

1

2,844,448

FUELS CONTAINING A DEPOSIT-CONTROL ADDITIVE

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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 polyglycol carbonate ester 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 polyglycol derivatives are outstanding in controlling the deposit-forming tendencies of hydrocarbon fuels.

The improved hydrocarbon fuels of this invention contain a polyglycol carbonate ester of the general formula



wherein R is a divalent aliphatic radical containing at least 2 carbon atoms, R' and R'' are aliphatic hydrocarbon radicals containing between 3 and 18 carbon atoms and n is an integer having a value of at least 2, in an amount sufficient to reduce the deposit-forming tendencies of the fuels. The polyglycol carbonate ester is effective in the motor fuel 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 polyglycol carbonate be present in the fuel.

The polycarbonate esters which inhibit the deposit-forming tendencies of hydrocarbon fuels are readily formed by a series of reactions involving the formation of an alcohol chloroformate by reaction of phosgene with an alcohol and subsequently reacting the alcohol chloroformate with a polyglycol in the presence of a hydrogen chloride acceptor, such as pyridine or quinoline. An alternate reaction procedure involves formation of a polyglycol dichloroformate by reaction of polyglycol with phosgene and subsequent reaction of polyglycol dichloroformate with an aliphatic alcohol in the presence of a hydrogen chloride acceptor. The preparation of compounds of this type is disclosed in U. S. Patents 2,370,567 and 2,370,569.

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

2

addition, the low deposit level reduces the engine's octane requirement increase. In addition, deposits on surfaces contacted by the lubricating oil, such as piston skirts and cylinder walls, are very markedly reduced.

Polyglycol carbonate esters usable in the process of the invention are exemplified by the following: diethylene glycol bis(allyl carbonate), triethylene glycol bis(allyl carbonate), tetraethylene glycol bis(allyl carbonate), diethylene glycol bis(n-amyl carbonate), triethylene glycol bis(n-amyl carbonate), tetraethylene glycol bis(n-amyl carbonate), dipropylene glycol bis(n-amyl carbonate), polyglycol (av. mol wt. 300) bis(n-amyl carbonate), polyglycol (av. mol wt. 400) bis(2-ethylhexyl carbonate), tetraethylene glycol bis(2-ethylhexyl carbonate), diethylene glycol bis(2-ethylbutyl carbonate), diethylene glycol bis(n-propyl carbonate), polyglycol (av. mol. wt. 400) bis(n-amyl carbonate), diethylene glycol bis(4-pentenyl carbonate), tripropylene glycol bis(2-ethylhexyl carbonate), diethylene glycol bis(isoamyl carbonate), and dipropylene glycol bis(2-ethylhexyl carbonate).

A surprising feature of this invention is that compounds closely related to compounds falling within the prescribed general formula



wherein R is a divalent aliphatic radical containing at least 2 carbon atoms, R' and R'' are aliphatic hydrocarbon radicals containing at least 3 carbon atoms and n is an integer having a value of at least 2, are ineffective as deposit-control additives in hydrocarbon fuels. For example, a monoglycol carbonate ester such as ethylene glycol bis(allyl carbonate) is ineffective while diethylene glycol carbonate esters such as diethylene glycol bis(allyl carbonate) are excellent deposit-control additives. Similarly, diethylene glycol-bis(ethyl carbonate) is ineffective in controlling deposits while diethylene glycol bis(allyl carbonate), is a very good deposit-control additive. As a result of intensive experimentation, the following generalizations have been made with regard to the properties required for a glycol carbonate ester to exhibit deposit-control properties.

The polyglycol carbonate esters that are effective in reducing the deposit formation in hydrocarbon fuels are all characterized by boiling points above 650° F., a molecular weight above 270 and a carbon to oxygen ratio by weight below 2.50. Apparently, the polyglycol carbonate ester must possess all of these properties simultaneously in order to impart deposit-control properties to hydrocarbon fuels. In Table I below the boiling point, molecular weight, and C to O ratio by weight for effective and ineffective glycol carbonate esters are shown.

TABLE I

	Approximate Boiling Point, ° F.	Molecular Wt.	Weight C to O Ratio
60 Ethylene glycol bis(allyl carbonate).....	560	230	2.00
Diethylene glycol bis(allyl carbonate).....	660	274	1.57
Diethylene glycol bis(n-amyl carbonate).....	720	334	1.71
Diethylene glycol bis(methyl amyl carbonate).....	700	362	1.93
Tetraethylene glycol bis(allyl carbonate).....	790	362	1.33
Tetraethylene glycol bis(2-ethylhexyl carbonate).....	(a)	506	2.18
Tetraethylene glycol bis(amyl carbonate).....	(a)	422	1.67
Polyglycol (av. mol wt. 300) bis(2-ethylhexyl carbonate).....	(a)	644	2.05
Polyglycol (av. mol wt. 400) bis(2-ethylhexyl carbonate).....	(a)	744	1.80
Diethylene glycol bis(n-butyl carbonate).....	670	306	1.50

* Not distilled—too high boiling.

