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MOTOR FUEL COMPOSITION

Stanley R. Newman, Robert Y. Heisler, and Kenneth L. Dille, Fishkill, and Norman Alpert, Poughkeepsie, N. Y., assignors to The Texas Company, New York, N. Y., a corporation of Delaware

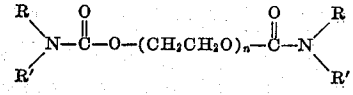
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8 Claims. (Cl. 44—71)

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 carbamate of a 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 carbamate ester of the general formula:



wherein R is hydrogen, an alkyl, alkenyl, or alkynyl group having from 1 to 18 carbon atoms, R' is an alkyl, alkenyl, or alkynyl group having from 1 to 18 carbon atoms, and *n* ranges from 2 to 6, in an amount sufficient to reduce the deposit-forming tendencies of the fuels. The polyglycol carbamate 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 of the polyglycol carbamate ester be present in the fuel.

Polyglycol carbamates of the present invention include for example: diethylene glycol bis(N,N-diallyl carbamate); diethylene glycol bis(N-2-ethylhexyl carbamate); diethylene glycol bis(N,N-dipropargyl carbamate); diethylene glycol bis (N-allyl carbamate); diethylene glycol bis[N,N-di-(1-methylsiopentyl) carbamate]; diethylene glycol bis(N-n-propyl carbamate); diethylene glycol bis-(N,N-diisopropyl carbamate); triethylene glycol bis(N,N-diallyl carbamate); triethylene glycol bis(N,N-dioctadecyl carbamate); triethylene glycol bis(N,N-dimethyl carbamate); triethylene glycol bis[N-(1,1-dimethyl-2-propynyl) carbamate]; tetraethylene glycol bis(N-2-ethylhexyl carbamate); tetraethylene glycol bis(N-allyl carbamate); pentaethylene glycol bis(N-propargyl carbamate); pentaethylene glycol bis(N-n-propyl carbamate); hexaethylene glycol bis(N,N-diallyl carbamate); hexaethylene glycol bis(N-n-butyl carbamate); and hexaethylene glycol bis(N-2-ethylhexyl carbamate).

The polyglycol carbamate esters which inhibit the deposit-forming tendencies of hydrocarbon fuels are readily formed by a series of reactions involving the formation of a polyglycol dichloroformate and thereafter reacting said dichloroformate with an aliphatic hydrocarbon amine. The reaction product is then separated from the unreacted substances by known purification steps. The preparation of the polyglycol dichloroformate type compound is disclosed in U. S. Patents 2,370,567 and 2,370,569.

They following examples are given to demonstrate the preparation of the esters of the invention.

EXAMPLE I

Preparation of diethylene glycol bis(n-allyl carbamate)

737 g. (12.94 moles) of allyl amine and 1115 g. (14.11 moles) of pyridine were placed in a 5 liter flask equipped with a stirrer, a condenser, a thermocouple probe, and an addition funnel, and the mixture was cooled to 50° F. 1360 g. (5.88 moles) of diethylene glycol dichloroformate was added to the mixture to yield a brick red solution lightening somewhat as a salt was formed. One liter of benzene was added to the mixture which was then stirred for about 48 hours after which one liter of water was added. The oil and water layers were separated and the oil layer was washed with 10 percent hydrochloric acid and then washed again with a saturated salt solution several times until the washes were neutral. The solution was then filtered, and the benzene and water were removed by distillation at atmospheric pressure. The residue, 1369 g., was crystallized to a waxy solid of low melting point. This solid was recrystallized from ether to yield 991 g. of white crystals having a melting point of 50 to 53° F. The theoretical analysis for diethylene glycol bis(N-allyl carbamate) shows the compound to have 53.0 percent carbon; 7.36 percent hydrogen, and 10.0 percent nitrogen. The actual analysis of the compound formed in accordance with this example showed it to have 52.7 percent carbon; 7.37 percent hydrogen; and 9.8 percent nitrogen. The yield of the purified compound was 62 percent of that theoretical obtainable.

