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[54] **HYDROCARBON FUEL COMPOSITIONS**

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[57]

ABSTRACT

Liquid hydrocarbon fuel compositions, especially gasolines, containing certain hydrocarbyl polyamines, effectively nullify and/or inhibit fouling of vital parts of internal combustion engines.

4 Claims, No Drawings

HYDROCARBON FUEL COMPOSITIONS

BACKGROUND OF THE INVENTION

The invention relates to fuel compositions having improved properties. In particular, it relates to gasoline compositions which effectively inhibit and/or prevent the fouling of the fuel and inlet system of internal combustion engines.

One means of combating air pollution is to reduce the emission of hydrocarbons by gasoline engines, due, inter alia, to crankcase ventilation. This ventilation is necessary to prevent dilution and contamination of the lubricating oil by unburnt or partly burnt gasoline components leaking from the combustion chamber along the piston and cylinder walls into the crankcase. The crankcase is ventilated by a forced draft as a result of which components known as blow-by gases, find their way into the atmosphere. To reduce this type of emission, some engine manufacturers have provided the engine with means for returning the mixture of blow-by gases and air to the inlet system preceding the carburetor, for instance, to the air filter. This measure, however, causes fouling of the fuel and inlet system, which, in turn causes the engine to malfunction. This tends to increase the concentration of unburnt and partly burnt hydrocarbons in the exhaust gases.

It is possible to counteract fouling of the engine by incorporating a minor amount of compounds with detergent properties into the fuel. These compounds, however, if they are to be effective for this purpose, must also possess good water-shedding properties. If the water-shedding properties of a fuel additive are poor, the additive promotes water pick-up and emulsion formation in the fuel. Fuels containing such additives are, inter alia, difficult to handle.

For non-surface vehicles such as supersonic aircraft, the fuels (called aviation turbine fuels) have to meet very stringent thermal stability requirements; they not only must absorb the large amounts of heat generated, at high speeds, due to air friction, but must also remain stable if they are to function properly.

These high temperatures further entail the risk of interreaction of the hydrocarbon components present in the aviation fuel composition with the resultant formation of products which may deposit on vital engine parts. This can cause serious problems, such as clogging of filters, control systems and fuel supply lines. Therefore, thermal stability constitutes one of the major problems of fuels for supersonic aircraft.

Previous attempts have been made to solve these problems. As a rule, however, the usual oxidation inhibitors have proven entirely unsatisfactory. In certain cases inhibitors have even promoted the formation of deposits. In other cases where the additives possessed excellent antioxidant properties, they gave rise to the formation of gasoline-water-emulsions when brought into contact with water. For example, polyisobutenyl tetraethylene pentamine showed this disadvantage when contacted with water.

SUMMARY OF THE INVENTION

A class of polyamine compounds has now been found which, when incorporated as additives into the fuel in minor amounts, effectively act to inhibit and prevent engine fouling. When added to a gasoline, these polyamine compounds effectively counteract engine fouling and specifically inhibit fouling of the carburetor

and to a certain extent also fouling of other parts of the fuel and inlet system, such as valves and valve rods. They possess excellent water-shedding properties and when incorporated into aviation fuels, they stabilize these fuels against deterioration at high temperatures, and are able to minimize the formation of noxious products in the fuel system of the aircraft engine.

The compounds concerned are polyamines wherein at least one monovalent hydrocarbon group having at least 50 carbon atoms and at least one monovalent hydrocarbon group having at most five carbon atoms are bound directly to separate nitrogen atoms and wherein the number of hydrogen atoms which are bound to nitrogen is smaller than the number of nitrogen atoms present in the polyamine molecule.

The invention therefore relates particularly to liquid hydrocarbon fuel compositions comprising a major proportion of a fuel and a minor proportion of one or more polyamines wherein at least one monovalent hydrocarbon group having at least 50 carbon atoms and at least one monovalent hydrocarbon group having at most five carbon atoms are bound directly to nitrogen and wherein the number of hydrogen atoms which are bound to nitrogen is smaller than the number of nitrogen atoms present in the polyamine molecules.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

The fuels to be used in the fuel compositions according to the invention may be distillate fuels, flashed distillates or residual fuels. Preferred are distillate fuels such as diesel fuels, gasolines and aviation turbine fuels, the latter two being particularly preferred.

