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LUBRICANTS CONTAINING A DEPOSIT-CONTROL ADDITIVE

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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 glycol bis(glycol ether carbonate) of 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 approach is through the lubricating oil. In our copending application filed of even date, Serial No. 555,193, it is disclosed that superior hydrocarbon fuels from the standpoint of engine deposits result from the incorporation of glycol bis(glycol ether carbonates) of prescribed composition. The subject application involves the discovery that the addition of a glycol bis(glycol ether carbonate) of prescribed composition 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.

In our copending application, Serial No. 554,941 filed of even date, now abandoned, there are disclosed novel glycol bis(glycol ether carbonates) of the general formula

$$R'O(CH_2CH_2O)_nOCO(RO)_xCO(OCH_2CH_2)_nOR'$$

wherein R is a divalent aliphatic radical containing 2 to 3 carbon atoms, R' is a C_1 to C_{18} aliphatic hydrocarbon radical, x has a value of 1 to 14 and n has a value of 1 to 10. This invention involves the discovery that a particular subclass of these novel compounds acts as a deposit-control additive for hydrocarbon fuels.

The improved lubricating oils of this invention contain a glycol bis(glycol ether carbonate) of the general formula

$$R'O(CH_2CH_2O)_nOCO(RO)_xCO(OCH_2CH_2)_nOR'$$

wherein R is a divalent aliphatic hydrocarbon radical containing 2 or 3 carbon atoms, R' is an aliphatic hydrocarbon radical containing 2 to 18 carbon atoms, x has a value of 1 to 4 and n has a value of 1 to 4, in an amount sufficient to eliminate deposits formed during fuel combustion and to maintain a clean engine. The glycol bis(glycol ether carbonates) 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 glycol bis(glycol ether carbonate) 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 glycol bis(glycol ether carbonate) in the combustion zone. This can be effected by using a fuel containing glycol bis(glycol ether carbonate) as disclosed in the aforedescribed copending application, by using a lubricant containing a glycol bis(glycol ether carbonate) as described herein, by employing a fuel and lubricant both of which contain a glycol bis(glycol ether carbonate) or by adding a glycol bis(glycol ether carbonate) to either the fuel, lubricant or both during engine operation. In the latter mode of operation, the glycol bis(glycol ether carbonate) 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 0.2 to 5 volume percent of the lubricating oil.

The glycol bis(glycol ether carbonates) which inhibit the deposit-forming tendencies of hydrocarbon fuels are readily prepared by the series of reactions described in the afore-identified copending application. In general, the preparation involves the formation of a monochloroformate by reaction of phosgene with an ethylene or polyethylene glycol monoalkyl ether and subsequent reaction of the chloroformate with a glycol in the presence of a hydrogen chloride acceptor such as pyridine or quinoline. An alternate reaction procedure involves formation of a glycol dichloroformate by reaction of glycol with phosgene and subsequent reaction of the dichloroformate with ethylene or polyethylene glycol 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.

Glycol bis(glycol ether carbonates) usable in the lubricants of the invention are exemplified by the following: ethylene glycol bis(ethoxyethyl carbonate), ethylene glycol bis(2-butoxyethyl carbonate), ethylene glycol bis(pentyloxyethyl carbonate), ethylene glycol bis(decoxyethyl carbonate), diethylene glycol bis(ethoxyethyl carbonate), diethylene glycol bis(propoxyethyl carbonate), diethylene glycol bis(hexoxyethylcarbonate), diethylene glycol bis(octoxyethyl carbonate), propylene glycol bis(butoxyethyl carbonate), dipropylene glycol bis(ethoxyethyl carbonate), diethylene glycol bis(pentoxyethyl carbonate), tetraethylene glycol bis(ethoxyethyl carbonate), triethylene glycol bis(butoxyethyl carbonate), tetraethylene glycol bis(propoxyethyl carbonate), triethylene glycol bis (octoxyethyl carbonate), triethylene glycol bis(butoxyethoxyethyl carbonate), diethylene glycol bis(n-pentoxyethoxyethyl carbonate) and tetraethylene glycol bis(2-ethylhexoxyethoxyethyl carbonate).

It is necessary for the glycol carbonate ester to have the prescribed formula in order to operate effectively as deposit-control additives. If there are more than 4 alkylene oxide units, the additive becomes oil-insoluble and too water-soluble for proper functioning as a lubricant additive.

