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UNSYMMETRICAL KETONES IN LUBRICATING OIL

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The present invention relates to mineral oil base lubricants of improved cleaning ability. The composition of the invention contains a sulfonate detergent in a mineral lubricating oil base and also includes an unsymmetrical long-chain ketone as a cleaning assistant.

As a result of less than perfect conditions of combustion in the operation of internal combustion engines, carbonaceous materials comprising carbon, gum, lacquer, etc., are deposited on cylinder walls, piston heads, valves, etc. These deposits may eventually build up to such an extent that the rings and/or valves stick, even though improved methods of refining motor fuels and lubricants have greatly reduced the amount of carbon and gum which is formed in an engine. Complete elimination of the deposit-forming agents has not been found practically possible and, furthermore carbon-free operation is dependent not only upon the fuel and lubricant but also upon proper engine performance. Because of the variety of conditions under which engines are operated, many of the conditions being adverse to proper engine performance, carbonaceous deposits are inherently formed. When these deposits have built up to such an extent that engine operation becomes uneconomical or when the engine fails to operate at all, costly mechanical repairs are required to recondition the engine. Deposits may similarly cause trouble in other automotive parts such as in automatic transmissions.

Although it is known that lubricating oil may contain sulfonates, particularly those of the alkaline earth metals to impart a detergency effect, that is, help to keep the carbonaceous waste products in suspension in the lubricating oil, the composition of this invention gives not only a mere suspensory effect on these waste products but goes beyond this to actually provide for the removal from engine parts of gums, lacquers, etc. which have previously been deposited on them. Even occasional use of the lubricant composition of this invention provides for rehabilitation of engines having sticky valves, clattering lash adjusters, etc., while continual use of the composition of the invention can provide for removal of the deposits as they are formed.

In accordance with this invention, unsymmetrical long chain ketones may be successfully used in sulfonate-containing engine oils as a cleaning assistant for resinous oxidation and condensation products of fuel and lubricating oil. In a series of tests results have indicated that these ketones are effective agents in freeing both sticking hydraulic type lash adjusters as well as intake and exhaust type valves. Cleaning of varnish deposits from engine parts is reflected in the improvement in engine performance ratings when the ketones are used in both low and high temperature tests. The composition of this invention is of utility as a component of an engine oil to prevent the accumulation of deposits in critical areas such as the ring belt and close tolerance parts where deposits inhibit the proper functioning of these parts. The composition also includes hydraulic transmission fluids, such as are used in automotive automatic transmissions. The lubricant composition may contain as little as 0.05% of the unsymmetrical ketone for "maintenance" purposes or as much as 20% for "rehabilitation" purposes, with certain areas in this range being preferred, depending on the contemplated use. As a rehabilitating fluid the unsymmetrical ketone is most advantageously used in about a 5 to 10 or 20% concentration in a high sulfonate detergent lubricating oil; as a component of compounded engine oil to give continuous solvency for resinous oxidation and condensation products of fuels and oils, the concentration may be lower, for instance, ranging from about 0.05 to 1.5% on a weight basis.

The unsymmetrical ketones used in the composition of this invention contain a lower alkyl carbonylic group attached to a long chain aliphatic radical of about 10 to 20 carbon atoms, preferably straight chain alkyl radicals varying from undecyl (C_{11}) to heptadecyl (C_{17}). The lower alkyl group has 1 to about 4 or more carbon atoms. Mixtures, preferably eutectic mixtures, of unsymmetrical ketones in the range outlined may be used. The preferred unsymmetrical ketone is an eutectic blend of about 4 parts methyl pentadecyl ketone to about 1 part methyl heptadecyl ketone. Since these compounds have high boiling points (B.P. of the 80:20 eutectic mixture—165° C. (330° F.)/3 mm.), they are not volatilized by engine temperatures and remain in the crankcase to give continuous solvent action for the normal drain interval of 1000 to 2000 miles. The flash point of this 80:20 eutectic ketone mixture is 255° F.