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 carbonate ester having deposit-control properties. The alkylene oxide unit, that is the $-(RO)_n-$ group, must contain at least 2 units; as many as 2 to 10 repeating units can be used in this portion of the molecule; ethylene oxide and propylene oxide derivatives are preferred from the standpoint of cost, availability and effectiveness. Two carbonate radicals are required since polyglycol mono carbonate ester compounds are ineffective as deposit-control additives. The terminal aliphatic radicals must contain at least three carbon atoms; aliphatic radicals containing 3 to 10 carbon atoms are preferred. In both the alkylene oxide group and in the terminal aliphatic radicals, straight chain radicals are preferred to the branched chain hydrocarbon radicals although if the overall molecule is large, moderate branching can be tolerated. Similarly, primary alkyl carbonate esters are preferred to secondary and tertiary carbonate esters.

As a general rule, longer chain terminal radicals are combined with polyglycols containing a larger number of repeating alkylene oxide units while lower molecular weight terminal aliphatic radicals are combined with polyglycols containing a small number of repeating alkylene oxide units. Thus, a 2-ethylhexyl terminal radical is preferably used in the formulation of a tetraethylene glycol carbonate ester than in the formulation of a diethylene glycol carbonate ester. Formulating the polyglycol carbonate esters following this general rule assures that the resulting additive has a carbon to oxygen weight ratio less than 2.5.

The polyglycol carbonate ester is effective as a deposit-control additive in concentrations between 0.01 and 1.0 volume percent of the fuel. Generally, dirtier fuels having a higher concentration of olefinic components require higher concentrations of the polyglycol carbonate ester whereas cleaner burning premium fuels are improved with respect to deposit-forming characteristics by smaller concentrations of the polyglycol carbonate ester. In general, dirtier gasolines require a polyglycol carbonate ester concentration between 0.1 and 0.3 volume percent whereas clean-burning premium fuels only need a polyglycol carbonate ester concentration of 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 polyglycol carbonate ester concentration be less than 1 volume percent.

The polyglycol carbonate esters 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 the polyglycol carbonate esters 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 polyglycol carbonate esters of this invention. In diesel fuels the presence of the polyglycol carbonate ester 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. Polyglycol carbonate esters find particular application in jet fuels which are used as cooling mediums prior to their consumption. A polyglycol carbonate ester-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 polyglycol carbonate esters. The gasolines to which the polyglycol

carbonate esters are added can be broadly defined as a hydrocarbon fuel having a boiling point up to approximately 400 F.

The action of polyglycol carbonate esters of the prescribed composition 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 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 II there is shown the decrease in deposit formation resulting from the addition of various polyglycol carbonate esters 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 936° 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'-disubstituted butyl-p-phenylenediamine, lecithin, and N,N'-disubstituted 1,2-diaminopropane. In all the runs in Table II, 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.

In Table II the concentration of additives in the base fuel was 0.1 volume percent in each instance.

TABLE II

Engine cleanliness in the modified Chevrolet S-II test

	Piston Skirt	Total engine deposits
Base fuel	4.7	77.7
Base fuel plus the following:		
Ethylene glycol bis(allyl carbonate)	3.5	70.5
Diethylene glycol bis(allyl carbonate)	8.5	84.5
Triethylene glycol bis(allyl carbonate)	8.7	86.7
Tetraethylene glycol bis(allyl carbonate)	9.2	89.2
Diethylene glycol bis(amylyl carbonate)	8.8	87.8
Tetraethylene glycol bis(amylyl carbonate)	7.5	82.5
Diethylene glycol bis(n-butyl carbonate)	8.5	87.5
Diethylene glycol bis(2-ethylhexyl carbonate)	5.8	80.8
Polyglycol (av. mol wt. 300) bis(2-ethylhexyl carbonate)	9.3	91.3
Tetraethylene glycol bis(2-ethylhexyl carbonate)	6.8	84.0
Triethylene glycol bis(allyl carbonate)	8.7	86.7
Triethylene glycol bis(amylyl carbonate)	9.0	91.0
Polyglycol (av. mol wt. 400) bis(2-ethylhexyl carbonate)	8.7	87.7
Polyglycol (av. mol wt. 300) bis(amylyl carbonate)	9.5	89.5
Polyglycol (av. mol wt. 400) bis(amylyl carbonate)	9.2	87.2

The data in the above table clearly show that a polyglycol carbonate ester of the prescribed formula is necessary in order to produce a motor fuel of decreased deposit-forming tendencies. Ethylene glycol bis(allyl carbonate) gave a dirtier piston skirt and a dirtier total engine rating than the base fuel whereas diethylene glycol bis(allyl car-

5

bonate) substantially improved both the piston skirt and total engine rate.

