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3,732,167

MOTOR OIL COMPOSITION

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8 Claims

ABSTRACT OF THE DISCLOSURE

Motor oil composition comprising a mineral lubricating oil containing in combination an alkylated diphenylamine, a zinc dihydrocarbyl dithiophosphate, a hydroxyalkyl hydrocarbyl thiophosphonate, a nitrogen-containing methacrylate polymer and an overbased calcium sulfonate and method for operating an internal combustion reciprocating engine.

BACKGROUND OF THE INVENTION

Conventional premium motor oil compositions are a balanced blend of a mineral lubricating oil and selected additives to provide lubrication, dispersant, detergent, corrosion inhibition and anti-wear properties in engine crankcase service. Such oils possess outstanding lubricating properties and surpass the specification requirements of the highest standards set for crankcase service presently denoted API Service SE.

Recently, certain types of extreme engine service have seriously impaired the life of the noted class of premium motor oils. In particular, a deterioration in the stability of the oil caused by unusually severe operating conditions with resultant rapid oxidation nitrogen fixation and/or soap formation in the mineral oil and subsequent loss of lubricating properties has been observed. Instances of engine seizure and failure have resulted from this lubricating oil breakdown. A combination of factors including very high sustained road speed, use of air conditioners, higher under-hood temperatures, exhaust emission controls, trailer hauling and roof-top loads, extended oil drain intervals, engine break-in and warm or hot atmospheric temperatures operate to bring about the unusually severe conditions leading to the noted problem.

The principal environmental factor which triggers the lubricating oil failure is the development in the engine of bulk crankcase oil operating temperatures in the order of 300 to 310° F. or above. These crankcase oil temperatures are abnormally high and compare to normal engine oil temperatures under high speed operating conditions in the range of 260 to 280° F. An interesting aspect of the problem is that it is associated primarily with the operation of very high-powered passenger cars at extremely high sustained road speeds of 80 to 90 miles per hour in conjunction with one or more of the additional load factors noted above. Automobiles with engines powered below the level of the high-powered vehicles are apparently incapable of imposing such extreme loads on the lubricating oil composition that a rapid failure of the oil ensues.

THE PRIOR ART

Many additives for lubricating oil compositions as well as formulated lubricating oil compositions employing additive combinations are known. U.S. 3,272,744 discloses a mineral lubricating oil composition containing hydroxyalkyl hydrocarbyl thiophosphonate detergents and a method for their preparation. U.S. 2,737,496 discloses a mineral lubricating oil composition containing dispersants of the basic amino-nitrogen-containing meth-

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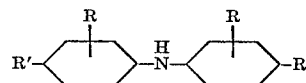
acrylate copolymer class. U.S. 2,344,395 and 3,293,181 disclose lubricating oil compositions containing the zinc dihydrocarbyl dithiophosphate class of anti-wear additives. U.S. 3,537,996 and 3,312,618 disclose lubricating oil compositions containing overbased calcium sulfonate detergents and method for preparing the overbased salts. Anti-oxidants of the alkylated diphenylamine class are marketed by the R. T. Vanderbilt Co.

SUMMARY OF THE INVENTION

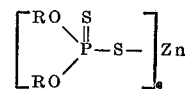
This invention is related to a novel mineral lubricating oil composition which provides an effective motor oil for the operation of a high-powered automobile under extremely severe operating conditions including crankcase bulk oil temperatures of 300° F. and above. The motor oil composition is a critically balanced formulation in a mineral oil base of lubricating viscosity. The additive components in the lubricating oil composition comprise a critical combination of an alkylated diphenylamine, a zinc dithiophosphate, a monohydroxyalkyl hydrocarbyl phosphonate, a basic amino nitrogen-containing addition type methacrylate copolymer and a calcium carbonate overbased calcium sulfonate. This invention also relates to a method for operating a reciprocating internal combustion engine.

DETAILED DESCRIPTION OF THE INVENTION

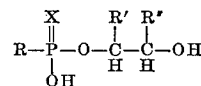
The motor oil composition of the invention will comprise a major proportion of a mineral lubricating oil containing in combination from about 0.1 to 2.5 percent of an alkylated diphenylamine represented by the formula:



in which R is an alkyl radical having from 1 to 4 carbon atoms and R' is an alkyl radical having from about 4 to 16 carbon atoms, from 0.1 to 0.5 percent of a zinc dithiophosphate represented by the formula:



in which R is a hydrocarbyl radical or a hydroxy substituted hydrocarbyl having from about 4 to 12 carbon atoms, from 0.5 to 5.0 percent of a monohydroxyalkyl hydrocarbyl phosphonate having the general formula:



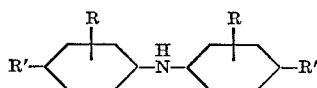
in which R is a hydrocarbyl radical having at least 12 carbon atoms, R' and R'' are selected from the group consisting of hydrogen and monovalent aliphatic hydrocarbyl radicals containing 1 to 6 carbon atoms and X is sulfur, from 0.5 to 5.0 percent of an oil soluble, basic amino nitrogen-containing addition type methacrylate copolymer derived from an alkyl methacrylate in which the alkyl radical has from 4 to 20 carbon atoms and dialkylamino-alkyl methacrylate in which the alkyl radicals have a total of 4 to 8 carbon atoms, said copolymer containing 0.1 to 3.0 percent by weight of basic amino nitrogen and having an inherent viscosity of 0.1 to 30, and from 0.25 to 3.5 percent of a calcium carbonate overbased calcium sulfonate having from about 5 to 30 moles of dispersed calcium carbonate per mole of calcium sulfonate and having a Total Base Number ranging from about 100 to 300.

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The method of the invention involves operating an internal combustion reciprocating engine employing the above lubricating oil composition.

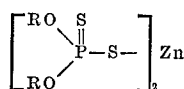
The hydrocarbon mineral oils employed in this invention can be paraffin base, naphthene base or mixed paraffin-naphthene base distillate or residual oils. Paraffin base distillate lubricating oil fractions are preferred for the formulation of the highest quality motor oils. The lubricating oil base generally 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 having 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.

The alkylated diphenylamine component of the lubricating oil composition is represented by the formula:



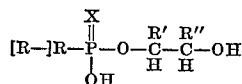
in which R is an alkyl radical having from 1 to 4 carbon atoms and R' is an alkyl radical having from about 4 to 16 carbon atoms. More preferred compounds are those in which R' is a tertiary alkyl hydrocarbon radical having from 6 to 12 carbon atoms. Examples of typical compounds include 2,2'-diethyl, 4,4'-tert. dioctyldiphenylamine, 2,2'-diethyl, 4,4'-tert. dioctyldiphenylamine, 2,2'-dimethyl-4,4'-tert. dioctyldiphenylamine, 2,5-diethyl, 4,4'-tert. dihexyldiphenylamine, 2,2,2',2'-tetraethyl, 4,4'-tert. didodecyldiphenylamine and 2,2' dipropyl-4,4'-tert. dibutyldiphenylamine. Mixtures of the foregoing compounds can be employed with equal effectiveness. The alkylated diphenylamine is normally employed in the oil composition in a concentration ranging from about 0.1 to 2.5 percent weight percent based on the weight of the lubricating oil composition. A preferred concentration is from about 0.25 to 1.0 percent.

The essential zinc dithiophosphate component of the lubricating oil is represented by the formula:



in which R is a hydrocarbyl radical or a hydroxy-substituted hydrocarbyl radical having from 4 to 12 carbon atoms. The preferred zinc dithiophosphates are those in which R represent an alkyl radical having from 4 to 8 carbon atoms. Examples of suitable compounds include zinc isobutyl 2-ethylhexyl dithiophosphate, zinc di(2-ethylhexyl) dithiophosphate, zinc isoamyl 2-ethylhexyl dithiophosphate, zinc di(phenoxylethyl) dithiophosphate and zinc di(2,4 diethylphenoxyethyl) dithiophosphate. In general, these compounds are employed in the oil composition in a concentration ranging from about 0.1 to 3.0 percent with the preferred concentration ranging from about 0.5 to 1.5 percent. 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. 2,344,395 and 3,293,181.

The mono-hydroxyalkyl hydrocarbyl thiophosphonate component of the oil composition is represented by the formula:



in which R is a hydrocarbyl radical having at least 12

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carbon atoms, R' and R'' are selected from the group consisting of hydrogen and monovalent aliphatic hydrocarbyl radicals containing 1 to 6 carbon atoms and X is sulfur.

Mono-hydroxyalkyl hydrocarbyl thiophosphates can be prepared by reacting alkylene carbonates, such as ethylene carbonate or propylene carbonate, with a hydrocarbyl thiophosphonic acid. The reaction of alkylene carbonate with hydrocarbyl thiophosphonic acid is usually effected in the presence of an alkaline catalyst, such as potassium carbonate.

The hydrocarbyl thiophosphonic acid employed in preparing the mono-hydroxyalkyl thiophosphate may be represented by the general formula:



wherein R is a hydrocarbyl 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 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 P₂S₅. The preferred hydrocarbyl radical is a polybutene radical having a molecular weight between 600 and 5000.