Commercially, these unsymmetrical ketones can be manufactured by passing the vapors of an acid, e.g. acetic acid, and a selected long chain fatty acid over an alkaline earth oxide catalyst at 400–500° C. Symmetrical ketone formation is suppressed by using an excess of the lower alkyl carboxylic acid. The reaction is, for example, as follows:

$$RCOOH + CH_3COOH \xrightarrow[\text{alkaline earth oxide}]{400\text{–}500^\circ\ C.} RCOCH_3 + CO_2 + H_2O$$

Unsymmetrical ketones in the weight range referred to are soluble in refined Mid-Continent, coastal naphthenic and Pennsylvania stocks or blends of these base lubricating oil stocks.

The lubricant composition of the invention contains an oil soluble basic alkaline earth metal salt of an aromatic sulfonic acid as an essential ingredient. The sulfonate is most frequently of calcium or barium and may be derived, for example, from the oil-soluble sulfonic acids produced in the treatment of aromatic-containing petroleum hydrocarbons with a sulfonating agent such as sulfuric acid or sulfur trioxide. The preferentially oil-soluble sulfonic acids, generally referred to as mahogany acids, are conveniently employed as a concentrate in the oil from which they are derived and may be prepared by sulfonating a suitable petroleum distillate with fuming sulfuric acid to obtain approximately a 10 weight percent concentration of mahogany acid in the acid oil, or by sulfonating with sulfur trioxide, in which case approximately a 20% concentration can be obtained. In the example recited below the barium sulfonate is a 20% concentrate in mineral oil; the calcium sulfonate is a 10% concentrate. The useful mahogany acids generally have a molecular weight of from about 300 to 500, or more, and although their exact chemical structures may vary, it appears that such acids are composed to a large extent of sulfonated aromatic hydrocarbons having either one or two aromatic rings per molecule possibly with one or more long-chain alkyl groups containing from about 8 to 30 carbon atoms attached to the ring nuclei. Suitable sulfonic acids in-

clude the alkylated benzene sulfonic acids, and alkylated naphthalene sulfonic acids. Other useful aromatic sulfonic materials for conversion to the basic alkaline earth form are the oil-soluble ammonia neutralized sulfonated mixtures of polyalkylated benzenes; alkyl aryl sulfonic acids in which the alkyl chain contains from about 8 to 18 carbon atoms; synthetic sulfonic acids prepared by reaction of paraffin wax chains of 20 or more carbons with aromatic nuclei which are then sulfonated by fuming sulfuric acid, e.g. wax substituted naphthalene; ammonium mahogany sulfonic acids obtained by reaction of ammonia with sulfuric acid treated hydrocarbon oil, ammonium sulfonates of the alkyl aryl sulfonic acids, particularly those having a monocyclic nucleus, all of which are available or may be readily prepared by known methods.

These sulfonic materials may be converted into the basic alkaline earth metal salts by reaction of the acid oil or ammonium sulfonate with an excess of a basic compound of the metal, with ammonia removal where necessary, to obtain a basic sulfonate of higher metal content than the normal or neutral salt. Generally, at least about 1.5 equivalents of the barium compound are reacted while in the case of calcium at least about 1.2 equivalents are reacted. If desired, the basic metal sulfonate can be carbonated by treatment with carbon dioxide as at atmospheric or slightly elevated pressure until the strong basicity of the sulfonate is reduced from a pH of about 14 to a pH between about 7 and 8.

In the practice of this invention a basic barium sulfonate canbe prepared by reacting a sulfonated sweet West Texas gas oil fraction with a theoretical excess of basic barium oxide. Although the mahogany acids may, for example, contain a sulfonate concentration of about 10%, introduction of barium (3.5%) gives a barium sulfonate concentration of about 13%. The sulfonate is generally employed in the amount of about 0.3 to 10%, preferably about 0.5 to 2% by weight, on an oil-free basis, in the composition of this invention.

The lubricants may contain an oxidation inhibitor such as a zinc or other heavy metal dialkyl dithiophosphate diester. A typical zinc dialkyl dithiophosphate is one in which the alkyl is the residue of a C_6–C_7 alcohol. These dithiophosphates are blended in the lubricant generally in the amount required to impart oxidation resisting characteristics. Such an amount may be about 0.2 to 4% by weight of the finished lubricant. A preferred dialkyl dithiophosphate is, for example, zinc dimethylamyl dithiophosphate which may be made by reacting the acid ester from the reaction of methyl amyl alcohol with P_2S_5, with zinc metal or zinc oxide to form the neutral reaction product. Other useful oil-soluble metal dithiophosphates contain generally about 3 to 18 carbon atoms preferably 6 to 12, in each ester group. Also, other dithiophosphates, such as nickel dithiophosphates may be substituted for part or all of the zinc salt for improved stability or anticorrosive characteristics. The zinc dithiophosphate used in the examples below was added as a 50% concentrate in mineral lubricating oil.