It is also significant that higher molecular weight alkyl radicals in the carbonate ester are advantageously combined with polyglycols of a large number of alkylene oxide units than with lower molecular weight polyglycols. This result is evident from a comparison of the ratings obtained with diethylene glycol bis(2-ethylhexyl carbonate) and tetraethylene glycol bis(2-ethylhexyl carbonate) and polyglycol (av. mol. weight 300) bis(2-ethylhexyl carbonate).

The data in Table II shows that regular gasoline fuels containing 0.1 volume percent polyglycol carbonate of prescribed composition are approximately equivalent to premium grade gasolines with regard to deposit-forming tendencies. The piston skirt ratings of 8.0 to 9.5 and the total engine ratings of 84 to 91+ are better ratings than are obtained with some premium fuels. The ability of polyglycol carbonates to boost regular grade fuels to the engine cleanliness level of premium grade fuels is a significant advance and a substantial step forward to solving the surface ignition problems encountered in high compression engines.

The effect of varying concentrations of diethylene glycol bis(allyl carbonate) in regular fuel are shown in Table III. The data in Table III indicate that a concentration between 0.1 and 0.2 volume percent is neces-

sary in order to obtain optimum results with diethylene glycol bis(allyl carbonate) in regular grade gasoline.

TABLE III

Additive, vol. percent.....	None	0.05	0.10	0.20
Visual Ratings:				
Piston Skirt.....	4.7	6.0	8.3	8.6
Total Engine.....	77.7	76.0	86.3	89.1

In Table IV the action of a polyglycol carbonate ester in reducing the deposit-forming properties of a premium grade fuel are shown. Since the premium grade fuel already has an excellent rating with respect to the tendency to form deposits, the action of a polyglycol carbonate ester is not as striking as in the regular grade fuel. However, significant improvement in the deposit-forming tendency in the premium grade fuel is effected by the addition of the polyglycol carbonate ester and smaller quantities of an additive are needed in order to obtain optimum results of the premium grade fuel.

The reference fuel employed in Table IV was a high quality premium grade fuel comprising mainly fluid catalytically cracked stock and straight run gasoline. The reference fuel had a 95 A. S. T. M. research octane rating, contained 2.74 ml. of TEL fluid per gallon, had an ° API gravity of 60 to 65 and a boiling point range between 100 and 398° F.; the base fuel was negative in the copper corrosion test and had an oxidation stability in the ASTM test of 240 minutes minimum. The reference fuel also contained minor amounts of conventional gasoline inhibitors, for example, approximately 6 pounds

6

of N,N'-disecundary butyl-p-phenylenediamine, a gum inhibitor, per thousand barrels of gasoline, about 1.2 pounds of N,N'-disalicylidene-1,2-diaminopropane, a metal deactivator, per thousand barrels of gasoline, and about 1.1 pounds of lecithin, a tetraethyl lead stabilizer, per thousand barrels of gasoline.

TABLE IV

Engine cleanliness in modified Chevrolet S-II test

	Piston Skirt	Total Engine Deposits
Base fuel.....	7.5	85.2
Base fuel+0.05 volume percent diethylene glycol bis(allyl carbonate).....	8.0	87.0
Base fuel+0.20 volume percent diethylene glycol bis(allyl carbonate).....	8.7	86.7

The specificity of the polyglycol carbonate ester structures is further shown by a consideration of the information recorded in Table V. Numerous compounds were evaluated that contained portions of the preferred overall structure, but in no case was an outstanding deposit control additive obtained. In some cases, the additive degraded the base fuel. Evaluation of the additives was made in the high quality regular grade gasoline previously described.

