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MOTOR LUBRICATING OIL COMPOSITION

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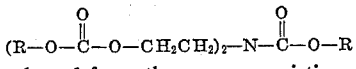
4 Claims. (Cl. 252—51.5)

This invention relates to motor lubricants containing a novel class of additives which reduce or suppress deposit formation in combustion engines. More specifically, this invention discloses that superior lubricating oils from the standpoint of removal of low temperature deposits are obtained by the addition of a minor amount of a carbonate derivative of diethanolamine of a prescribed composition.

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 preignition 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 is through the lubricating oil. In a co-assigned copending application filed of even date, Serial No. 627,563, it is disclosed that superior hydrocarbon fuels from the standpoint of engine deposits result from the incorporation of carbonate derivatives of diethanolamine of a prescribed composition. The present invention involves the discovery that the addition of these same carbonate derivatives of diethanolamine, which are also termed substituted urethane compounds, to a lubricating oil produce lubricants marked by the ability to maintain a clean engine even with dirty fuels under low temperature conditions of operation.

Modern lubricating oils for internal combustion engines usually contain a combination of additives which impart detergent and dispersant properties as well as resistance to oxidation to lubricating oils. The detergent and dispersant properties are normally obtained by the addition of alkaline earth metal petroleum sulfonates, alkaline earth metal salts of alkyl-substituted aromatic compounds or derivatives of these compounds. The most commonly used anti-oxidant and inhibitor is a divalent metal dialkyl dithiophosphate. Lubricating oils containing additives of these types are compounded to a supplement I level. Oils of suplement I level are very satisfactory lubricants for modern automobile engines from all standpoints with the exception of effectiveness in controlling deposits formed under low temperature conditions. The lubricating compositions of this invention are particularly designed for control of deposits resulting at low temperature conditions of operation.

The improved lubricating oils of this invention contain a carbonate derivative of diethanolamine hereinafter also referred to as a urethane compound having the following general formula:



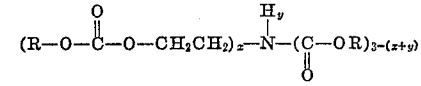
where R is selected from the group consisting of aliphatic radicals having from 1 to 8 carbon atoms and alkoxyalkyl radicals having from 2 to 10 carbon atoms, in an amount sufficient to reduce deposits.

The urethane compounds of this invention are effective in the lubricating oil 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 of the urethane compounds of the present invention be present in the lubricating oil.

This invention also contemplates a process for maintaining an internal combustion engine free from deposits, particularly those formed during low temperature operation, by the presence of a urethane compound of the above-described composition in the combustion zone. This can be effected by using a fuel containing a urethane as disclosed in the afore-described copending application, by using a lubricant containing a urethane as described herein, by employing a fuel and lubricant both of which contain a urethane compound or by adding a urethane compound to either the fuel, lubricant or both during engine operation. In the latter mode of operation, the urethane compound 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.

The urethane compounds which inhibit or suppress deposits through incorporation in the lubricating oil in accordance with this invention are readily formed by a series of reactions involving the formation of a chloroformate by reaction of phosgene with an alcohol and subsequently reacting the formed chloroformate with diethanolamine in the presence of a hydrogen chloride acceptor, such as pyridine or quinoline.

Our copending application Serial No. 627,564, filed of even date, claims as novel compounds carbonate derivatives of ethanolamines having the general formula:



wherein R is an aliphatic hydrocarbon radical or an alkoxyalkyl radical having from 1 to 18 carbon atoms, x is an integer ranging from 1 to 3, and y is either 0 or 1. The specific urethane compounds useful in this invention as lubricating oil additives are a subgenus of the novel compounds of that invention.

The lubricating oil composition of this invention is effective in maintaining deposits at a low level with the results 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 pre-ignition 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.

Examples of useful urethane compounds of this invention are as follows: ethyl urethane of diethanolamine bis (ethyl carbonate), allyl urethane of diethanolamine bis-(allyl carbonate), butyl urethane of diethanolamine bis-(butyl carbonate), propargyl urethane of diethanolamine bis(propargyl carbonate), n-amyl urethane of diethanolamine bis(n-amyl carbonate), 2-ethylhexyl urethane of diethanolamine bis(2-ethylhexyl carbonate), methoxyethyl urethane of diethanolamine bis(methoxyethyl carbonate), ethoxyethyl urethane of diethanolamine bis (ethoxyethyl carbonate), butoxyethyl urethane of diethanolamine bis(butoxyethyl carbonate).