An anti-wear agent, which may be one or a combination of additives, may be used to impart extreme pressure properties. The combination usually includes sulfurized fatty esters, fatty oils or saturated or olefin hydrocarbons. These materials have been found necessary if the lubricant is to maintain its extreme pressure usefulness under high speed conditions. A preferred type of sulfurized fatty ester or fatty oil containing about 5 to 15% sulfur is made by treating sperm oil with about 12% sulfur at 340 to 350° F. for 6 hours, with a 1 hour air blow at 250° F.

The other sulfurized materials are usually prepared by the reaction of hydrocarbons, preferably branched chain, of 8–32 carbon atoms with sulfur and comprise about 25 to 75% sulfur by weight. Although sulfurized hydrocarbons having as little as 10% sulfur by weight are sometimes used, the more highly sulfurized materials, in an amount from about 0.5 to 5% by weight of the lubricant composition, are most often used to give a fully satisfactory multi-purpose material. Along with a sulfurized hydrocarbon, other materials can be used to help this material impart the desired extreme pressure properties to the lubricant. Among these materials are chlorinated hydrocarbons, and phosphosulfurized mineral oil. Of course all of the components of these additives are selected to give materials soluble in the base mineral oil.

The mineral oil base stock conventionally used is of lubricating viscosity and can be, for instance, a solvent extracted or solvent refined oil obtained in accordance with conventional methods of solvent refining lubricating oils. Generally, lubricating oils have viscosities from about 35 to 250 SUS at 210° F. The base oil may be derived from paraffinic, naphthenic, asphaltic, or mixed base crudes, and if desired, a blend of solvent treated Mid-Continent neutrals and Mid-Continent bright stocks may be used.

When the composition of the invention is to be used for rehabilitating a dirty engine, a concentrate may be used. A pint of this concentrate is suitable for dilution with lubricating oil to make up 4 or 5 quarts of crankcase oil, giving a lubricant of about 1% ketone concentration.

Typical formulations for the concentrate are as follows:

	Weight
Mid-Continent base stock (vis. 100–110 SUS at 100° F.)	62.00
Barium sulfonate (20% concentrate)	25.00
Zinc dialkyl dithiophosphate (50% concentrate)	1.50
V.I. improver	1.50
Unsymmetrical ketone	10.00
W. Texas naphthenic base stock (vis. 100–200 SUS at 100° F.)	52.00
Barium sulfonate (20% concentrate)	35.00
Zinc dialkyl dithiophosphate (50% concentrate)	1.50
V.I. improver	1.50
Unsymmetrical ketone	10.00
Pennsylvania base stock (vis. 100–145 SUS at 100° F.)	63.00
Barium sulfonate (20% concentrate)	25.00
Zinc dialkyl dithiophosphate (50% concentrate)	1.50
V.I. improver	0.50
Unsymmetrical ketone	10.00

Typical formulations for a compounded engine oil containing the unsymmetrical ketone are as follows:

Mid-Continent base stock (Saybolt vis. 100–110 SUS at 100° F.)	70.25
Barium sulfonate (20% concentrate)	25.00
Zinc dialkyl dithiophosphate (50% concentrate)	1.70
V.I. improver	1.70
Anti-wear agent	1.25
Unsymmetrical ketone	0.10
W. Texas naphthenic base stock (Say. vis. 100–200 SUS at 100° F.)	60.20
Calcium sulfonate (10% concentrate)	35.00
Zinc dialkyl dithiophosphate (50% concentrate)	1.50
V.I. improver	2.00
Anti-wear agent	1.25
Unsymmetrical ketone	0.05
Pennsylvania base stock (Say. vis. 150 SUS at 100° F.)	71.65
Barium sulfonate (20% concentrate)	25.00
Zinc dialkyl dithiophosphate (50% concentrate)	1.50
V.I. improver	0.50
Anti-wear agent	1.25
Unsymmetrical ketone	0.10

All the above formulations may be blended at 150° F. and filtered before packaging.