TABLE V

Additive	Concentration, Volume Percent	Molecular Weight	Weight C to O Ratio	Piston Skirt Rating	Total Engine Rating
None.....				4.7	77.7
Diallyl.....	0.05	98	4.5	5.0	75.0
Do.....	0.10			5.3	82.3
Diallyl ether of diethylene glycol.....	0.10	186	2.5	3.7	74.7
Dibutyl ether of tetraethylene glycol.....	0.20	306	2.4	5.0	76.0
Diethyl ether of diethylene glycol.....	0.20	162	2.0	5.0	71.0
Allyl alcohol.....	0.05	70	2.25	4.2	72.2
Diallyl carbonate.....	0.10	142	1.75	4.8	75.8
Di-2-ethylhexyl carbonate.....	0.10	296	4.25	5.7	81.7

Octane requirement increase.—Octane requirement increase of engines in service is an old problem that becomes more severe with the modern high compression engines. An engine which has an initial octane requirements of 85 often will develop a need for a 95 octane fuel during service. It has been postulated that octane requirement increase is attributable partially to engine design and partially to the fuel and lubricant.

Reduced octane requirement increase was demonstrated in the laboratory for the additive-containing motor fuel of this invention in comparison with the reference fuel by the following procedure:

LAUSON H-2 ORI TEST PROCEDURE

Test operation.—The engine was operated under the following standard operating conditions and the data recorded as outlined in the following table:

TABLE VI

Variable	Condition
Test, Hours.....	To equilibrium O. R.=200 hr.
Wattmeter Reading.....	1,500-1,600.
Fuel Flow, lbs. per hr.....	1.6 ± .04.
Coolant Temp., °F.....	210 ± 5.
Oil Temp., °F.....	175 ± 5.
Oil Level.....	Check once each day.
Maintain Intake Manifold Press.....	0 inches (each hour).
Orifice Press. Drop.....	Record each hour.

Octane requirement of the engine was determined approximately every 24 hours. Before taking octane requirement the oil level was checked and necessary addi-

tions made and the following items determined and recorded.

Compression pressure at operating throttle position
Air temperature, ° F.
Barometer reading, in. Hg
Spark advance, ° B. T. D. C. (should be 20 degrees)
Amount of oil added

Equilibrium octane requirement was reached when the engine had operated for 50 hours with a change in ORI of 2 numbers or less.

A modified Model H-2 Lauson engine, which is a single cylinder, liquid cooled, four stroke spark ignition engine with a bore of 2¾ inches and a stroke of 2¾ inches giving a displacement of 14.89 cubic inches, was used. Power output was rated at 4.3 H. P. at 2400 R. P. M. Compression ratio of the engine was 6.5:1 using a modified head. The original flywheel magneto was replaced with a Bendix-Scintella magneto, Type CBR-4R and coupled to the forward end of the engine crankshaft to provide ignition. The engine was operated under the following conditions:

Engine speed----- 1800 R. P. M.
Engine load----- 1600 watts.
Spark advance----- 20° B. T. C.
Fuel flow rate----- 1.6#/hr.
Air-fuel ratio----- 13.5:1
Coolant temperature----- 210° F.
Carburetor air temp----- 100° F.
Oil temperature----- 175° F.
Test duration----- App. 200 hr. to equilibrium octane requirement.

The octane requirement of the engine was determined with primary reference fuels on the clean engine and after each period of operation until equilibrium octane requirement was attained. The difference between the initial (clean) octane requirement and the equilibrium octane requirement is known as the octane requirement increase or ORI.

The premium grade fuel employed in Table IV gave an octane requirement increase of 20 units in the above test whereas the same fuel plus 0.2 volume percent diethylene glycol bis(allyl carbonate) showed a maximum increase of 17 units in this test. Of more significance is the fact that the octane requirement increase would successively build up to a maximum of about 17 using the additive-containing fuel and then would quickly drop to an increase of 7 units followed by successive buildups and drops of a similar magnitude. It has been theorized that these periodic drops in octane requirement increase in the engine are a consequence of large areas of deposits being rapidly removed by the action of the polyglycol carbonate esters during engine operation.

Effect of additives on engine wear. Frequently, in the course of development of useful additives for improved fuels, deleterious effects will be encountered. The deleterious effects may greatly overshadow possible benefits. Deleterious action is frequently associated with increase in engine wear of such engine parts as piston rings, cylinder walls, bearings, and valves. The fuels obtained by the addition of a minor amount of a polyglycol carbonate ester of prescribed composition 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 both low and high temperature conditions.

