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2,866,758

LUBRICANTS CONTAINING A DEPOSIT-
CONTROL ADDITIVE

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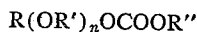
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8 Claims. (Cl. 252-57)

This invention relates to a lubricating oil containing a novel class of additives which act to control deposits in the combustion zone and to minimize the effects of deposits resulting from the combustion of the fuel, particularly under low temperature conditions. More specifically, this invention discloses that superior lubricating oils from the standpoint of removal of low temperature deposits, are obtained by addition of a minor amount of mixed carbonic acid diester of an aliphatic alcohol and of a polyglycol monoether.

As automobile manufacturers annually raise the compression ratio of their engines in the race for higher horsepower, the problem of engine deposits resulting from the fuel becomes increasingly more severe. Engine deposits which find their origin in the fuel are primarily responsible for surface ignition phenomena such as pre-ignition and octane requirement increase (ORI) which is the tendency of spark ignition engines in service to require higher octane fuels for proper performance. There are two avenues by which this problem can be attacked. One approach is through the fuel and the other approach is through the lubricating oil. In our copending application filed of even date, Serial No. 559,761, it is disclosed that superior hydrocarbon fuels from the standpoint of engine deposits result from the incorporation of mixed carbonic acid diester of an aliphatic alcohol and of a polyglycol monoether. The subject application involves the discovery that the addition of mixed carbonic acid diester of an aliphatic alcohol and of a polyglycol monoether to a lubricating oil produces a lubricant marked by the ability to maintain a clean engine even with dirty fuels under low temperature conditions of operation.

The improved lubricating oils of this invention contain a mixed carbonic acid diester of an aliphatic alcohol and of a polyglycol monoether of the general formula



wherein R is an monovalent hydrocarbon radical containing 6 to 18 carbon atoms, R' is a divalent aliphatic hydrocarbon radical containing 2 to 3 carbon atoms, R'' is an aliphatic hydrocarbon radical containing 1 to 14 carbon atoms, and n is an integer having a value of 3 to 15. The mixed carbonic acid diesters of an aliphatic alcohol and of a polyglycol monoether of prescribed composition, hereafter called "mixed carbonic acid diesters," are effective in lubricating oils in concentrations as low as 0.2 volume percent, but concentrations of 0.5 to 3.0 volume percent are normally employed. There is no critical upper limit of concentration, but economic considerations dictate that concentrations less than 5.0 volume percent "mixed carbonic acid diesters" be present in the lubricating oil.

In our copending application Serial No. 559,762, filed of even date, now Patent No. 2,821,538, the "mixed carbonic acid diesters" employed as a lubricating oil additive in this invention are claimed as novel chemical compounds and their preparation is described in detail.

This invention also contemplates a process for main-

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taining an internal combustion engine free from deposits, particularly those formed during low temperature operation, by the presence of a "mixed carbonic acid diester" in the combustion zone. This can be effected by using a fuel containing "mixed carbonic acid diesters" as disclosed in the aforescribed copending application, by using a lubricant containing a "mixed carbonic acid diester" as described herein, by employing a fuel and lubricant both of which contain a "mixed carbonic acid diester," or by adding a "mixed carbonic acid diester" to either the fuel, lubricant or both during engine operation. In the latter mode of operation, a "mixed carbonic acid diester" is added to the gasoline in an amount to constitute 0.01 to 1.0 volume percent of the fuel and/or to the lube to constitute 0.5 to 5 volume percent of the lubricating oil.

In general, "mixed carbonic acid diesters" which inhibit the deposit-forming tendencies of hydrocarbon fuels are prepared by a series of reactions involving the reaction of phosgene with a hydroxy compound to form a chloroformate which is subsequently reacted with another hydroxy compound. One reaction procedure involves the formation of a chloroformate by reaction of phosgene with a polyglycol monoether and subsequent reaction of the chloroformate with an aliphatic alcohol in the presence of a hydrogen chloride acceptor such as pyridine or quinoline. An alternate reaction procedure involves formation of chloroformate by reaction of an aliphatic alcohol with phosgene and subsequent reaction of the chloroformate with a polyglycol monoether in the presence of a hydrogen chloride acceptor.

The lubricating oil of this invention is effective in maintaining deposits at a low level with the result that an engine lubricated therewith shows exceptionally clean cylinder head, combustion space, valves and ring belt area. The low deposit level in the engine minimizes surface ignition in all its manifestations, mainly preignition and "knock." In addition, the low deposit level reduces the engine's octane requirement increase. Deposits on surfaces contacted by the additive-containing lubricating oil, such as piston skirts and cylinder walls, are very markedly reduced.