A surprising feature of this invention is that compounds closely related to compounds falling within the general formula shown above are ineffective in deposit-control-

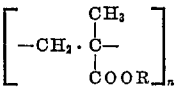
ling engine lubricants. For example, the compound tris(N-β-pentoxy-carboxyethyl) amine is totally ineffective while the urethane type compounds of the invention are excellent deposit-control additives.

The urethane compounds of this invention are effective in controlling deposit formation in lubricants employed in spark ignition engines, diesel motors and gas turbines. However, they 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 these urethane compounds are effective in eliminating deposits resulting from the use of the so-called "economy" diesel fuels, e.g., fuels having a high sulfur content or containing cracked or residual stocks. The urethane compounds 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 urethane compounds of the invention are added with the formation of superior lubricants from the standpoint of deposit-removal 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 urethane compounds of this invention 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 V.I. improver normally used is a polymethacrylate of the general formula:



wherein R is an aliphatic radical ranging from butyl to stearyl and n is an integer of more than one.

The most commonly used detergent-dispersant additive is an alkaline earth metal petroleum 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 anti-oxidant 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 mole 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 polyakylene glycols; sulfur analogs of polyesters are exemplified by the reaction product of adipic acid, thioglycol and 2-ethylhexyl mercaptan.

The action of the urethane compound 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 worst condition. Similarly, a rating of 100 on total engine deposits represents a perfectly clean engine, etc.

The fuel 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 an 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 fuel also contained minor amounts of gasoline inhibitors, namely, N,N'-di-secondary butyl-p-phenylene diamine, lecithin, and N,N'-disalicylidene 1,2-diamino propane.

The reference lubricating oil was a 20–20W heavy duty oil meeting supplement I requirements. This reference oil contained a methacrylate V.I. improver and a

balanced combination of additives which impart detergent, dispersant and anti-oxidant properties to the oil. The additive mixture comprised a barium petroleum sulfonate, and a zinc alkyl dithiophosphate in which the alkyl group is a methylcyclohexyl radical.

In Table I are shown the results obtained in the Modified Chevrolet Deposits Test with lubricating oils which showed additive concentrations of urethane compounds of this invention, for comparision, and the closely related compound tris(N - β - pentoxycarboxyethyl)amine. In these experiments the concentration of additive in the lubricant was determined at the conclusion of the run by analysis.

Table I

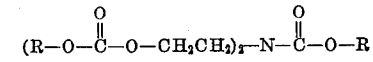
	Piston Skirt	Total Engine Deposits	Concentration Of Additive In Oil at Run Termination, Vol. Percent
Reference Oil	5.9	79.9	0
Reference Oil containing:			
tris (N-β-pentoxycarboxyethyl) amine	5.3	75.3	4.0
n-amyl urethane of diethanolamine, bis (n-amyl carbonate)	7.8	86.8	3.0
ethoxyethyl urethane of diethanolamine, bis (ethoxyethyl carbonate)	9.2	89.2	3.0

The data in Table I show that the urethane compounds of the prescribed formula are effective deposit control lubricating additives. The closely related tris(N-β-pentoxycarboxyethyl)amine was ineffective as a deposit control additive and actually gave dirtier piston skirt and total engine ratings pointing out the high specificity of the invention.

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:

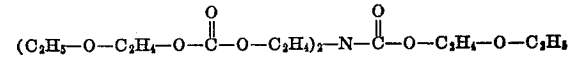
1. A lubricating oil containing a minor amount of a compound having the following general formula:



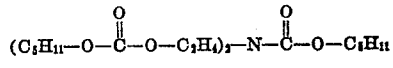
where R is selected from the group consisting of aliphatic hydrocarbon radicals having from 1 to 8 carbon atoms and alkoxyalkyl radicals having from 2 to 10 carbon atoms in an amount sufficient to improve the cleanliness properties of the lubricant composition.

2. The lubricating oil of claim 1 where the amount of the compound is from 0.2 to 5.0 volume percent.

3. A mineral lubricating oil containing from 0.5 to 3.0 volume percent of a urethane compound having the following formula:



4. A mineral lubricating oil containing from 0.5 to 3.0 volume percent of a urethane compound having the following formula:



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