Aviation turbine fuel can be defined as a hydrocarbon oil having a Reid vapor pressure below 3 lb/sq. inch at 100°F and a final boiling point below 325°C.

Gasoline can be defined as a mixture of hydrocarbons having a boiling range determined according to ASTM method D 86 between about 30° and 210°C.

It is very surprising that the additive according to the invention shows such excellent water-shedding properties especially in gasolines, since the water-shedding properties of very closely related compounds are so poor that these compounds are unsuitable, in this respect, as gasoline additives. If the performance of an additive according to the invention, e.g., a reaction product of one mole of a polyisobutenyl (PIB) chloride with one mole of N,N-dimethylpropylene-1,3-diamine is compared with the performance of a closely related compound, which, however, lies outside the scope of the present invention, e.g., a reaction product of one mole of the same polyisobutenyl chloride with one mole of tetraethylenepentamine, it appears that although both compounds have very good detergent properties, the former has excellent water-shedding properties, while the water-shedding properties of the latter are unacceptable for a gasoline additive, since it tends to form undesirable water-gasoline emulsions when contacted by water.

Apparently, the fact that the terminal diamine structures of the additives according to the invention are tertiary having a more hydrophobic character rather than primary having a more hydrophilic character as in the PIB-tetraethylenepentamine coupled with the fact that the alkyl groups, according to the invention (e.g. methyl) are too small to significantly effect the polar nature of the diamine, contribute, at least in part, to the

advantageous use of the additives according to the invention.

The polyamines which according to the invention are incorporated into the fuel compositions (hereafter called the additives) may contain, if desired, more than one of each of the above-mentioned types of hydrocarbon groups. The monovalent groups may be bound to the same nitrogen atom or to different nitrogen atoms. Here, by monovalent hydrocarbon groups should be understood a monovalent radical, built up substantially from carbon and hydrogen, in which, however, dependent on the chosen method of preparation of the additives, a minor amount of one or more other elements, e.g., halogen, may be present. Examples of suitable hydrocarbyl groups are alkyl or alkenyl groups derived from alkanes or alkenes with a straight or a branched carbon chain, which may carry aromatic or cycloaliphatic hydrocarbon substituents. The hydrocarbon groups having at least 50 carbon atoms are preferably non-substituted alkenyl or alkyl groups, such as polyethylene groups, polypropylene groups, polybutenyl groups and polyisobutenyl groups, regularly branched being preferred. Additives containing less than 500 carbon atoms are preferred as hydrocarbon groups having at least 50 carbon atoms; particularly preferred are hydrocarbon groups having less than 200 carbon atoms. Polyisobutenyl groups are preferred most as hydrocarbon groups having at least 50 carbon atoms.

The hydrocarbon groups having at most 5 carbon atoms are preferably alkyl groups with an unbranched carbon chain. Preferred are methyl, ethyl and propyl. Methyl groups are preferred most.

In the additives according to the invention the number of hydrogen atoms which are bound to nitrogen should be smaller than the number of nitrogen atoms present in the additives. Preferred are additives wherein the number of hydrogen atoms which are bound to nitrogen is about half the number of nitrogen atoms present in the additive molecule.

The polyamines acting as carriers of the monovalent hydrocarbon groups in the additives according to the invention may be either aliphatic or aromatic polyamines. Both diamines and higher amines are suitable.

Examples of suitable diamines are ethylene-1,2-diamine, propylene-1,2-diamine, propylene-1,3-diamine, N,N-dimethylpropane-1,3-diamine, the butylene diamines and benzene-1,4-diamine. Examples of suitable higher amines are the polyalkylenepolyamines such as the polyethylenepolyamines, the polypropylenepolyamines and polybutylenepolyamines. Specific examples of the polyethylenepolyamines are diethylenetriamine, triethylenetetramine and tetraethylenepentamine, pentaethylenhexamine and higher polyamines with a molecular weight above 1000. As carriers of the monovalent hydrocarbon groups in the additives according to the invention, alkylene diamines are preferred, especially polymethylene- α,ω -diamine particularly propylene-1,3-diamine.