EXAMPLES AND TESTS

Example I

A lubricant composition was made of the following ingredients in the following proportions:

Component:	Weight percent
Neutral petroleum lubricating oil	80.25
Basic barium petroleum sulfonate (approx. 20% conc. in petroleum oil)	14.10
Zn dialkyl (C_6–C_7 alcohols) dithiophosphate (about 50% conc. in petroleum oil)	2.20
Sulfurized sperm oil (12% S) antiwear agent	1.25
"Acryloid" polyacrylate V.I. improver	1.20
80:20 eutectic mixture of methyl pentadecyl and methyl heptadecyl ketones	1.0

This composition was put in the crankcase of 16 automobiles in place of the crankcase oil they had been using. Each of the cars had one or more sticking lash adjusters or intake valves at the time the lubricant of this invention was applied.

The criterion for judging improvement in engine operation was the disappearance of the clatter associated with a sticking lifter or the smooth running of an engine which had a sticking valve.

Detailed below in Table I is a list of cars in which the sticking lifters were freed. In the first group are examples of sticking lifters which were freed and the condition did not reoccur. In the second group are examples wherein the sticking reoccurred in mileages ranging from 5000 to 8000 miles. This group was relieved by a second treatment after the 5000 to 8000 miles interval. The table below records the number of miles of operation of each car required to relieve the conditions using the composition of the invention.

TABLE I

Car No.	Make	Miles to Lifter Freeing
1	Oldsmobile	25
2	Buick	50
3	Oldsmobile	25
4	Cadillac	75
5	Buick	50
6	Oldsmobile	35
7	Chrysler	25
8	Chrysler	25
9	Buick	10
10	Chevrolet	Unknown
GROUP II		
11	Buick Super	25
12	Chrysler	50
13	Oldsmobile	75
14	Buick	20

Cars No. 15 and No. 16 each having an intake valve giving intermittent sticking and, as a result, rough engine operation, were freed after treatment with the 1% ketone lubricant in approximately fifteen miles of driving.

Example II

A composition was made by incorporating 1% methyl heptadecyl ketone in a lubricant having the same ingredients as the lubricant of Example I in the following proportions.

Component:	Weight percent
Neutral base oil	81.25
Barium sulfonate	14.10
Zn dialkyl dithiophosphate	2.20
Sperm oil	1.25
"Acryloid" V.I. improver	1.20

This lubricant blend was subjected to a low temperature test (EL–2) which simulated stop and go driving. The test consists of 60 hours of running the engine under alternating cycling conditions of high and low temperatures (four hours each) with engine demand at a maximum of 20 horsepower. The overall rating in this test (No. 1545) was 84.5 with piston skirt and cylinder wall ratings being 5.0 respectively. Most engine oils have a rating that averages only 77.0 to 80.0 when evaluated by this test method. The engine was reassembled without cleaning or other changes and run under L–4 conditions (Test No. 1546), which comprised a simulated 36 hour drive at 60 m.p.h. The inspection results, which use the same criterion scale as the EL–2 test, showed that the engine rating had improved to 95.0 and there was no evidence of varnish or gum.

Example III

To an oil having the composition of the lubricant described in Example II, and also to a "MIL–O–2104" oil comprising the same ingredients in the following proportions:

Component:	Weight percent
Neutral oil	91.2
Barium sulfonate	7.0
Zn dithiophosphate	1.8

10 cc. samples of a standard synthetic insoluble oxidized oil sludge were added. The first, ketone-containing, oil disperses the insoluble sludge and keeps it in suspension. In the MIL oil, the same quantity of insoluble sludge precipitates as a black, heavy tar. When the experiment is repeated using a 5% concentration of the eutectic ketone mixture of Example I in the MIL oil, both the oils disperse the insoluble synthetic sludge. These tests indicate that the unsymmetrical ketone lubricant has solvency for petroleum oxidation and condensation products enabling the lubricant to dissolve and resuspend these products and can prevent the products from redepositing on vital engine parts. The same type of test, using cyclic, symmetrical, and aromatic ketones such as isophorone, 8-pentadecanone and phenyl undecyl ketone in place of the methyl unsymmetrical ketones indicate that the former ketones are not as efficient.