"Mixed carbonic acid diesters" usable in the lubricants of this invention are exemplified by the following: the carbonic acid diester of amyl alcohol and of pentaethylene glycol monodecylphenyl ether, the carbonic acid diester of ethyl alcohol and of pentapropylene glycol mono-octylphenyl ether, the carbonic acid diester of lauryl alcohol and of pentaethylene glycol monoamylphenyl ether, the carbonic acid diester of methyl alcohol and of decaethylene glycol monolauryl ether, the carbonic acid diester of amyl alcohol and of octaethylene glycol mono-octyl ether, the carbonic acid diester of octyl alcohol and of decapropylene glycol monohexyl ether, the carbonic acid diester of 2-ethylhexyl alcohol and of pentapropylene glycol mono-octyl ether, the carbonic acid diester of myristyl alcohol and of pentaethylene glycol monoheptyl ether, the carbonic acid diester of nonyl alcohol and of hexaethylene glycol monolauryl ether and the carbonic acid diester of poly-oxyethylene-oxy-1,2-propylene mono-octyl ether (av. mol. wt. 600).

It is necessary for the "mixed carbonic acid diesters" to have the prescribed formula in order to operate effectively as deposit-control additives. As will be demonstrated later, related carbonates are ineffective as deposit-control additives. Carbonic acid esters such as di(2-butoxyethoxyethyl) carbonate and allyl ricinoleyl carbonate are ineffective as deposit-control additives. As a result of extensive experimentation, the following conclusions can be made as to the requirements of the additive molecule for the production of a "mixed carbonic acid diester" having deposit-control properties: (1) the

polyalkylene oxide radical, that is the $-(OR)_n-$ radical, must contain at least 3 repeating units and preferably 4 to 10 units, (2) the hydrocarbon monoether radical may be aliphatic or aryl in nature and should contain at least 6 to 18 carbon atoms and preferably 6 to 12 carbon atoms, and (3) the aliphatic hydrocarbon radical esterified with the carbonate radical should contain 1 to 14 carbon atoms and preferably 2 to 10 carbon atoms.

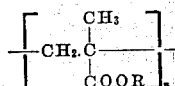
The "mixed carbonic acid diesters" are effective as a deposit-control additive in a concentration of at least 0.2 volume percent of the lubricant. The concentration of the "mixed carbonic acid diester" usually falls between 0.5 and 3.0 volume percent of the lubricant. Since the improvement in concentrations higher than 5.0 volume percent is only marginal, a practical upper limit is about 5.0 percent level even though there is no critical upper limit. Economic considerations also dictate that the additive concentration be less than 5 percent.

The "mixed carbonic acid diesters" of this invention are effective in controlling deposit formation in lubricants employed in spark ignition engines, diesel motors and gas turbines. However, these additives are normally used in motor oils for spark ignition engines wherein fuel derived deposits formed during low temperature operation are a particularly vexing problem. Diesel lubricants containing "mixed carbonic acid diesters" are effective in eliminating deposits resulting from the use of the so-called "economy" diesel fuels, i. e. fuels having a high sulfur content or containing cracked or residual stocks. "Mixed carbonic acid diesters" are also useful as deposit-control additives in gas turbine lubricants which are generally ester base lubricants; they are also useful in aviation oils which lubricate reciprocating aviation engines. The scope of the lubricating oils to which the "mixed carbonic acid diesters" of the invention are added to form superior lubricants is broad and includes mineral oils, synthetic lubricating oils and mixtures thereof.

The hydrocarbon mineral oils usable 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 used in the formulation of premium grade motor oils such as are contemplated in this invention. The lubricating 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 improve the pour of the oil. Broadly speaking, mineral lubricating oils having an SUS viscosity at 100° F. between 50 and 1,000 may be used in the formulation of the improved lubricants of this invention but usually the viscosity range falls between 70 and 300 at 100° F.

The mineral lubricating oils to which the "mixed carbonic acid diesters" are added usually contain other additives designed to impart other desirable properties thereto. For example, V. I. improvers such as the polymethacrylates are normally included therein as are materials which act as detergents and dispersants for the removed combustion chamber deposits. The detergent additives, such as basic barium sulfonate and barium alkyl phenolate, provide the required dispersing properties.

The V. I. improver normally used is a polymethacrylate of the general formula



wherein R is an aliphatic radical and n is an integer having a value of more than 1.

