United States Patent Office 3,434,814 Patented Mar. 25, 1969

3,434,814

EMISSION CONTROL ADDITIVE

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No Drawing. Filed June 29, 1966, Ser. No. 561,415
Int. Cl. C10m 10/02, 1/22
U.S. Cl. 44—69 5 Claims

ABSTRACT OF THE DISCLOSURE

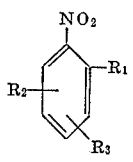
Increase of combustion chamber deposits and exhaust hydrocarbon emission of internal combustion engines is reduced by operating the engine on gasoline containing ortho-substituted aromatic nitro compounds.

This invention relates to a fuel composition for use in internal combustion engines which results in reduced hydrocarbon emission in the exhaust gas and a reduced amount of combustion chamber deposits. In particular, this invention relates to a liquid hydrocarbon fuel containing an aromatic nitro compound.

The exhaust gas of internal combustion engines contains some quantity of unburned hydrocarbons. Hydrocarbons are reported by researchers to react with ozone in the atmosphere, forming irritants. Research has attributed photochemical smog to the presence of hydrocarbons in the atmosphere. Thus, a need exists for a method to reduce the amount of hydrocarbon introduced into the atmosphere from the exhaust gas of internal combustion engines. Previous means of accomplishing this have been through the secondary oxidation of the unburned exhaust hydrocarbons employing catalytic oxidizing methods or direct flame oxidation in the exhaust system. If the amount of unburned hydrocarbons initially in the exhaust can be reduced, the need for secondary oxidation is diminished. Previous attempts to reduce the initial hydrocarbon content of the exhaust gas have concentrated on mechanical methods such as improved carburetion. The present invention relates to a method of reducing exhaust emission and engine deposits through the use of a fuel containing an exhaust emission reducing additive.

An object of this invention is to provide an improved fuel composition. A further object is to provide a fuel composition which, when used to operate an internal combustion engine, results in reduced hydrocarbon emission. A still further object is to provide a fuel that will substantially reduce the amount of deposits formed in the combustion chamber of engines.

These and other objects are accomplished by providing an improved fuel composition comprising a major portion of a liquid hydrocarbon fuel and a minor quantity, sufficient to reduce exhaust emission and engine deposits, of an aromatic nitro compound having the formula:



(I)

wherein R_1 is selected from the group consisting of alkyl radicals having from 1–20 carbon atoms, aryl radicals having from 6–20 carbon atoms, aralkyl radicals having from 7–20 carbon atoms, alkanoyloxy radicals containing from 1–12 carbon atoms, alkoxy radicals containing from 1–12 carbon atoms, hydroxyl radicals and halogens having an atomic No. from 17–35, and R_2 and R_3 are selected from the group consisting of hydrogen, nitro radicals,

hydroxyl radicals, alkoxy radicals containing from 1–12 carbon atoms, alkyl radicals containing from 1–20 carbon atoms, aryl radicals containing from 6–20 carbon atoms, and aralkyl radicals containing from 7–20 carbon atoms.

In more preferred embodiments of the invention, R_1 in Formula I is selected from the group consisting of alkyl radicals having from 1–20 carbon atoms, aryl radicals having from 6–20 carbon atoms, aralkyl radicals having from 7–20 carbon atoms, alkanoyloxy radicals containing from 1–12 carbon atoms, alkoxy radicals containing from 1–12 carbon atoms, and halogens having an atomic No. from 17–35, and R_2 and R_2 are selected from the group consisting of hydrogen, nitro radicals, alkoxy radicals containing from 1–12 carbon atoms, alkyl radicals containing from 1–20 carbon atoms, aryl radicals containing from 6–20 carbon atoms and aralkyl radicals containing from 7–20 carbon atoms.

Not all nitro aromatics are useful in reducing exhaust emissions. For example, nitrobenzene itself causes an increase in both exhaust emission and combustion chamber deposits. The useful aromatic nitro compounds are those having some fuel solubility and an ortho substituent as shown in Formula I. Some examples of these aromatic nitro compounds are

o-nitro toluene,
2,6-dinitrochlorobenzene,
2,5-dimethoxy nitrobenzene,
o-sec-dodecyl-nitrobenzene,
2-dodecoxy-4-methyl-nitrobenzene,
2-methyl-4-hydroxy-5-tert-butyl-nitrobenzene,
2-chloro-4-methoxy-nitrobenzene,
2-bromo-5-tert-eicosyl-nitrobenzene,
2-hexanoyloxy-4-phenyl-nitrobenzene,
2-methoxy-4-tert-butyl-5-hydroxy-nitrobenzene,
2-tert-octyl-6-chloro-nitrobenzene,
2,4-dibromo-nitrobenzene,
2-(α-methylbenzyl)nitrobenzene,
2-acetoxy-5-tert-cetyl-nitrobenzene,
2-methoxy-3,5-dichloro-nitrobenzene,
2,6-dinitro-chlorobenzene,
2-dodecanoyloxy-4-tert-octadecyl-nitrobenzene,
2-chloro-4-benzyl-nitrobenzene,
2 - methyl - 5-(2,4-di-tert-butyl-α,α-dimethylbenzyl)-nitrobenzene,
1,3-dinitro-6-(2-methyl-4-sec-tridecylphenyl)benzene, and
the like.