The test used for low temperature wear evaluations uses a 1949 Pontiac 8 piston and Sealed Power IB-10 compression piston rings installed in a CFR high-speed crankcase. The cylinder liner is nitrided cast iron. The operating conditions are as follows:

Jacket coolant in., ° F----- 45-50
Engine speed, R. P. M----- 1200±20
Intake manifold pressure, in. Hg abs----- 25±0.05
Fuel-air ratio----- 0.067-0.068
Intake air temperature, ° F----- 150±3
Oil temperature, ° F----- 105±3
Oil pressure, p. s. i. g----- 75-80
Spark timing, ° BTC----- 35
Exhaust back pressure, in. H₂O----- 6±0.3
Crankcase ventilation, air, C. F. M----- 0.5
Duration of test (including warm-up), hrs-- 10

The loss in weight of the two compression rings is taken as a measure of the low temperature wear properties of the fuel and oil combination. By holding the oil constant, the relative wear characteristics of fuels can be determined. Using Advanced Custom Made Havoline oil, previously described, the results shown in Table VII, below, were obtained with a premium fuel with and without a polyglycol carbonate ester:

TABLE VII
Low temperature wear

Fuel	Mg. Weight Loss of Compression Rings
Premium fuel	50
Premium fuel plus 0.2% by volume diethylene glycol bis (allyl carbonate)	42

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 VIII, below, no deleterious effect was noted for a polyglycol carbonate ester.

TABLE VIII
High temperature wear CRC-L-4 extended test

Fuel	Gram Weight Loss of Bearing
Regular Grade Fuel	0.079
Regular Grade Fuel plus 0.2% by volume diethylene glycol bis(allyl carbonate)	0.044

The foregoing data prove that the polyglycol carbonate esters of prescribed composition are outstanding fuel additives for controlling deposits and at the same time do not possess any deleterious effects with regard to engine wear.

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 polyglycol carbonate ester having a carbon to oxygen weight ratio below 2.5 and a boiling point above 650° F. and the following general formula



wherein R is a divalent aliphatic hydrocarbon radical containing at least 2 carbon atoms, R' and R'' are aliphatic hydrocarbon radicals containing between 3 and 18 carbon atoms and n is an integer having a value of 2 to 10, said glycol carbonate ester being present in an amount sufficient to reduce the deposit-forming property of said fuel.

2. A hydrocarbon fuel according to claim 1 containing 0.01 to 1.0 volume percent of polyglycol carbonate ester.

3. A hydrocarbon fuel according to claim 1 containing 0.04 to 0.3 volume percent of a polyglycol carbonate ester. 5

4. A hydrocarbon fuel according to claim 1 in which said R' and R'' contain 3 to 10 carbon atoms.

5. A gasoline containing a polyglycol carbonate ester having a carbon to oxygen weight ratio below 2.5 and a boiling point above 650° F. and the following general formula 10



wherein R is a divalent aliphatic hydrocarbon radical containing at least 2 carbon atoms, R' and R'' are aliphatic hydrocarbon radicals containing between 3 and 18 carbon atoms and n is an integer having a value of 2 to 10, said glycol carbonate ester being present in an amount sufficient to reduce the deposit-forming property of said fuel. 20

6. A gasoline according to claim 5 containing 0.01 to 1.0 volume percent of polyglycol carbonate ester.

7. A gasoline according to claim 5 containing 0.04 to 0.3 volume percent of a polyglycol carbonate ester.

8. A gasoline according to claim 5 in which said R' and R'' contain 3 to 10 carbon atoms.

9. A gasoline containing 0.1 to 1.0 volume percent diethylene glycol bis(allyl carbonate).

10. A gasoline containing 0.1 to 1.0 volume percent diethylene glycol bis(amyl carbonate).

11. A gasoline containing 0.1 to 1.0 volume percent tetraethylene glycol bis(allyl carbonate). 10

12. A gasoline containing 0.1 to 1.0 volume percent polyglycol (av. molecular weight 300) bis(2-ethylhexyl carbonate).

13. A gasoline containing 0.1 to 1.0 volume percent triethylene glycol bis(allyl carbonate). 15

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UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 2,844,448

July 22, 1958

Robert Y. Heisler et al.

It is hereby certified that error appears in the printed specification of the above numbered patent requiring correction and that the said Letters Patent should read as corrected below.

Column 2, line 62, Table I, first column thereof, third item, for "bis(n-amyl carbonase)" read ==bis(n-amyl carbonate)==; column 4, line 34, for "936° F." read ==396° F.==; columns 5 and 6, Table V, first column thereof, second item, for "Diallyl" read ==Diallyl ether==.

Signed and sealed this 14th day of October 1958.

(SEAL)
Attest:

KARL H. AXLINE
Attesting Officer

ROBERT C. WATSON
Commissioner of Patents