction and an aqueous fraction; neutralizing the latter aqueous fraction with a base to yield further organic- and water-containing phases; and recovering said organic phase comprising said heterocyclic nitrogen-containing mixture therefrom.

2. The lubricant oil composition claimed in claim 1 wherein said organic phase occurring after acid-treatment, hydrolysis, neutralization and final removal of said water-containing phase therefrom, is desalted, dried and recovered upon distillation thereof up to a temperature of 580°F.

3. The lubricant oil composition as claimed in claim 1 wherein said organic phase occurring after acid-treatment, hydrolysis, neutralization and final removal of said water-containing phase therefrom, is desalted, dried and the fraction boiling at and below 580°F removed upon distillation; and the residue remaining recovered upon distillation above 580°F.

4. A lubricant oil composition as claimed in claim 1 wherein said composition comprises a mineral lubricating oil and from 0.10 to 10% by weight of the said heterocyclic nitrogen-containing mixture.

5. A lubricant oil composition as claimed in claim 2 wherein said composition comprises a mineral lubricating oil and from 0.10 to 10% by weight of the said heterocyclic nitrogen-containing mixture.

6. A lubricant oil composition as claimed in claim 3 wherein said composition comprises a mineral lubricating oil and from 0.10 to 10% by weight of the said heterocyclic nitrogen-containing mixture.

7. A lubricating oil as claimed in claim 1 wherein said oil includes 0.1 to 5.0% of a zinc diethio phosphate characterized by the formula:

\[
\begin{array}{c}
\text{Zn} \\
\text{RO} \\
\text{S} \\
\text{S} \\
\text{RO} \\
\end{array}
\]

in which \( R \) is a hydrocarbonyl radical or a hydroxy substituted hydrocarbonyl radical having from 4 to 12 carbon atoms, 0.5 to 5.0% of monohydroxyalkyl hydrocarbonyl thiophosphonate characterized by the general formula:

\[
\begin{array}{c}
\text{R}^1 \text{PO} \text{C} \text{C} \text{C} \text{OH} \\
\text{OH} \\
\end{array}
\]

in which \( R^1 \) is a hydrocarbonyl radical having at least 12 carbon atoms, \( R^2 \) and \( R^3 \) are selected from the group consisting of hydrogen and monovalent aliphatic hydrocarbonyl radicals containing 1 to 6 carbon atoms and \( X \) is sulfur, from 0.5 to 5.0% of an oil-soluble, basic amino nitrogen-containing addition type methacrylate copolymer derived from an alkyl methacrylate in which the alkyl radical has from 4 to 20 carbon atoms and di-alkylaminoalkyl methacrylate in which the alkyl radicals have a total of 4 to 8 carbon atoms, said copolymer containing 0.05 to 3.5% by weight of basic amino nitrogen and having an inherent viscosity of 0.1 to 3.0 and from 0.25 to 5% of calcium carbonate overbased calcium sulfonate having from about 5 to 30 moles di-
persed calcium carbonate per mole of calcium sulfonate and having a Total Base Number ranging from 100 to 500.

8. A crankcase engine oil as claimed in claim 2 wherein said oil includes 0.1 to 5.0% of a zinc dithiophosphate characterized by the formula:

in which R is a hydrocarbyl radical or a hydroxy substituted hydrocarbyl radical having from 4 to 12 carbon atoms, 0.5 to 5.0% of monohydroxyalkyl hydrocarbyl thiophosphonate characterized by the general formula:

in which R is a hydrocarbyl radical having at least 12 carbon atoms, R² and R³ are selected from the group consisting of hydrogen and monovalent aliphatic hydrocarbyl radicals containing 1 to 6 carbon atoms and X is sulfur, from 0.5 to 5.0% of an oil-soluble, basic amino nitrogen-containing addition type methacrylate copolymer derived from an alkyl methacrylate in which the alkyl radical has from 4 to 20 carbon atoms and di-alkylaminomethyl methacrylate in which the alkyl radicals have a total of 4 to 8 carbon atoms, said copolymer containing 0.05 to 3.5% by weight of basic amino nitrogen and having an inherent viscosity of 0.1 to 3.0 and from 0.25 to 5% of calcium carbonate overbased calcium sulfonate having from about 5 to 30 moles dispersed calcium carbonate per mole of calcium sulfonate and having a Total Base Number ranging from 100 to 500.