EXAMPLE II

Preparation of diethylene glycol bis(N-2-ethylhexyl carbamate)

193 ml. (2.4 moles) of pyridine and 354 ml. (2.2 moles) of 2-ethylhexylamine were placed in a 2 liter, triple-necked flask equipped with a stirrer, condenser, thermometer, and addition funnel. This mixture was stirred and maintained below 50° F. while 231 g. (1 mole) of diethylene glycol dichloroformate were slowly added. The solution changed from yellow to green to brown and finally to dark red. After about 15 hours of stirring, 500 ml. of ether was added and the resulting mixture was washed 5 times, each time with 400 ml. of 10 percent hydrochloric acid followed by 4 washes with 300 ml. of saturated salt solution per wash. The neutral water insoluble layer was dried over anhydrous calcium sulfate. The calcium sulfate was next removed by filtration and the ether removed by vacuum distillation. The crude product of 350 g. was dissolved in benzene and twice passed through synthetic magnesium silicate to give a light orange solution. The benzene was removed by vacuum distillation. The product had a calculated analysis of 63.4 percent carbon; 10.54 percent hydrogen; 6.74 percent nitrogen; and a molecular weight of 416. An actual analysis of the product showed 62.2 percent carbon; 10.4 percent hydrogen; 6.6 percent nitrogen; and a molecular weight of 402.

EXAMPLE III

Preparation of diethylene glycol bis(N-n-propyl carbamate)

865 g. of n-propylamine and 1290 ml. of pyridine were placed into a 5 liter, triple-neck flask equipped with stirrer, condenser, thermometer, and addition funnel. This mixture was stirred and maintained below 50° F. while 1556 g. (6.73 moles) of diethylene glycol dichloroformate were slowly added. 800 ml. of benzene were added to the mixture to keep the reaction mobile and then the mixture was stirred for about 5 hours. The crude product-benzene solution was then washed 3 times with 800 ml. of a 10 percent hydrochloric acid solution followed by 3 washes with 1000 ml. of water. The crude product was further purified by a synthetic magnesium silicate percolation, and the benzene was evaporated to give approximately 700 g. of the crude product. The product was again dissolved in benzene and decolorized by passing through decolorizing charcoal, and cooled to recover 330 g. of white crystals. A small sample was dried over P_2O_5 at 65° F. under 2 mm. pressure. The product had a theoretical 52.1 percent carbon, 8.7 percent hydrogen, and 10.12 percent nitrogen. The actual analysis of the compound showed it to have 51.8 percent carbon, 7.5 percent hydrogen, and 9.9 percent nitrogen.

EXAMPLE IV

Preparation of diethylene glycol bis(N,N-diallyl carbamate)

970 g. of diallylamine, 500 ml. of benzene, and 880 ml. of pyridine were placed into a triple-neck flask equipped with a stirrer, condenser, thermometer, and addition funnel. The mixture was stirred and maintained below 50° F. while 1155 g. of diethylene glycol dichloroformate were slowly added. After stirring for about 15 hours, the mixture was washed with a 10 percent hydrochloric acid solution and thereafter washed again with a saturated salt solution. The remaining benzene and water were removed by distillation. The crude product weighed 1580 g. Further purification was made by vacuum distillation. Analysis of the fraction boiling at 173 to 195° F. at 300 to 750 microns was made. This product theoretically had 61.1 percent carbon; 7.95 percent hydrogen; and 7.95 percent nitrogen. Actual analysis of this compound showed that it contained 60.6 percent carbon; 7.95 percent hydrogen; and 7.8 percent nitrogen.

The hydrocarbon fuels of this invention are characterized by low deposit-forming tendencies with the result that an engine operated therewith shows an exceptionally clean combustion space, valve ring belt area and injection system as in the case of a diesel engine. The low deposit level in the engine minimizes surface ignition in all its manifestations, mainly preigniton and "knock." In addition, the low deposit level reduces the engine's octane requirement increase. In addition, deposits on surfaces contacted by a lubricating oil, such as piston skirts and cylinder walls, are very markedly reduced.

