FUELS CONTAINING DEPOSIT CONTROL ADDITIVES

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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 disclosed that superior motor fuels are obtained by the addition of a minor amount of a polymerlylene 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 gasoline 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 polyethylene glycol derivatives are outstanding in controlling the deposit-forming tendencies of hydrocarbon fuels.

In our copending application, Serial No. 567,476 filed of even date there are disclosed novel polyethylene glycol carbonates of the general formula

\[ R'\text{O}(\text{CH}_2\text{CH}_2\text{O})_n\text{OCCOROCO}(\text{OCH}_2\text{CH}_2)_n\text{OR} \]

wherein \( R' \) is a divalent symmetrical polyethylene radical containing at least 4 carbon atoms, \( R' \) is an aliphatic hydrocarbon radical containing 1 to 12 carbon atoms and \( n \) has a value of 0 to 10. This invention involves the discovery that a particular group of these novel compounds, namely the polyethylene glycol bis(glycol ether carbonates) are deposit control fuel additives.

The improved hydrocarbon fuels of this invention contain a polyethylene glycol bis(glycol ether carbonate) of the general formula

\[ R'\text{O}(\text{CH}_2\text{CH}_2\text{O})_n\text{OCCOROCO}(\text{OCH}_2\text{CH}_2)_n\text{OR} \]

wherein \( R' \) is a divalent symmetrical polyethylene radical containing at least 4 carbon atoms and preferably 4 to 12 carbon atoms, \( R' \) is an aliphatic hydrocarbon radical containing 1 to 12 carbon atoms and \( n \) has a value of 1 to 6. The polyethylene glycol bis(glycol ether carbonate) 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 polyethylene 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 aforementioned copending application. In general, the preparation involves the formation of a chloroformate by reaction of phosgene with an ethylene or polyethylene glycol monooxylyl ether and subsequent reaction of the chloroformate with a polyethylene glycol in the presence of a hydrogen chloride acceptor such as pyridine or quinoline. An alternate reaction procedure involves formation of a dichloroformate by reaction of a polyethylene glycol with phosgene and subsequent reaction of the dichloroformate with a monooxylyl or polyethylene glycol 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 of a diesel engine. The low deposit level in the engine minimizes surface ignition in all its manifestations, namely 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.

The polyethylene glycol bis(glycol ether carbonates) usable in the fuels of the invention are exemplified by the following: tetramethylene glycol bis(butoxyethoxyl carbonates), pentamethylene glycol bis(methoxyethoxyl carbonates), hexamethylene glycol bis(ethoxyethoxyl carbonates), hexamethylene glycol bis(propoxyethoxyl carbonates), hexamethylene glycol bis(butoxyethoxyl carbonates), pentamethylene glycol bis(methoxyethoxyl carbonates), octamethylene glycol bis(ethoxyethoxyl carbonates), octamethylene glycol bis(methoxyethoxyl carbonates), decamethylene glycol bis(ethoxyethoxyl carbonates), decamethylene glycol bis(butoxyethoxyl carbonates), pentamethylene glycol bis(2-butene-1-oxy-ethoxyl carbonates), tetramethylene glycol bis(methoxyethoxyl carbonates), tetramethylene glycol bis(ethoxyethoxyl carbonates), pentamethylene glycol bis(butoxyethoxyl carbonates), pentamethylene glycol bis(octoxyethoxyl carbonates), pentamethylene glycol bis(pentoxyethoxyl carbonates), heptamethylene glycol bis(pentoxynethoxyl carbonates).

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 6 ethylene 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 polyethylene glycol bis(glycol ether carbonate) 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 polyethylene glycol bis(glycol ether carbonate) having deposit-control properties: (1) The polyethylene radical, that is, the \( R' \) group, contains at least 4 and preferably less than 10 carbon atoms. (2) The ethylene oxide unit, i. e. the \( \text{OCH}_2\text{CH}_2\text{O} \), contains 1 to 6 units. (3) Two carbonate radicals are required since polyethylene glycol carbonates and carbonate ester derivatives are ineffective as deposit-control additives. (4) Terminal aliphatic radicals contain 1 to 12 carbon atoms with aliphatic radicals containing 2 to 6 carbon atoms being preferred.

The polyethylene glycol bis(glycol ether carbonates) are effective as deposit-control additives in concentrations between 0.01 and 1.0 volume percent of the fuel. Gen-
erally, dirtier fuels having a high concentration of olefinic components require high concentrations of the additive whereas cleaner burning premium fuels are improved with respect to deposit-forming characteristics by smaller concentrations of the polyethylene glycol bis(glycol ether carbonate) ester. In general, dirtier, diesel fuels 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 polyethylene 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 polyethylene glycol bis(glycol ether carbonates) are added to fuels containing residual stocks of tar or having a boiling point above 700 °F. 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 jet and gas turbines are also improved by the polyethylene glycol derivatives 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. Polyethylene glycol bis(glycol ether carbonates) find particular application in jet fuels used as a cooling medium prior to their consumption. A polyethylene glycol bis(glycol ether carbonate)-containing jet fuel is an excellent heat exchange medium since it is relatively free from deposits in storage for extended periods 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 polyethylene 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 Motometer—Chevrolet Deposit Test. The laboratory engines are operated under the standard conditions of this test with the exception that crankcase oil temperatures were 10 °F below 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 where-in 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 parts 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 10 on total engine deposits represents a perfectly clean engine, etc.