The hydrocarbyl thiophosphonic acids of the above formula are conventionally prepared by the reaction of P₂S₅ with a hydrocarbon, the reaction mixture constituting between about 5 and 40 weight percent P₂S₅, 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 P₂S₅ hydrocarbon reaction product results in its hydrolysis to form inorganic phosphorus acids and a hydrocarbyl thiophosphonic 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 hydrocarbyl thiophosphates. Removal of the inorganic phosphorus acids from the hydrolyzed product can be effected by the procedures disclosed in U.S. 2,951,835 and 2,897,512 wherein removal is effected by contact with synthetic hydrous alkaline earth metal silicates and synthetic hydrous alkali metal silicates respectively. Inorganic phosphorus acid can also be removed by extraction with anhydrous methanol as disclosed in U.S. 3,135,729.

An alkylene oxide is reacted with the hydrocarbyl thiophosphonic acid in about an equimolar basis in the absence of catalyst to form the mono-hydroxyalkyl thiophosphonate additives of this invention. The preparation of this component is fully described in U.S. 3,272,744 and this disclosure is incorporated in the present application.

The basic amino nitrogen-containing copolymer is an addition-type polymer 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, said polymer containing 0.05 to 3.5 weight percent thereof, of basic amino nitrogen.

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 naphthenic 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 percent. 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 ammonio, 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.

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'-azodiisobutyronitrile. The polymerization processes usually are carried out in an inert atmosphere, e.g. nitrogen or carbon dioxide, at temperatures ranging from 30° C. to 150° C., depending on the catalyst used and generally at temperatures between 50° C. and 70° C. when alpha, alpha'-azodiisobutyronitrile is used as the 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. 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 percent with the preferred concentration ranging from about 1 to 4 percent.

The calcium carbonate overbased calcium sulfonate component of the lubricating oil is characterized by consisting of from about 5 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.

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, 135–160° 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. 3,537,996 and the disclosure of this reference is incorporated herein.

The motor oil composition of the invention was tested in a laboratory engine test designed to simulate extreme service conditions and called an "Oxidative Oil Test" and in a road test. In the laboratory engine test, 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 fiberglass insulation around 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 water temperature.

The engine in the laboratory engine test was operated under the following conditions:

Engine speed, r.p.m. -----	3200
Load, BHP -----	105
5 Jacket outlet, ° F. -----	233±2
Intake air, ° F. -----	115
Exhaust back pressure, in Hg -----	5
Oil pressure, p.s.i. ----- min--	30
Spark advance, ° BTC -----	32
10 Air-fuel ratio -----	14.0±.5

The base oil, designated Base Oil A, employed in preparing the lubricating oils of the invention was a blend of mineral oils of lubricating viscosity having the following inspection tests.

15 Gravity, ° API -----	31.0
Flash, COC° F. -----	410
Viscosity, SSU at—	
0° F. (extrap.) -----	7500
20 100° F. -----	160
210° F. -----	44

The compositions of a lubricating oil of the invention and a comparison oil on a weight percent basis and the terminal increase in viscosity are set forth in the table below:

TABLE I.—OXIDATIVE OIL TEST

Motor oil -----	A	B	C	D	E
Base oil A -----	92.56	92.06	92.03	92.06	92.06
30 Mono (2-hydroxyethyl) polybutene (1,100 average mol wt. thiophosphonate) -----	3.00	3.00	3.00	3.00	3.00
Basic amino nitrogen-containing addition type methacrylate copolymer ¹ -----	2.00	2.00	2.00	2.00	2.00
Zinc isopropyl methyl isobutyl carbonyl dithiophosphate -----	1.09	1.09	1.09	1.09	1.09
35 Calciumcarbonate overbased calcium sulfonate ² -----	1.35	1.35	1.35	1.35	1.35
2,2'-diethyl-4,4-tertiary dioctyldiphenylamine ³ -----		0.5			
Anti-oxidant 450 ⁴ -----			0.5		
Dimethylaniline -----				0.5	
Anti-oxidant 237 -----					0.5
40 Terminal increase in viscosity at 100° F., percent -----	741	113	543	666	790

¹ Copolymer of butyl, lauryl, stearyl and dimethylaminoethyl methacrylates in 21.53:22.4 weight ratio.

² Approximately 15 moles of dispersed calcium carbonate per mole of calcium sulfonate, 300 TBN.

³ Commercial mixture in which approximately 1/2 is 2,2'-diethyl-4-tert-octyldiphenylamine.