The glycol bis(glycol ether carbonates) effective in

reducing deposit formation are all characterized by boiling points above 650° F., a molecular weight above 300 and a carbon to oxygen weight ratio below 2.5. Apparently, the glycol carbonate ester must possess all of these properties simultaneously in order to impart deposit-forming properties to hydrocarbon fuels.

In summary, the following conclusions can be made as to the requirements of each section of the additive molecule for the production of a glycol bis(glycol ether carbonate) having deposit-control properties. (1) The alkylene oxide unit, that is the —(RO)— group must contain 1 to 4 units. The ethylene oxide unit, e. g. the $-(OCH_2CH_2)_n-$ group, can contain 1 to 4 units but 1 to 2 units, which are respectively Cellosolve and Carbitol derivatives, are preferred. (2) Two carbonate radicals are required since glycol mono carbonate ester derivatives are ineffective as deposit-control additives. (3) Terminal aliphatic radicals contain 1 to 18 carbon atoms with aliphatic radicals containing 2 to 10 carbon atoms being preferred.

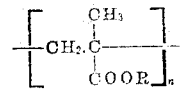
The glycol bis(glycol ether carbonates) are effective as a deposit-control additive in a concentration of at least 0.2 volume percent of the lubricant. The concentration of the glycol bis(glycol ether carbonate) usually falls between 0.5 and 3.0 volume percent of the lubricant. Since the improvement 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 glycol bis(glycol ether carbonates) of this invention are effective in controlling deposit formation in lubricants employed in spark ignition engines, diesel motors and gas turbines. However, the glycol bis(glycol ether carbonates) of prescribed composition 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 glycol bis(glycol ether carbonates) 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. The glycol bis(glycol ether carbonates) are also useful as deposit control additives in gas turbine lubricants which are generally ester base lubricants. The glycol bis(glycol ether carbonates) are useful in aviation oils which lubricate reciprocating aviation engines. The scope of the lubricating oils to which the glycol bis(glycol ether carbonates) 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 the 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 glycol bis(glycol ether carbonates) 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 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.

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 United States Patent 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 the glycol bis(glycol ether carbonate) 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.

In Table I are shown the results obtained in the modified Chevrolet deposits test with lubricating oils which possessed various concentrations of glycol bis(glycol ether carbonates). 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 paraphenylene diamine, lecithin, and N,N'-disalicylidene-1,2-diaminopropane.

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 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 I

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	4.8	76.1	0.0
Base Oil Plus:			
Tripropylene glycol bis(2-ethoxyethyl carbonate)	6.7	81.7	2.0
Diethylene glycol bis(2-ethoxyethyl carbonate)	8.7	89.7	2.0
Triethylene glycol bis(2-ethoxyethyl carbonate)	8.7	87.7	2.0
Diethylene glycol bis(2-butoxyethyl carbonate)	6.7	84.7	3.0
Tetraethylene glycol bis(2-butoxyethyl carbonate)	9.5	86.5	3.0

The data in Table I show that the glycol bis(glycol ether carbonates) of this invention are effective deposit-control lubricating additives. Ratings above 8.0 in piston skirt and above 85 in total engine deposits are very excellent results in this low temperature deposits test.

In Table II there is a comparison of a reference oil with a reference oil containing 0.6 volume percent of tetraethylene glycol bis(2-butoxyethyl carbonate) in the modified Chevrolet deposits test. The fuel used in the run of Table II is the same as the regular grade high quality gasoline described in connection with Table I. The reference lubricating oil was the 20–20W heavy duty lubricating oil described in connection with Table I.

TABLE II

Engine cleanliness in the modified Chevrolet S–II test

[0.6 volume percent additive in oil.]

	Piston Skirt	Total Engine Deposits
Base Oil	5.8	80.3
Base Oil plus tetraethylene glycol bis(2-butoxyethyl carbonate)	8.2	82.2

The data in Table II show that substantial improvement of engine cleanliness is obtained even with low concentrations of additive in the lubricating oil. The improvement with a low concentration of additive is particularly noticeable in the piston skirt rating.