Example IV

5 percent methyl amyl ketone was used in the MIL–O–2104 lubricant of Example III in place of the methyl heptadecyl ketone. This oil was subjected to a test which comprised mixing 70 cc. of the oil under test, 10 cc. of a carbon dispersion oil (0.25% carbon black in a neutral oil) and 10 cc. of solvent dispersed oil-insoluble, resinous synthetic sludge. Each oil mixture is placed in a stoppered glass graduate which is inverted to mix and then heated in an open container to 150° F. for about one minute to drive off volatiles. Each oil is then poured over a steel plate. If the resinous oxidation material is dispersed, the oil remains clear. If the sludge is not dispersed, it will collect as a tarry black residue on the bottom of the beaker and can be poured onto the plate while still warm.

The original dispersancy of the lubricant to which methyl amyl ketone had been added was almost as good as the oil containing the methyl heptadecyl ketone, however, after the former had settled for approximately one hour, the suspended and dissolved sludge precipitated. The sample was reheated to 150° F. and the deposit was partly resuspended but the bulk of it remained on the bottom of the beaker. Increasing the temperature to 200° F. did not appear to bring more of the material into solution or suspension. A parallel experiment using a 40% methyl heptadecyl ketone and a 60% methyl pentadecyl ketone mixture in a 5% concentration in the MIL oil gave a nearly clear solution. On the cooling and setting for a similar period, a light readily dispersable precipitate came down. On reheating most of this material was redissolved giving a clear oil. On cooling, the same general amount and type of precipitate reappeared.

Example V

The superior cleaning properties of long chain unsymmetrical ketones is illustrated by use in an automatic transmission fluid in an automobile with a three speed Torque Flight automatic transmission having approximately 36,000 miles of service. The transmission developed trouble over a period of time: it would not down shift to low gear and, in general was sluggish. The transmission fluid used in the operation was a commercial mineral oil base transmission fluid containing a basic barium petroleum sulfonate. A quart sample of this transmission fluid drawn from the car was olive green in color.

A transmission fluid may generally be made up of the following ingredients in percent by weight:

12% basic barium sulfonate concentrate	12
55–60% barium dithiophosphate concentrate	0.72
Sulfurized sperm oil (12% S)	2.5
Methacrylate V.I. improver	3.5
Dimethyl silicone anti-foam agent	0.002
Lanolin	0.5
Base lubricating oil	Rest

A replacement quart of transmission fluid was made up having a 10% concentration of the 60–40 mixture of methyl hepta- and pentadecyl ketone, the balance being similar to the transmission fluid described above. This make-up quart was put in the automatic transmission which had a 10 quart capacity. In about 300 additional miles of operation, the transmission would down shift on demand and would go through its three speed shift sequence as well as when the unit was new. The fluid was drained and a sample collected. The fluid was now black and had an appreciable increase in viscosity. The color and viscosity change along with the substantial improvement in operation of the transmission demonstrated that the methyl hepta- and pentadecyl ketone mixture had dissolved and suspended the resinous oxidation products and permitted the unit to operate without expensive overhaul. The refilled unit continued to give good service and the car was subsequently sold.

We claim.

1. A lubricant composition consisting essentially of about 0.3 to 10% of a basic oil-soluble aromatic sulfonate of an alkaline earth metal and a small amount, sufficient to enhance the cleaning ability of the lubricant, of a dialkyl ketone, one of said alkyl groups having 1 to about 4 carbon atoms and the other alkyl group having about 10 to 20 carbon atoms, in a mineral oil base of lubricating viscosity.

2. The lubricant composition of claim 1 in which an alkyl group is methyl.

3. The lubricant composition of claim 2 in which the ketone is present in the amount of about 0.5 to 1.5% by weight.

4. The lubricant composition of claim 2 in which the ketone is present in the amount of about 5 to 10% by weight.

5. The lubricant composition of claim 2 in which the higher alkyl is straight chain.

References Cited in the file of this patent

UNITED STATES PATENTS

2,100,287	Conquest	Nov. 23, 1937
2,316,754	Backoff et al.	Apr. 20, 1943
2,350,145	Backoff et al.	May 30, 1944
2,799,650	McDermott et al.	July 16, 1957

OTHER REFERENCES

Georgi: "Motor Oils and Engine Lubrication," 1950, Reinhold Pub. Corp., pages 174–177.