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FUELS CONTAINING A DEPOSIT-CONTROL ADDITIVE

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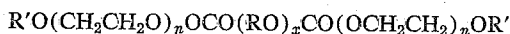
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This invention relates to hydrocarbon fuels containing a novel class of additives which reduce the deposit-forming tendency of hydrocarbon fuels. More specifically, this invention discloses that superior motor fuels are obtained by the addition of a minor amount of a glycol bis(glycol ether carbonate) of prescribed composition.

As automobile manufacturers annually raise the compression ratio of their automobile engines in the race for higher horsepower, the need becomes greater for gasolines which burn cleanly, that is, have low deposit-forming tendencies. 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. As a consequence, gasoline manufacturers have placed increasing stress on reducing the deposit-forming tendencies of their fuels and have resorted to various additives either to reduce the amount of deposits or to minimize their effects. The present invention involves the discovery that a particular class of glycol derivatives are outstanding in controlling the deposit-forming tendencies of hydrocarbon fuels.

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



wherein R is a divalent aliphatic radical containing 2 to 3 carbon atoms, R' is a C₁ to C₁₈ 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 hydrocarbon fuels of this invention contain a glycol bis(glycol ether carbonate) of the general formula



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. The glycol bis(glycol ether carbonates) prescribed in this invention are effective deposit-control additives in concentrations as low as 0.01 volume percent, but concentrations of 0.04 to 0.3 volume percent are normally employed. There is no critical upper limit of concentration, but economic considerations dictate that concentrations less than 1.0 volume percent glycol carbonate ester be present in the fuel.

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 aforeidentified copending application. In general, the preparation involves the formation of a chloroformate by reaction of phosgene with an ethylene or polyethylene

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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 a C₂ or C₃ glycol with phosgene and subsequent reaction of the dichloroformate with ethylene or polyethylene glycol monoether in the presence of a hydrogen chloride acceptor.

The hydrocarbon fuels of this invention are characterized by low deposit-forming tendencies with the result that an engine operated therewith shows exceptionally clean intake system, combustion space, valves, ring belt area and injection system if a diesel engine. 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 lubricating oil, such as piston skirts and cylinder walls, are very markedly reduced.

Glycol bis(glycol ether carbonates) usable in the fuels of the invention are exemplified by the following: ethylene glycol bis(ethoxyethyl carbonate), ethylene glycol bis(n-2-butoxyethyl carbonate), ethylene glycol bis(pentoxymethyl carbonate), glycol bis(decoxyethyl carbonate), diethylene glycol bis(ethoxyethyl carbonate), diethylene glycol bis(propoxyethyl carbonate), diethylene glycol bis(hexoxyethyl carbonate), diethylene glycol bis(octoxyethyl carbonate), propylene glycol bis(butoxyethyl carbonate), dipropylene glycol bis(ethoxyethyl carbonate), diethylene glycol bis(pentoxymethyl 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-pentoxymethoxyethyl 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 too water-soluble for proper functioning as a fuel additive. An additive with high water solubility is generally lost from a hydrocarbon fuel during storage which is usually over water.

The glycol bis(glycol ether carbonates) effective in reducing deposit formation in hydrocarbon fuels 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, i. e. the (OCH₂CH₂)_n can contain 1 to 4 units but 1 to 2 units, which are respectively Cellosolve and Carbitol derivatives, are preferred. (2) Carbonate radicals are required since glycol mono carbonate ester derivatives are ineffective as deposit-control additives. (3) Terminal aliphatic radicals must contain at least 1 carbon atom; aliphatic radicals containing 2 to 10 carbon atoms are preferred.

The glycol bis(glycol ether carbonates) are effective as deposit-control additives in concentrations between 0.01 and 1.0 volume percent of the fuel. Generally, dirtier fuels having a high concentration of olefinic components require high concentrations of the glycol derivative whereas cleaner burning premium fuels are improved

with respect to deposit-forming characteristics by smaller concentrations of the glycol bis(glycol ether carbonate). In general, dirtier gasolines require an additive concentration between 0.1 and 0.3 volume percent whereas clean-burning premium fuels only need an additive concentration between 0.01 and 0.08 volume percent. As indicated previously, there is no critical upper limit from a functional viewpoint but economics dictate that the glycol additive be less than 1 volume percent.

The glycol bis(glycol ether carbonates) of the type described in this invention are effective in controlling deposits in hydrocarbon fuels having boiling points up to about 700° F., although benefits also result when glycol bis(glycol ether carbonates) are added to fuels containing residual stocks of higher boiling point. The major application of the additive is in gasoline for automotive engines wherein fuel-derived engine deposits have become a particularly vexing problem. The deposit-forming properties of diesel fuels and fuels designed for use in jets and gas turbines are also improved by the glycol carbonate esters of this invention. In diesel fuels the presence of the additive maintains the injection system and combustion zone in a clean condition. This is particularly important with the increasing use of the so-called "economy" diesel fuels, that is fuels having a high sulfur content or containing cracked or residual stocks. Glycol bis(glycol ether carbonates) find particular application in jet fuels used as a cooling medium prior to their consumption. A glycol bis(glycol ether carbonate) containing jet fuel is an excellent heat exchange medium since it is relatively free from deposits in the cooling system and burner nozzle where deposits cannot be tolerated.