EFFECT OF ADDITIVES ON ENGINE WEAR

Frequently, in the course of development of useful additives for improved lubricants and fuels, deleterious side effects are encountered. The deleterious effects may greatly overshadow the one or more advantages obtained from the use of the additive. Deleterious action is frequently encountered as increase in engine wear of such engine parts as piston rings, cylinder walls, bearings and valves. The glycol bis(glycol ether carbonates) described in this invention are unusual in that no deleterious effects have been encountered in the large amount of engine testing conducted. In fact, with respect to wear of vital engine parts, it has been found that wear is actually decreased under high temperature conditions which are most severe with respect to engine wear.

The test used for high temperature wear and corrosion is an extended version of the CRC–L–4–1252 test. In the extended test, the total test time is 72 hours instead of the usual 36. This increase in test time makes the test more severe. Bearing weight loss is the criterion for possible corrosive or wear action. As indicated in Table III, below, no deleterious effect was noted for the glycol bis(glycol ether carbonates) of this invention.

In this test the glycol bis(glycol ether carbonate) was added to both the fuel and lubricating oil. The base fuel in these runs was the same regular grade gasoline used in Table I, and the base lubricating oil was the same 20–20W heavy duty Supplement I level oil employed in Table I. The additive employed in this test was diethylene glycol bis(2-ethoxyethyl carbonate).

TABLE III

High temperature wear—CRC–L–4 extended test

Additive, volume percent:		
Fuel	0	0.05
Oil	0	1
Visual Ratings:		
Piston Skirt	8.8	9.5
Total Engine	88.8	92.5
Wear Data:		
Compression Ring Wt. Loss, g./cyl.	0.044	0.072
CuPb Bearing Wt. Loss, g./2 whole bearing	0.215	0.052

The high temperature conditions of the extended L–4 test normaly give a clean engine because the high temperature conditions promote the removal of deposit. Accordingly, the increases in piston skirt rating from 8.8 to 9.5 and in total engine deposits from 88.8 to 92.5 are significant improvements.

The compression ring weight loss is of the same order of magnitude in both the runs shown in Table II. The wear loss of the compression rings was low with and without diethylene glycol bis(2-ethoxyethyl carbonate). The five-fold decrease in the CuPb bearing weight loss resulting from the use of the additive in both the fuel and the oil is a significant improvement.

The foregoing data prove that lubricants containing glycol bis(glycol ether carbonates) of prescribed composition are outstanding in controlling deposits. Moreover, glycol bis(glycol ether carbonates) appear to fill the one

main need of Supplement I detergent oils, namely ability to control low temperature deposits.

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 glycol bis(glycol ether carbonate) having a carbon to oxygen weight ratio below 2.5 and a boiling point above about 650° F. and the general formula

$$R'O(CH_2CH_2O)_nOCO(RO)_xCO(OCH_2CH_2)_nOR'$$

wherein R is a divalent aliphatic hydrocarbon radical containing 2 to 3 carbon atoms, R' is an aliphatic hydrocarbon radical containing 2 to 18 carbon atoms, x has a value of 1 to 4 and n has a value of 1 to 4, 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 glycol bis(glycol ether carbonate).

3. A lubricating oil according to claim 1 containing 0.5 to 3.0 volume percent glycol bis(glycol ether carbonate).

4. A mineral lubricating oil containing a glycol bis(glycol ether carbonate) having a carbon to oxygen weight ratio below 2.5 and a boiling point above about 650° F. and the general formula

$$R'O(CH_2CH_2O)_nOCO(RO)_xCO(OCH_2CH_2)_nOR'$$

wherein R is a divalent aliphatic hydrocarbon radical containing 2 to 3 carbon atoms, R' is an aliphatic hydrocarbon radical containing 2 to 18 carbon atoms, x has a value of 1 to 4 and n has a value of 1 to 4, 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 glycol bis(glycol ether carbonate).

6. A lubricating oil according to claim 4 containing 0.5 to 3.0 volume percent glycol bis(glycol ether carbonate).

7. A lubricating oil according to claim 4 containing tripropylene glycol bis(2-ethoxyethyl carbonate).

8. A lubricating oil according to claim 4 containing diethylene glycol bis(2-ethoxyethyl carbonate).

9. A lubricating oil according to claim 4 containing triethylene glycol bis(2-ethoxyethyl carbonate).

10. A lubricating oil according to claim 4 containing diethylene glycol bis(2-butoxyethyl carbonate).

11. A lubricating oil according to claim 4 containing tetraethylene glycol bis(2-butoxyethyl carbonate).

References Cited in the file of this patent

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