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2,885,274

MOTOR FUEL COMPOSITION

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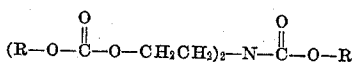
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6 Claims. (Cl. 44—71)

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 certain carbonate derivatives of diethanolamines.

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 pre-ignition 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 type of diethanolamine derivative, which is a substituted urethane compound, is outstanding in controlling the deposit-forming tendencies of hydrocarbon fuels.

The improved hydrocarbon fuels of this invention contain a carbonate derivative of diethanolamine hereinafter also termed a urethane compound having the following general formula:



where R is selected from the group consisting of aliphatic hydrocarbon radicals having from 1 to 8 carbon atoms and alkoxyalkyl radicals having from 2 to 10 carbon atoms, in an amount sufficient to reduce the deposit-forming tendencies of the fuels.

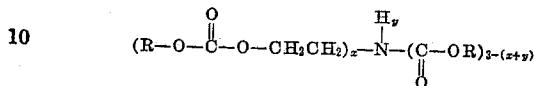
The urethane compounds of this invention are effective in the motor fuel in concentrations as low as 0.01 volume percent but concentrations of 0.04 to 0.3 volume percent are normally employed. There is no critical upper limit of concentration but economic considerations dictate that concentrations less than 1.0 volume percent of these urethane compounds be present in the fuel.

Examples of useful urethane compounds of this invention are as follows: ethyl urethane of diethanolamine bis (ethyl carbonate), allyl urethane of diethanolamine bis (allyl carbonate), butyl urethane of diethanolamine bis (butyl carbonate), propargyl urethane of diethanolamine bis (propargyl carbonate), n-amyl urethane of diethanolamine bis (n-amyl carbonate), 2-ethylhexyl urethane of diethanolamine bis (2-ethylhexyl carbonate), methoxyethyl urethane of diethanolamine bis (methoxyethyl carbonate), ethoxyethyl urethane of diethanolamine bis (ethoxyethyl carbonate), butoxyethyl urethane of diethanolamine bis (butoxyethyl carbonate).

The urethane compounds which inhibit the deposit-forming tendencies of hydrocarbon fuels in accordance with this invention are readily formed by a series of re-

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actions involving the formation of a chloroformate by reaction of phosgene with an alcohol and subsequently reacting the formed chloroformate with diethanolamine in the presence of a hydrogen chloric acceptor, such as pyridine or quinoline. Our copending application Serial No. 627,564, filed of even date, claims as novel compounds carbonate derivatives of ethanolamines having the general formula:



wherein R is an aliphatic hydrocarbon radical or an alkoxyalkyl radical having from 1 to 18 carbon atoms, x is an integer ranging from 1 to 3, and y is either 0 or 1. The specific urethane compounds useful in this invention as fuel additives are a subgenus of the novel compounds of this invention.

The urethane compounds of the present invention are effective in controlling deposits in hydrocarbon fuels having boiling points up to about 700° F. although benefits also result when the urethane compounds of this invention are added to fuels containing residual stocks of a 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 urethane compounds of this invention. In diesel fuels the presence of the urethane compound 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. Urethane compounds find particular application in jet fuels which are used as cooling mediums prior to their consumption. A urethane compound-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 these urethane compounds. The gasoline to which they are added can be broadly defined as a hydrocarbon fuel having a boiling point up to approximately 400° F.

The action of urethane compounds of the prescribed composition in controlling the deposit-forming tendencies of motor fuel was demonstrated by a modified Chevrolet deposits tests, 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 there is shown the decrease in deposit formation resulting from the addition of various urethane compounds to a high quality regular grade gasoline com-

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prising a mixture of thermal cracked stock, fluid catalytically cracked stock and straight run gasoline. This regular base fuel had and 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'-disecundary butyl-p-phenylene diamine, 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	5.9	79.9
Base Fuel plus ethoxyethyl urethane of diethanolamine bis (ethoxyethyl carbonate)	9.2	89.2
Base Fuel plus n-amyl urethane of diethanolamine bis (n-amyl carbonate)	7.8	86.8

The above Table I shows the advantage gained by utilizing urethane compounds of this invention in the fuel combustion engine in the preferred additive amount. The hydrocarbon fuels of this invention are characterized by low deposit-forming tendencies with the result that an engine operated therewith also shows a clean intake system, combustion space, valve, ring belt area, and injection system, of a diesel engine. A low level of deposit in the engine minimizes surface ignition in all its manifestations, mainly preignition and "knock." In addition, the low deposit level reduces the engine octane requirement increase.

In contradistinction to the excellent results obtained by utilizing the urethane compounds of this invention, closely related nitrogen compounds do not advantageously affect the deposit-forming tendencies of a fuel. For example, the compound tris(N-β-pentoxycarboxyethyl) amine which does not contain a urethane portion in its molecule degraded a fuel to which it was added with respect to engine deposits as demonstrated in the following Table II.

In Table II tris(N-β-pentoxycarboxyethyl) amine was added to a fuel having the same qualities as that previously used in obtaining the results shown in Table I. The lubricant was the same as that employed in Table I.

TABLE II

Chevrolet S-II test results

	Piston Skirt Results	Total Engine Results
Base Fuel	5.9	79.9
Base Fuel plus 0.1% tris (β-Z-pentoxycarboxy ethyl) amine	5.3	75.3

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The above Table II demonstrates that the compounds of this invention are unique among closely related compounds which might be expected to demonstrate similar qualities. The above data proves that tris(N-β-pentoxycarboxy ethyl)amine degraded the fuel with respect to low temperature engine 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:

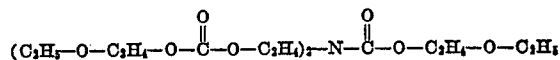
1. A liquid hydrocarbon fuel for a combustion engine boiling within the range of gasoline to light gas oil containing a compound having the following general formula:



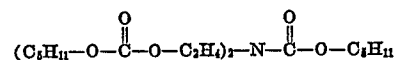
20 where R is selected from the group consisting of an aliphatic hydrocarbon radical having from 1 to 8 carbon atoms and an alkoxyalkyl radical having from 2 to 10 carbon atoms in an amount sufficient to suppress engine deposits.

25 2. A liquid hydrocarbon fuel as described in claim 1 wherein the amount of said compound present in the fuel ranges from 0.01 to 1 percent by volume.

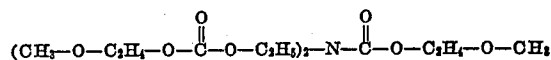
3. A liquid hydrocarbon fuel for a combustion engine boiling within the gasoline to light gas oil range containing from 0.04 to 0.3 percent by volume of a compound having the following formula:



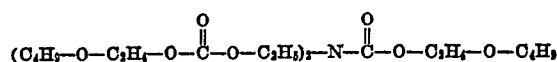
35 4. A liquid hydrocarbon fuel for a combustion engine boiling within the gasoline to light gas oil range containing from 0.04 to 0.3 percent by volume of a compound having the formula:



40 5. A liquid hydrocarbon fuel for a combustion engine boiling within the gasoline to light gas oil range containing from 0.04 to 0.3 volume percent of a compound having the formula:



50 6. A liquid hydrocarbon fuel for a combustion engine boiling within the gasoline to light gas oil range containing from 0.04 to 0.3 volume percent of a compound having the following formula:



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