The additives according to the invention may be prepared, for instance, by allowing a polyamine which already carries the desired number of monovalent hydrocarbon groups having at most five carbon atoms to react with a halogen-containing hydrocarbon having at least 50 carbon atoms in the molecule. One may very suitably start from a chlorine-containing hydrocarbon obtained by chlorination substitution of an alkene having at least 50 carbon atoms in the molecule and a dou-

ble bond in the terminal position whose beta-carbon atoms carries a methyl group. The chlorination can very suitably be performed with an amount of chlorine that is just sufficient to convert the alkene into the corresponding alkenyl chloride. One may start, for instance, from polyisobutene which - in an inert solvent - is converted, with a stoichiometric amount of chlorine, into polyisobutenyl chloride. The reaction between the halogen-containing hydrocarbon and the polyamine is carried out at a temperature between 20° and 200°C, preferably in the presence of an inert solvent. In the reaction between a halogen containing hydrocarbon and a polyamine, hydrogen halide is formed in addition to the desired additives. The hydrogen halide formed combines with the polyamine used as starting material. Therefore, unless special measures are taken, the polyamine has to be present in large excess. Since it is desirable that the amount of polyamine required for the preparation be kept as small as possible, it is preferred that the reaction be carried out in the presence of a hydrogen halide acceptor that differs both from the polyamine used as starting material and from the additive formed. Examples of hydrogen halide acceptors suitable for use in the preparation of the present additives are, for instance, carbonates, bicarbonates, oxides and hydroxides. Favorable results are obtained by using sodium carbonate or potassium carbonate as the hydrogen halide acceptor.

The molar ratio in which the halogen-containing hydrocarbon having at least 50 carbon atoms in the molecule and the polyamine are reacted depends on the number of such hydrocarbon groups one wishes to introduce. For the preparation of additives according to the invention in which substantially a single hydrocarbon group having at least 50 carbon atoms in bound direct to one of the nitrogen atoms of the polyamine, one preferably uses at most 2 gram molecules of the starting polyamine per gram atom of halogen-containing hydrocarbon.

If the additives according to the invention are prepared by a process comprising the reaction of a halogen-containing hydrocarbon having at least 50 carbon atoms in the molecule with a polyamine in which one or more monovalent hydrocarbon groups with at most five carbon atoms are bound direct to nitrogen, very suitable products are produced from N,N-dimethylpropylene-1,3-diamine, N,N-diethylpropylene-1,3-diamine, N,N-dipropylpropylene-1,3-diamine, N,N-dibutylpropylene-1,3-diamine, N,N-dipentylpropylene-1,3-diamine, N-methylpropylene-1,3-diamine, N-ethylpropylene-1,3-diamine, N-butylpropylene-1,3-diamine, N-dienalpropylene-1,3-diamine and the like. Especially preferred is N,N-dimethylpropylene-1,3-diamine.

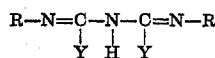
Excellent results have been obtained by the reaction of polyisobutenyl chlorides in which the average number of carbon atoms amounted to about 91 and about 117 with an N,N-di lower-alkyl-lower-alkylene- α,ω -diamine, specifically N,N-dimethylpropylene-1,3-diamine, in which reaction about 1.3 gram molecules of polyamine were used per gram atom of chlorine, present in the polyisobutenyl chloride. In this way, additives according to the invention were prepared wherein two lower-alkyl (one to four carbon atom alkyls), such as methyl groups and substantially one polyisobutenyl group having about 91 and 117 carbon atoms were bound direct to nitrogen and wherein the

number of hydrogen atoms which were bound to nitrogen was substantially half the number of nitrogen atoms present in the additive. These compounds, added in a small amount, for example to an aviation turbine fuel, imparted to that fuel stability against high temperatures, as was shown by the performance of aviation turbine fuel compositions according to the invention in a modified Fuel Coker Test. The aviation turbine fuels used may have been freed of sulfur by means of hydro-treating, or the sulfur compounds may have been converted by means of an acid (e.g., sulfuric acid) treatment. When the compounds according to the invention were added in a small amount to a gasoline, they showed a high activity as cleanliness agents for the carburetor as well as for other parts of the inlet system, such as the inlet valves and the inlet valve rods. Moreover, their water-shedding properties were excellent.