The most commonly used detergent-dispersant additive is an alkaline earth metal sulfonate such as calcium

petroleum sulfonate or barium petroleum sulfonate. These products are so well known as detergent-dispersant additives they require no further description. Similarly, divalent metal alkyl phenolates are widely used as detergents either alone or in combination with the alkaline earth metal petroleum sulfonates.

The most commonly used inhibitor and antioxidant is a divalent metal alkyl dithiophosphate which results from the neutralization of a P_2S_5 -alcohol reaction product with a divalent metal or divalent metal oxide. The most widely used inhibitors are barium and zinc alkyl dithiophosphates.

The synthetic lubricating bases are usually of the ester or ether type. High molecular weight, high boiling liquid aliphatic dicarboxylic acid esters possess excellent viscosity-temperature relationships and lubricating properties and are finding ever increasing utilization in lube oils adapted for high and low temperature lubrication; esters of this type are used in the formulation of jet engine oils. Examples of this class of synthetic lubricating bases are the diesters of acids such as sebacic, adipic, azelaic, alkenyl succinic, etc.; specific examples of these diesters are di-2-ethylhexyl sebacate, di-2-ethylhexyl azelate, di-2-ethylhexyl adipate, di-n-amyl sebacate, di-2-ethylhexyl-n-dodecyl succinate, di-2-ethoxyethyl sebacate, di-2'-methoxy-2-ethoxyethyl sebacate (the methyl Carbitol diester), di-2'-ethyl-2-n-butoxyethyl sebacate (the 2-ethylbutyl Cellosolve diester), di-2-n-butoxyethyl azelate (the n-butyl Cellosolve diester) and di-2'-n-butoxy-2-ethoxyethyl-n-octyl succinate (the n-butyl Carbitol diester).

Polyester lubricants formed by a reaction of an aliphatic dicarboxylic acid of the type previously described, a glycol and a monofunctional aliphatic monohydroxy alcohol or an aliphatic monocarboxylic acid in specified mol ratios are also employed as the synthetic lubricating base in the compositions of this invention; polyesters of this type are described in U. S. 2,628,974. Polyesters formed by reaction of a mixture containing specified amounts of dipropylene glycol, sebacic acid and 2-ethylhexanol and of a mixture containing adipic acid, diethylene glycol and 2-ethylhexanoic acid illustrate this class of synthetic polyester lubricating bases.

Polyalkylene ethers as illustrated by polyglycols are also used as the lubricating base in the compositions of this invention. Polyethylene glycol, polypropylene glycol, polybutylene glycols and mixed polyethylene-polypropylene glycols are examples of this class of synthetic lubricating bases.

The sulfur analogs of the above-described diesters, polyesters and polyalkylene ethers are also used in the formulation of the lubricating compositions of this invention. Dithioesters are exemplified by di-2-ethylhexyl thiosebacate and di-n-octyl thioadipate; polyethylene thioglycol is an example of the sulfur analogs of the polyalkylene glycols; sulfur analogs of polyesters are exemplified by the reaction product of adipic acid, thioglycol and 2-ethylhexyl mercaptan.

The action of "mixed carbonic acid diesters" in improving the deposit-removing properties of a lubricating oil was demonstrated by a modified Chevrolet deposits test—CRC-FL-2-650. The laboratory engines are operated under the standard conditions of this test with the exception that crankcase oil temperatures were 10° F. lower, the water jacket temperatures were 5° F. lower, and the crankcases of the test engines were ventilated. These modifications are in every case in the direction of making the test more severe and are intended to simulate low temperature conditions wherein deposit formation is most pronounced. After the termination of each run, the engine is disassembled and its parts are evaluated by a merit system adapted from the CRC-L-4-1252 test. This merit system involves visual examination of the engine part in question and their rating according

to deposits by comparison with standards which have assigned ratings. For example, a rating of 10 on piston skirt designates a perfectly clean piston while a rating of zero represents the worse condition. Similarly, a rating of 100 on total engine deposits represents a perfectly clean engine, etc.

In the following table are shown the results obtained in the modified Chevrolet deposits test with lubricating oils which possessed various concentrations of "mixed carbonic acid diesters." Base fuel A used in this test was a high quality regular grade gasoline comprising a mixture of thermal cracked stock, fluid catalytically cracked stock and straight run gasoline. This regular base fuel had a 87.0 ASTM research octane rating, contained 2.90 ml. of TEL per gallon, had an API gravity of 58.0 and a boiling range between 106° F. and 396° F.; the base fuel was negative in the copper corrosion test and had an oxidation stability in the ASTM test of 530 minutes minimum. The reference fuels also contained minor amounts of gasoline inhibitors, namely N,N'-disubstituted butyl paraffinylamine, lecithin, and N,N'-disubstituted-1,2-diaminopropane. Base fuel B had a 90.5 ASTM research octane rating, contained 2.67 ml. TEL per gallon, had an API gravity of 59.0 and a boiling range between 93 and 395; it was negative in the copper corrosion test and had an oxidation stability of 445 minutes minimum in the ASTM test.