9. A crankcase engine oil as claimed in claim 3 wherein said oil includes 0.1 to 5.0% of a zinc dithiophosphate characterized by the formula:

in which R is a hydrocarbyl radical or a hydroxy substituted hydrocarbyl radical having from 4 to 12 carbon atoms, 0.5 to 5.0% of monohydroxyalkyl hydrocarbyl thiophosphonate characterized by the general formula:

in which R is a hydrocarbyl radical having at least 12 carbon atoms, R² and R³ are selected from the group consisting of hydrogen and monovalent aliphatic hydrocarbyl radicals containing 1 to 6 carbon atoms and X is sulfur, from 0.5 to 5.0% of an oil-soluble, basic amino nitrogen-containing addition type methacrylate copolymer derived from an alkyl methacrylate in which the alkyl radical has from 4 to 20 carbon atoms and di-alkylaminomethyl methacrylate in which the alkyl radicals have a total of 4 to 8 carbon atoms, said copolymer containing 0.05 to 3.5% by weight of basic amino nitrogen and having an inherent viscosity of 0.1 to 3.0 and from 0.25 to 5% of calcium carbonate overbased calcium sulfonate having from about 5 to 30 moles dispersed calcium carbonate per mole of calcium sulfonate and having a Total Base Number ranging from 100 to 500.

10. A lubricating oil as claimed in claim 4 wherein the oil includes 0.1 to 5.0% of a zinc dithiophosphate characterized by the formula:

in which R is a hydrocarbyl radical or a hydroxy substituted hydrocarbyl radical having from 4 to 12 carbon atoms, 0.5 to 5.0% of monohydroxyalkyl hydrocarbyl thiophosphonate characterized by the general formula:

in which R is a hydrocarbyl radical having at least 12 carbon atoms, R² and R³ are selected from the group consisting of hydrogen and monovalent aliphatic hydrocarbyl radicals containing 1 to 6 carbon atoms and X is sulfur, from 0.5 to 5.0% of an oil-soluble, basic amino nitrogen-containing addition type methacrylate copolymer derived from an alkyl methacrylate in which the alkyl radical has from 4 to 20 carbon atoms and di-alkylaminomethyl methacrylate in which the alkyl radicals have a total of 4 to 8 carbon atoms, said copolymer containing 0.05 to 3.5% by weight of basic amino nitrogen and having an inherent viscosity of 0.1 to 3.0 and from 0.25 to 5% of calcium carbonate overbased calcium sulfonate having from about 5 to 30 moles dispersed calcium carbonate per mole of calcium sulfonate and having a Total Base Number ranging from 100 to 500.

11. A lubricating oil as claimed in claim 5 wherein said oil includes 0.1 to 5.0% of a zinc dithiophosphate characterized by the formula:
in which R¹ is hydrocarbaryl radical having at least 12 carbon atoms, R² and R³ are selected from the group consisting of hydrogen and monovalent aliphatic hydrocarbaryl radicals containing 1 to 6 carbon atoms and X is sulfur, from 0.5 to 5.0% of an oil-soluble, basic amino nitrogen-containing addition type methacrylate copolymer derived from an alkyl methacrylate in which the alkyl radical has from 4 to 20 carbon atoms and dialkylaminoalkyl methacrylate in which the alkyl radicals have a total of 4 to 8 carbon atoms, said copolymer containing 0.05 to 3.5% by weight of basic amino nitrogen and having an inherent viscosity of 0.1 to 3.0 and from 0.25 to 5% of calcium carbonate overbased calcium sulfonate having from about 5 to 30 moles dispersed calcium carbonate per mole of calcium sulfonate and having a Total Base Number ranging from 100 to 500.

12. A crankcase engine oil as claimed in claim 6 wherein said oil includes 0.1 to 5.0% of a zinc dithiophosphate characterized by the formula:

\[
\begin{align*}
\text{Zn} & \quad \begin{bmatrix}
\text{RO} & \text{S} \\
\text{P-S-} & \text{RO}'
\end{bmatrix}^2
\end{align*}
\]

in which R is a hydrocarbaryl radical or a hydroxy substituted hydrocarbon radical having from 4 to 12 carbon atoms, 0.5 to 5.0% of monoxyalkyl hydrocarbaryl thiophosphonate characterized by the general formula:

in which R¹ is hydrocarbaryl radical having at least 12 carbon atoms, R² and R³ are selected from the group consisting of hydrogen and monovalent aliphatic hydrocarbaryl radicals containing 1 to 6 carbon atoms and X is sulfur, from 0.5 to 5.0% of an oil-soluble, basic amino nitrogen-containing addition type methacrylate copolymer derived from an alkyl methacrylate in which the alkyl radical has from 4 to 20 carbon atoms and dialkylaminoalkyl methacrylate in which the alkyl radicals have a total of 4 to 8 carbon atoms, said copolymer containing 0.05 to 3.5% by weight of basic amino nitrogen and having an inherent viscosity of 0.1 to 3.0 and from 0.25 to 5% of calcium carbonate overbased calcium sulfonate having from about 5 to 30 moles dispersed calcium carbonate per mole of calcium sulfonate and having a Total Base Number ranging from 100 to 500.

13. A composition according to claim 7 wherein said oil includes a mineral lubricating oil having an SUS viscosity at 100°F. of between 50 and 1000.

14. A composition according to claim 8 wherein said oil includes a mineral lubricating oil having an SUS viscosity at 100°F. of between 50 to 1000.

15. A composition according to claim 9 wherein said oil includes a mineral lubricating oil having an SUS viscosity at 100°F. of between 50 and 1000.