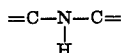
The concentration of the present additives in the fuel may vary within wide limits. In general, the desired stabilizing effect is obtained when the amount added is from 0.001 to 5%w preferably from 0.001 to 0.1%w. The additives may be added to the fuel as such or in the form of a concentrate with a small amount of hydrocarbon oil, such as a distillate fuel or lubricating oil.

In addition to a major amount of fuel and a minor amount of the present additives, the fuel compositions according to the invention may contain minor amounts of other additives by which the quality of the fuel is further improved, such as agents improving the ignition, scavenging agents, anti-icing additives, antioxidants, conductivity improving agents, metal deactivating compounds.

Suitable metal deactivators are compounds having the formula



wherein R represents a heterocyclic radical containing a $-\text{C}=\text{N}-$ group in a five-membered or six-membered ring and Y represents hydrogen or a cyclic or acyclic substituent, or the two Y's together with the



group form a cyclic structure. Examples are compounds of the above formula, in which the R group represents a thiazole, pyridine, quinoline or isopyrrole ring which may contain one or more substituents, and in particular compounds wherein this ring is attached to the nitrogen atom in the alpha-position. A very active metal deactivator, in particular copper deactivator, in this class of compounds is 1,3-di(2'-pyridyl)-iminoisindoline.

Especially suitable metal deactivators, which may be used in the fuel compositions according to the invention are compounds belonging to the class of the N,N'-disalicylidene-1,2-diaminoalkanes. Preferred in this class of compounds is N,N'-disalicylidene-1,2-diaminopropane.

The amount of metal deactivators which may be present in the fuel compositions according to the invention may vary within wide limits, between about 0.0001 and 0.01%w.

Anitoxidants, in particular alkylphenolic anitoxidants such as 2,6-di-tert-butyl-4-methylphenol and 2,4-dimethyl-6-tert-butylphenol may also be present in the

fuels according to the invention, preferably between about 0.005 and 0.05%w.

Conductivity improving agents, which decrease the tendency for self-inflammation during handling of fuels, in particular during pumping of aviation turbine fuels, may also be incorporated in the fuels. Suitable conductivity improving agents consist of a mixture of the calcium or barium salt of dialkyl (e.g., dioctyl) sodium sulfosuccinate, chromium salts of alkyl (e.g., $\text{C}_{14}-\text{C}_{18}$) salicylic acids and a copolymer of alkyl methacrylates (e.g., lauryl and/or stearyl methacrylates) and a vinyl-pyridine (e.g., 2-methyl-5-vinyl-pyridino and/or 4 vinyl-pyridine).

The invention will be further characterized by the following examples.

EXAMPLE I

Additive Synthesis

Two additives consisting of N'-polyisobutenyl-N,N-dimethylpropylene-1,3-diamine with different molecular weights were prepared.

Additive 1: Polyisobutene with a molecular weight of 1280 was dissolved in isooctane. After addition of a crystal of iodine to this solution, chlorine was introduced - at room temperature - until the color of the solution faded. Subsequently, the solvent was vaporized. The residue contained 2.84%w chlorine, corresponding to a mono-chloro-product.

A mixture of 123.2 g of polyisobutenyl chloride prepared in this way, 60 ml toluene and 10 g pulverized potassium carbonate was heated to 130°C - in a nitrogen atmosphere, with stirring - and subsequently, while the mixture was being stirred, 13.0 g N,N-dimethylpropylene-1,3-diamine was added dropwise over a period of 5 hours. Afterward, an additional amount of 4 g pulverized potassium carbonate was added and the reaction mixture - while being stirred - was kept at 130°C for 15 hours. After cooling down, the reaction product was taken up in a 60/80 gasoline and washed with water until the washwater was free from chlorine. The reaction product was isolated by vaporizing the solvent.

The product obtained weighed 124.5 g and had a nitrogen content of 1.24%w. It contained both secondary and tertiary amino nitrogens and one carbon-to-carbon double bond.

Additive 2: Polyisobutene with a molecular weight of 1635 was chlorinated, in the same way as described for additive 1, to a product with a chlorine content of 2.0%w.