The reference lubricating oil was a 20-20W heavy duty oil meeting supplement I requirements. This reference oil contained a methacrylate VI improver and a balanced combination of additives which impart detergent, dispersant and antioxidant properties to the oil. The additive mixture comprises a barium petroleum sulfonate, and a zinc alkyl dithiophosphate in which the alkyl group is a methylcyclohexyl radical.

TABLE

Engine cleanliness in the modified Chevrolet S-II test

	Piston Skirt	Total Engine Deposits	Concentration of Additive in Oil at Run Termination, Vol. Percent
Base Oil plus Base Fuel A.....	4.8	76.1	-----
Base Oil plus:			
Carbonic acid diester of allyl alcohol and of a polyethylene glycol monolauryl ether (av. mol wt. 600).....	6.8	83.8	2.5
Carbonic acid diester of allyl alcohol and of pentaethylene glycol monoethylphenyl ether.....	8.2	88.2	2.0
Carbonic acid diester of allyl alcohol and ricinoleyl alcohol.....	5.2	79.2	2.0
Base Oil plus Base Fuel B.....	6.0	79.9	-----
Base Oil plus:			
Di (2-butoxyethoxyethyl) carbonate.....	5.8	80.8	1.0
Di-isooctyl carbonate.....	5.7	81.7	4.0

The data in the above table clearly show that "mixed carbonic acid diesters" of prescribed compositions are effective deposit-control additives for lubricating oils. Piston skirt deposit and total engine deposit ratings of

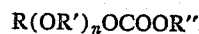
8.2 and 88.2, respectively, are excellent results in the low temperature deposits test.

It is also significant that carbonic acid diesters related to the "mixed carbonic acid diesters" of this invention are ineffective deposit-control lubricating oil additives. Some of the carbonate diesters shown in the foregoing table actually had a harmful effect on engine cleanliness.

Obviously, many modifications and variations of the invention, as hereinbefore set forth, may be made without departing from the spirit and scope thereof, and therefore, only such limitations should be imposed as are indicated in the appended claims.

We claim:

1. A lubricating oil containing a carbonic acid diester of an aliphatic alcohol and of a polyglycol monoether of the following general formula

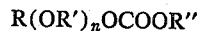


wherein R is a monovalent hydrocarbon radical containing 6 to 18 carbon atoms, R' is a divalent aliphatic hydrocarbon radical containing 2 to 3 carbon atoms, R'' is an aliphatic hydrocarbon radical containing 1 to 14 carbon atoms, and n has a value of 3 to 15, said carbonic acid diester being present in an amount sufficient to eliminate deposits formed during fuel combustion and to maintain a clean engine.

2. A lubricating oil according to claim 1 containing 0.2 to 5.0 volume percent of said carbonic acid diester.

3. A lubricating oil according to claim 1 containing 0.5 to 3.0 volume percent of said carbonic acid diester.

4. A mineral lubricating oil containing a carbonic acid diester of an aliphatic alcohol and of a polyglycol monoether of the following general formula



wherein R is a monovalent hydrocarbon radical containing 6 to 18 carbon atoms, R' is a divalent aliphatic hydrocarbon radical containing 2 to 3 carbon atoms, R'' is an aliphatic hydrocarbon radical containing 1 to 14 carbon atoms, and n has a value of 3 to 15, said carbonic acid diester being present in an amount sufficient to eliminate deposits formed during fuel combustion and to maintain a clean engine.

5. A lubricating oil according to claim 4 containing 0.2 to 5.0 volume percent of said carbonic acid diester.

6. A lubricating oil according to claim 4 containing 0.5 to 3.0 volume percent of said carbonic acid diester.

7. A lubricating oil containing 0.2 to 5.0 volume percent of a carbonic acid diester of allyl alcohol and of a polyethylene glycol monolauryl ether, said polyethylene glycol having an average molecular weight of 600.

8. A lubricating oil containing 0.2 to 5.0 volume percent of a carbonic acid diester of allyl alcohol and of pentaethylene glycol monoethylphenyl ether.

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