45 ⁴ Commercial anti-oxidants.

Run B in the above table illustrates the surprising and outstanding improvement in Motor Oil B as compared to other motor oil compositions including Motor Oils C, D and E which contained a variety of oxidation inhibitors. Under the extreme conditions of this test, Motor Oil B experienced a 113% increase in viscosity as measured at 100° F. while Motor Oils A, C, D and E had viscosity increases ranging from over 500 percent to as high as 790 percent.

Motor Oil B passed the ASTM sequence Test IIIC by a wide margin as shown by the following table.

TABLE II.—ASTM SEQUENCE TEST IIIC

	Motor Oil B	Specification to pass
60 Test hours -----	64	64
Percent viscosity increase 100° F. at 40 hours -----	64.0	1400
Average engine sludge -----	9.9	29.0
Piston skirt varnish -----	9.9	29.5
Oil ring land faces -----	9.3	26.0

¹ Maximum.

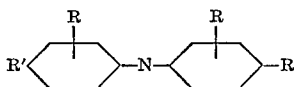
² Minimum.

Motors Oils A and B above were tested in a high speed road test. The cars used were 1969 Cadillacs equipped with 472 CID engines. A rooftop carrier was mounted on each car to provide 1062 additional square inches of frontal area. These vehicles were operated at a speed of 80 miles per hour. Under the noted operating conditions, the jacket outlet temperature in the engine ranged from 240–245° F. and the oil temperature varied 75 from 300–315° F.

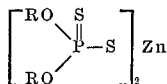
The viscosity curve of Motor Oil A broke sharply when the car employing this oil reached 2600 miles. In contrast, the viscosity curve of Motor Oil B broke sharply when the car employing this oil reached 5700 miles. This road test demonstrated a surprising and unexpected improvement in Motor Oil B, or a 100% plus improvement over Motor Oil A. The test results were in good correlation to the laboratory test results on the same oils.

We claim:

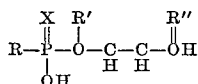
1. A lubricating composition resistant to oxidation at bulk oil temperatures of 300° F. and above comprising a major proportion of a mineral lubricating oil containing from about 0.1 to 2.5 percent of an alkylated diphenylamine represented by the formula:



in which R is an alkyl radical having from 1 to 4 carbon atoms and R' is an alkyl radical having from about 4 to 16 carbon atoms, 0.1 to 5.0 percent of a zinc dithiophosphate represented 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 percent of monohydroxyalkyl hydrocarbyl thiophosphonate having the general formula:



in which R is a hydrocarbyl radical having at least 12 carbon atoms, R' and R'' 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 percent 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 0.1 to 3.0 percent by weight of basic

amino nitrogen and having an inherent viscosity of 0.1 to 3.0, and from 0.25 to 3.5 percent of calcium carbonate overbased calcium sulfonate having from about 5 to 30 moles of dispersed calcium carbonate per mole of calcium sulfonate and having a Total Base Number ranging from about 100 to 300.

2. A lubricating composition according to claim 1 in which the R in said alkylated diphenylamine is an ethyl radical and R' is a tertiary radical having from about 6 to 12 carbon atoms.

3. A lubricating composition according to claim 1 in which said alkylated diphenylamine is essentially 2,2'-diethyl-4,4'-tert. dioctyldiphenylamine.

4. A lubricating composition according to claim 1 in which the olefin portion of said hydroxyalkyl hydrocarbyl thiophosphonate has a molecular weight from about 600 to 5000.

5. A lubricating composition according to claim 1 in which said zinc dithiophosphate is zinc isopropyl methyl isobutyl carbinyl dithiophosphate.

6. A lubricating composition according to claim 1 in which said basic amino nitrogen-containing addition type methacrylate copolymer is a copolymer of butyl, lauryl, stearyl and dimethylaminoethyl methacrylates in approximately 21:53:22:4 weight ratios respectively.

7. A lubricating composition according to claim 1 in which said calcium carbonate overbase calcium sulfonate contains about 15 moles of dispersed calcium carbonate per mole of calcium sulfonate and has a Total Base Number of about 300.

8. A lubricating composition according to claim 1 in which the mineral lubricating oil has an SUS at 100° F. from 70 to 300.

References Cited

UNITED STATES PATENTS

3,232,873	2/1966	Wilson et al.	252—32.7
3,216,936	11/1965	Le Suer	252—32.7
3,493,516	2/1970	Allphin et al.	252—32.7
3,462,367	8/1969	Booher	252—33

CARL F. DEES, Primary Examiner

U.S. Cl. X.R.

252—46.7, 402