A mixture of 140.6 g of this polyisobutenyl chloride, 75 ml toluene and 10 g pulverized potassium carbonate was heated to 130°C - in a nitrogen atmosphere, with stirring - and subsequently, while the mixture was being stirred, 10.5 g N,N-dimethylpropylene-1,3-diamine was added dropwise over a period of five hours. After that, an additional amount of 4 g pulverized potassium carbonate was added and the reaction mixture - while being stirred - was kept at 130°C for 15 hours. The reaction mixture was finished in the same way as described for additive 1.

The product obtained weighed 141.5 g and had a nitrogen content of 0.93%w. Analysis established it as being N,N-dimethyl-N'-polyisobutenyl-propylene-1,3-diamine.

Additives A, B, C, and
D(N-polyisobutenyltetraethylenepentamines)

For comparison, four related compounds which, however, lie outside the scope of the present invention, were prepared, starting from tetraethylenepentamine and polyisobutenes with molecular weights of 950, 1280, 1380 and 1635, respectively. The preparation of these additives was carried out in a way substantially the same as described for the additives 1 and 2.

Additive E and F: Also for comparison, two commercial gasoline dispersants were incorporated into the testing program.

Additive E is a reaction product of polyisobutenyl chloride, maleic anhydride and tetraethylenepentamine.

Additive F is a mixture of alkylamine salts of alkyl-phosphoric acids.

EXAMPLE II

The additives 1, 2, A, D, E and F were tested as gasoline additives in a Sunbeam Talbot engine and in a Ford engine. The concentration of the additives in the gasoline was 0.01%. For comparison, the two engine tests were also carried out with the same base gasoline containing no such additives. As base gasoline, a premium grade leaded gasoline was used.

Ford E 105 engine test: The extent of fouling of the carburetor was determined in a Ford E 105 engine equipped with a Solex B 30 PSE carburetor. The carburetor was of the standard design except for the gas valve chamber having been bored and lined with a duralumin insert. After the test, the fouling of the carburetor was evaluated. In order to accelerate the formation of deposits, small, accurately metered amounts of blow-by gas from the engine and exhaust gas (representative of driving a car in heavy traffic) were returned to the carburetor. The engine remained in operation for a total test period of 90 hours according to a scheme providing for operation in cycles consisting of running for 3.5 minutes at no load and running for 30 seconds with partly opened gas valve under conditions simulating driving on a road at normal load.

Sunbeam Talbot engine test: In this test, the inlet system fouling is determined on the basis of fouling of the inlet valves and the inlet valve rods. The test was carried out on a Sunbeam Talbot engine with a piston displacement of 2264 cm³, a compression ratio of 6.45 : 1, and a maximum capacity of 70 bhp at 4000 rpm. Before the test was started, the engine, including the two carburetors, was cleaned whereupon the engine was kept in continuous operation for 32 hours, at a speed of 1500 rpm, a capacity of 15 bhp and a fuel consumption of 5.0 kg per hour. After the test had been finished, the fouling of the inlet valves and the inlet valve rods was evaluated.

The water-shedding properties of additive 1 and 2 and additives A-F were determined in a test in which the fuel comprising 100 ppm (parts per million) additive is shaken with distilled water at ambient temperature under standard conditions. After adequate settling, the water content of a sample taken at a specified depth is determined by titration with Fischer reagent. The amount of free water is calculated from the total water content and basic solubility data.

The results of the engine tests and the water-shedding tests are given in Table I.

TABLE I

Additive.....	1	2	A	B	C	D	E	F
Molecular weight of the polyisobutene used for the preparation of the additive.....	1,280	1,635	950	1,280	1,380	1,635		
Composition of the additive:								
Number of nitrogen atoms.....	2	2	5	5	5	5		
Number of hydrogen atoms bound to nitrogen.....	1	1	6	6	6	6		
Number of monovalent hydrocarbon groups having at least 50 carbon atoms.....	1	1	1	1	1	1		
Number of monovalent hydrocarbon groups having at most 5 carbon atoms.....	2	2	0	0	0	0		
Ford E 105 engine test:								
Carburetor cleanliness effectiveness, percent:.....	85	84	96			74	68	84
Sunbeam Talbot engine test:								
Inlet system cleanliness improvement over base fuel, percent:.....	93	93	57			95	20	20
Water-shedding properties, p.p.m. free water.....	20	25	168	186	386	75	160	55

* 100 is perfect.