In the following table there are shown the depositcontrol properties of polyethylene glycol bis(glycol ether carbonates) in comparison with those of polyethylene glycol bis(alkyl carbonates). Base fuels A and B are high quality regular grade gasolines comprising a mixture thermal cracked stock, fluid catalytically cracked, and straight run gasoline. Base fuel A has an 87.0 ASTM research octane rating containing 2.90 ml. of TEL per gallon, had an API gravity of 58.0 and a boiling range between 106 and 396 °F; it was negative in the copper strip corrosion test and had an oxidation stability in the ASTM test of 310 minutes minimum. Base fuel B had a 90.5 ASTM research octane rating, contained 2.67 ml. of TEL per gallon, had an API gravity of 59.0 and a boiling range between 93 and 395 °F; it was negative in the copper strip corrosion test and had an oxidation stability of 35 minutes minimum. The reference fuels also contained minor amounts of gasoline inhibitors, namely N,N'-diisobutyryl aminobenzene, lecithin, and N,N'-bis(dialkyl) amino compounds. In all runs, 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 1: Engine cleanliness in the modified Chevrolet S-II Test

<table>
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<tr>
<th>Fuel Type</th>
<th>Piston Skirt</th>
<th>Total Engine Deposits</th>
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<tbody>
<tr>
<td>Base Fuel A</td>
<td>4.7</td>
<td>77.7</td>
</tr>
<tr>
<td>Base Fuel A plus 0.1 vol. percent of:</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1,5-pentamethylene glycol bis(2-ethylhexyl carbonate)</td>
<td>7.8</td>
<td>83.8</td>
</tr>
<tr>
<td>1,5-pentamethylene glycol bis(2,6-dimethylcyclopentyl carbonate)</td>
<td>6.7</td>
<td>70.7</td>
</tr>
<tr>
<td>Base Fuel B</td>
<td>6.1</td>
<td>70.9</td>
</tr>
<tr>
<td>Base Fuel B plus 0.1 vol. percent of:</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1,5-pentamethylene glycol bis(2,6-dimethylcyclopentyl carbonate)</td>
<td>9.7</td>
<td>90.7</td>
</tr>
<tr>
<td>1,5-pentamethylene glycol bis(2-ethylhexyl carbonate)</td>
<td>4.8</td>
<td>78.8</td>
</tr>
</tbody>
</table>

The fuels formed by the addition of the polyethylene glycol bis(glycol ether carbonates) to a regular grade gasoline are equivalent to some premium grade gasolines from the standpoint of engine cleanliness. The piston skirt rating of the "cooling" test and total engine rating of 92.8 to 90.7 are better ratings than are obtained with some premium fuels. The ability of the polyethylene glycol bis(glycol ether carbonates) to raise regular grade fuels to the engine cleanliness level of premium grade fuels is a substantial step forward in solving the surface ignition problems encountered in high compression engines.

It is significant that the polyethylene glycol bis(alkyl carbonates), which are also disclosed in Serial No. 567,476 filed of even date, are ineffective and, in some respects, deleterious deposit control additives. It has been theorized that the ether linkage in the polyethylene glycol bis(glycol ether carbonates) is necessary for the additive to solubilize the low temperature deposits. Whatever the explanation of the effectiveness of polyethylene glycol bis(glycol ether carbonates) and of the ineffectiveness of polyethylene glycol bis(alkyl carbonates) the results are striking.

An outstanding feature of the polyethylene 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. Fuels containing polyethylene glycol bis(glycol ether carbonates) of prescribed composition actually decrease engine wear under high temperature conditions.

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 normally liquid hydrocarbon fuel for internal combustion engines containing a polyethylene glycol bis(glycol ether carbonate) of the general formula

   \[ R'O(CH_2CH_2O)_nCOR'O \]

   wherein R is a divalent symmetrical polyethylene radical containing 4 to 10 carbon atoms, R' is an alicyclic...
hydrocarbon radical containing 1 to 12 carbon atoms and n has a value of 1 to 6, said glycol derivative having a carbon to oxygen weight ratio below 2.5 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 polymethylene glycol bis (glycol ether carbonate).

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

4. A gasoline containing a polymethylene glycol bis (glycol ether carbonate) of the general formula

\[ R'O(CH_2CH_2O)_nOOCOROCO(OCH_2CH_2)_mOR' \]

wherein R is a divalent symmetrical polymethylene radical containing 4 to 10 carbon atoms, R' is an aliphatic hydrocarbon radical containing 1 to 12 carbon atoms and n has a value of 1 to 6 said glycol derivative having a carbon to oxygen weight ratio below 2.5 and being present in an amount sufficient to reduce the deposit-forming properties of said gasoline.

5. A gasoline according to claim 4 containing 0.01 to 1.0 volume percent of polymethylene glycol bis (glycol ether carbonate).

6. A gasoline according to claim 4 containing 0.04 to 0.3 volume percent of polymethylene glycol bis (glycol ether carbonate).

7. A gasoline according to claim 4 in which said polymethylene 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.

8. A gasoline containing 0.01 to 1.0 volume percent 1,5-pentamethylene glycol bis (2-ethoxyethyl carbonate).

9. A gasoline containing 0.01 to 1.0 volume percent 1,5-pentamethylene glycol bis (2,2',2''-triethoxyethyl carbonate).

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