The major application of the additive of the invention 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 carbamates of this invention. In diesel fuels the presence of the polyglycol carbamate 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 carbamates fined particular application in jet fuels which are used as cooling mediums prior to their consumption. A polyglycol carbamate 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 carbamates. The gasolines to which the polyglycol carbamates are added can be broadly defined as a hydrocarbon fuel having a boiling point up to approximately 400° F.

The action of polyglycol carbamates of the prescribed composition in controlling the deposit-forming tendencies of a motor fuel was demonstrated by a modified Chevrolet deposits test—CRC FL–2–650 (Chevrolet S–II test). The laboratory engines were 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. The modifications were in every case in the direction of making the test more severe and were intended to simulate low temperature conditions wherein deposit formation is most pronounced. After the termination of each run, the engine was disassembled and its parts evaluated by a merit system adapted from the CRC–L–4–1252 test. This merit system involved visual examination of the engine parts in question and their rating according to deposits by comparison with standards which had assigned ratings. For example, a rating of 10 on piston skirt designated a perfectly clean piston while a rating of zero represented the worst condition. Similarly, a rating of 100 on total engine deposits represented a perfectly clean engine, etc.

In Table I there is shown the decrease in deposit formation resulting from the addition of various polyglycol carbamates 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'-disecondary butyl-p-phenylenediamine, lecithin, and N,N'-disalicylidene-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.

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

TABLE I.—CHEVROLET S-II TEST RESULTS

	Piston Skirt Rating	Total Engine Rating
Base Fuel	6.1	79.9
Base Fuel plus 0.1% DEG bis (2-ethylhexylcarbamate).	8.0	88.0
Base Fuel plus 0.05% DEG bis (N, N-diallyl carbamate).	8.0	88.0

DEG=diethylene glycol.

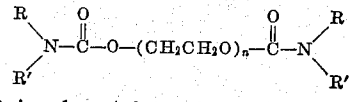
The above Table I demonstrates the ability of typical compounds of this invention to suppress engine deposits when incorporated in additive amounts in the fuel.

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 liquid hydrocarbon fuel for a combustion engine

boiling within the gasoline range containing a polyethylene glycol carbamate having the following general formula:



wherein R is selected from the group consisting of hydrogen, alkyl, alkenyl, and alkynyl radicals containing from 1 to 18 carbon atoms, R′ is selected from the group consisting of an alkyl, alkenyl, and alkynyl radical containing from 1 to 18 carbon atoms, and *n* is an integer ranging from 2 to 6, in an amount sufficient to inhibit engine deposits.

2. A liquid hydrocarbon fuel as described in claim 1 wherein the polyethylene glycol carbamate is present in an amount ranging from 0.01 to 1 percent by volume.

3. A liquid hydrocarbon fuel as described in claim 2 wherein R is hydrogen and R′ is an alkyl group containing from 1 to 18 carbon atoms and *n* is 2.

4. A liquid hydrocarbon fuel as described in claim 2 wherein R is hydrogen and R′ is an alkenyl group containing from 1 to 18 carbon atoms and *n* is 2.

5. A liquid hydrocarbon fuel as described in claim 2

wherein R and R′ are alkyl groups containing from 1 to 18 carbon atoms and *n* is 2.

6. A liquid hydrocarbon fuel as described in claim 2 wherein R and R′ are alkenyl groups containing from 1 to 18 carbon atoms and *n* is 2.

7. A liquid hydrocarbon fuel boiling within the gasoline range containing diethylene glycol bis(N-2-ethylhexyl carbamate) in an amount ranging from about 0.04 to 0.3 percent by volume.

8. A liquid hydrocarbon fuel boiling within the gasoline range containing diethylene glycol bis(N,N-diallyl carbamate) in an amount ranging from 0.04 to 0.3 percent by volume.

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