The compositions according to the invention are thus shown to possess effective cleanliness properties and concomitantly excellent water-shedding characteristics.

EXAMPLE III

Thermal Stability Test

The thermal stability of aviation turbine fuels containing additive 1 was tested according to a modified version of the ASTM/CRC Fuel Coker Test, (ASTM D 1660). A test fuel reservoir and a preheater different from those prescribed in the ASTM method were used viz.:

1. As test fuel reservoir a stainless steel reservoir of 25 l provided with a heating element was used wherein the fuel to be tested could be brought in one hour to 275°F and kept at that temperature during the test in contact with the atmosphere.
2. The preheater contained an aluminium preheater tube, which was internally supported by a stainless steel tube. The outer tube of the preheater was surrounded by a 3 cm thick layer of insulating material.

Moreover, no in line micron filter was present between the fuel reservoir and the preheater.

The aviation turbine fuel compositions were tested for five hours at a preheater fuel outlet temperature of 435°F and a filter temperature of 525°F, maintaining a fuel temperature of 275°F in the reservoir.

This modified version is considered to be a more severe test for the fuel than the ASTM D 1660 test proper, in view of the high preheater temperature and in view of the fact that the fuel to be tested is in contact with air at a high temperature.

The drop over the filter in inches mercury and the rating of the preheater tube deposits were determined as described in ASTM method D 1660.

An aviation turbine fuels there were used an acid treated kerosene and a hydrodesulfurized kerosene both with a Reid vapor pressure of 0.1 lb/sq inch at 100°F and a boiling range from 150°-250°C.

Table 2 shows the results; tests 1, 2 and 6 are for comparison, and not according to the invention.

on a gasoline fuel containing from 0.001 to 5 percent by weight of N'-polyisobutenyl-N,N-dialkylpropylene-1,3-diamine wherein the polyisobutenyl group has at least 50 and less than 200 carbon atoms and each alkyl group of said dialkyl is unbranched alkyl of one to three carbon atoms.

TABLE 2

Test No.	Acid treated kerosine	Hydro-treated kerosine	Additives parts per million				Results	
			Additive 1 according to the invention	N,N'-disalicylidene-1,2-diamino propane	1,3-di(2'-pyridyl)-iminolso-indoline	Conductivity improving additive*	Press. drop (inch mercury)	Preheater tube rating
1.....	-	+	0	0	0	0	**184	4
2.....	-	+	0	7	0	0	10.8	<3
3.....	-	+	200	0	0	0	0.1	4
4.....	-	+	100	0	0	0	0.05	4
5.....	-	+	50	7	0	0	0.01	1
6.....	+	-	0	0	0	0	**179	4
7.....	+	-	50	0	0	0	0.02	4
8.....	+	-	50	7	0	0	0.1	2
9.....	+	-	50	0	7	0	0.1	3
10.....	+	-	50	0	0	0.75	0.05	4

*50% solution of the calcium salt of dioctyl sodium sulfosuccinate, chromium salts of alkylsalicylic acids and a copolymer of alkyl methacrylates and 2-methyl-5-vinylpyridine.

**Time in minutes in which pressure drop amounted to 25 inch mercury.

Thus, the inventive compositions showed markedly superior thermal stability. Further, the addition of N,N'-disalicylidene-1,2-diamino propane to the inventive compositions apparently enhanced their effectiveness.

It is clear from the test results and preceding data that liquid hydrocarbon distillate fuel compositions containing polyamines according to the invention effectively counteract, nullify and/or inhibit fouling of vital parts of internal combustion engines.

We claim as our invention:

1. A method for reducing hydrocarbon exhaust gas emissions by operating an internal combustion engine

2. A method for reducing hydrocarbon exhaust gas emissions by operating an internal combustion engine on a gasoline fuel containing between 0.001 and 0.1 percent by weight of N'-polyisobutenyl-N,N-dimethylpropylene-1,3-diamine wherein the polyisobutenyl group has at least 50 and less than 200 carbon atoms.

3. The composition of claim 1 in which the alkyl groups are methyl.

4. The composition of claim 1 in which the amount of the diamine is between 0.001 and 0.1 percent by weight.

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