The deposit-forming properties of both regular and premium gasolines, both of the leaded and of the non-leaded type, are improved by the addition of glycol bis(glycol ether carbonates).

The gasolines to which the polyglycol carbonate esters are added can be broadly defined as hydrocarbon fuels having boiling points up to approximately 400° F.

The action of the additives in controlling the deposit-forming tendencies of motor fuel 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 standard 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 there is shown the decrease in deposit formation resulting from the addition of various glycol bis(glycol ether carbonates) to 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 para-phenylene diamine, lecithin, and N,N'-di-salicylidene 1,2-diaminopropane. In all the runs in Table I, the laboratory engines in the Chevrolet S-II

test were lubricated with Advanced Custom Made Havoline, a heavy duty type oil meeting Supplement I requirements and manufactured by The Texas Company.

TABLE I

Engine cleanliness in the modified Chevrolet S-II test

	Piston Skirt	Total Engine Deposits
Base fuel.....	4.8	76.1
Base fuel plus 0.1 vol. percent of:		
Tripropylene glycol bis(2-ethoxyethyl carbonate).....	6.7	81.7
Diethylene glycol bis(2-ethoxyethyl carbonate).....	8.7	89.7
Triethylene glycol bis(2-ethoxyethyl carbonate).....	8.7	87.7
Diethylene glycol bis(2-butoxyethyl carbonate).....	6.7	84.7
Tetraethylene glycol bis(2-butoxyethyl carbonate).....	9.5	86.5

The data of the above table clearly show that glycol bis(glycol ether carbonates) are effective deposit control additives in motor fuels. Both ethylene and propylene glycol derivatives are effective in controlling deposit formation, but the ethylene glycol derivatives are preferred from the standpoints of both cost and efficiency.

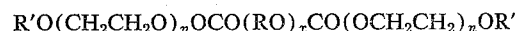
The fuels formed by the addition of the glycol carbonate ester disclosed in the invention to a regular grade gasoline are approximately equivalent to premium grade gasolines from the standpoint of engine cleanliness. The piston skirt ratings of 8.7 and 9.5 and total engine ratings 84 to 89.7 are better ratings than are obtained with most premium fuels. The ability of the glycol bis(glycol ether carbonates) to raise regular grade fuels above the engine cleanliness level of premium grade fuels is a substantial step forward in solving the surface ignition problems encountered in high compression engines.

An outstanding feature of the glycol bis(glycol ether carbonates) of this invention is that they do not possess any deleterious effect on other properties of the fuel. In many fuel additives, engine wear of parts such as piston rings, cylinder walls, bearings and valves, is a definite problem. The fuels of this invention containing a glycol bis(glycol ether carbonate) of prescribed composition actually decrease engine wear under high temperature conditions.

Obviously many modifications and variations of the invention are 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 normally liquid hydrocarbon fuel for internal combustion engines containing a glycol bis(glycol ether carbonate) having a carbon to oxygen weight ratio below 2.5 and the general formula



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, said glycol derivative being present in an amount sufficient to reduce the deposit-forming properties of said fuel.

2. A hydrocarbon fuel according to claim 1 containing 0.01 to 1.0 volume percent of glycol bis(glycol ether carbonate).

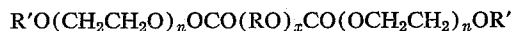
3. A hydrocarbon fuel according to claim 1 containing 0.04 to 0.3 volume percent of glycol bis(glycol ether carbonate).

4. A hydrocarbon fuel according to claim 1 in which said glycol bis(glycol ether carbonate) has terminal aliphatic radicals containing 3 to 10 carbon atoms and said n has a value of 1 to 2.

5. A gasoline containing a glycol bis(glycol ether car-

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bonate) having a boiling point above 650° F., a molecular weight above 300, a carbon-to-oxygen weight ratio below 2.5 and the general formula



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, said glycol derivative being present in an amount sufficient to reduce the deposit-forming properties of said fuel.

6. A gasoline according to claim 5 containing 0.01 to 1.0 volume percent of glycol bis(glycol ether carbonate).

7. A gasoline according to claim 5 containing 0.04 to 0.3 volume percent of glycol bis(glycol ether carbonate).

8. A gasoline according to claim 5 in which said glycol bis(glycol ether carbonate) has terminal aliphatic radicals containing 3 to 10 carbon atoms and said n has a value of 1 to 2.

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9. A gasoline containing 0.01 to 1.0 volume percent tripropylene glycol bis(2-ethoxyethyl carbonate).

10. A gasoline containing 0.01 to 1.0 volume percent diethylene glycol bis(2-ethoxyethyl carbonate).

11. A gasoline containing 0.01 to 1.0 volume percent triethylene glycol bis(2-ethoxyethyl carbonate).

12. A gasoline containing 0.01 to 1.0 volume percent diethylene glycol bis(2-butoxyethyl carbonate).

13. A gasoline containing 0.01 to 1.0 volume percent tetraethylene glycol bis(2-butoxyethyl carbonate).

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