Highly preferred aromatic nitro additives are 1,4-dimethoxy-2-nitrobenzene, 2,4-dinitro-toluene and picryl acetate.

The additives of this invention can be used to reduce emissions and combustion chamber deposits resulting from the use of a broad range of liquid hydrocarbon fuels including both spark ignition and diesel fuels. It is especially useful in gasoline used in spark ignition engines. These liquid hydrocarbon fuels have a boiling range of from about 95 to about 400° F., and contain aliphatic, aromatic, olefinic and naphthenic hydrocarbons. The hydrocarbon fuels may contain other materials frequently used in such fuels. For example, the fuels may contain antiknock agents such as tetraethyllead, tetramethyllead, triethylmethyllead, diethyldimethyllead, trimethylethyllead, tetravinyllead, triethylvinyllead, diethyldivinyllead, trivinylethyllead, ferrocene, methyl ferrocene, iron carbonyl, methylcyclopentadienyl manganese tricarbonyl, methylcyclopentadienyl nickel nitrosyl, N,N-dimethylaniline, and the like. When metallic antiknock agents are employed the fuels generally contain a scavenging agent. A particularly useful scavenging agent when lead alkyls are employed are the halohydrocarbons such as ethylenedichloride, ethylenedibromide, and the like. An especially useful

fuel in this invention is a fuel containing from 0.5 to 6 grams of lead per gallon as tetraethyllead and from 1.5 to 2.5 gram atoms of chlorine as a chlorohydrocarbon per gram atom of lead and from 0.5 to 1.5 gram atoms of bromine as a bromohydrocarbon per gram atom of lead. The most prefered chlorohydrocarbon is ethylenedichloride, and the most preferred bromohydrocarbon is ethylenedibromide.

The fuels can also contain deposit modifying agents such as phosphorus containing additives, for example, tricresylphosphate, cresyldiphenylphosphate, trimethylphosphate, dimethylcresylphosphate, tris(β-chloropropyl)phosphate, and the like.

The fuels frequently contain antioxidant additives such as 2,6-di-tert-butylphenol; 2,6-di-tert-butyl-4-methylphenol; 4,4'-methylenebis(2,6-di-tert-butylphenol); 2,2'-methylenebis(4-methyl-6-tert-butylphenol); phenylenediamines; p-nonylphenol; mixed alkylated phenols, 4,4'-thiobis(3-methyl-6-tert-butylphenol), and the like.

Other materials can be present in the fuel such as deicers, metal deactivators, pour point depressants, boron esters, nickel alkyl phosphates and dyes.

The following examples illustrate the preparation of typical improved fuel compositions of this invention.

EXAMPLE 1

To a blending vessel is added 1000 gallons of a gasoline having the following properties:

Boiling range	°F.	101–375
Research octane number		93
Aromatics	(volume percent)	38
Olefinics	do	10
Aliphatics	do	52

To this gasoline is added a tetraethyllead antiknock agent containing two gram atoms of chlorine as ethylenedichloride per gram atom of lead and one gram atom of bromine as ethylenedibromide per grams atom of lead. The quantity of tetraethyllead antiknock agent added is sufficient to provide 3.17 grams of lead per gallon of fuel. There is then added sufficient 1-chloro-2,4-dinitrobenzene to give a concentration of 0.25 weight percent. The mixture is agitated until thoroughly mixed, resulting in a gasoline having reduced exhaust emission properties.

EXAMPLE 2

To a blending vessel is added 1000 gallons of a gasoline having the following properties:

Boiling range	°F.	94–403
Research octane number		97
Aromatics	(volume percent)	62
Olefinics	do	5
Aliphatics	do	33

To this gasoline is added a tetraethyllead antiknock mixture containing one theory of chlorine as ethylenedichloride and 0.5 theory of bromine as ethylenedibromide. A quantity sufficient to provide 2.12 grams of lead per gallon is added. There is also added, as an antioxidant, a mixture of butylated phenols containing about 75 percent 2,6-di-tert-butylphenol, such that the gasoline contains 0.1 weight percent of the antioxidant mixture. Then 0.15 weight percent of 1,4-dimethoxy-2-nitrobenzene is added and the mixture thoroughly stirred, resulting in a gasoline giving reduced emission and combustion chamber deposits weight when used to operate a spark ignition internal combustion engine.

Good results are also obtained in the above example when 2,4-dinitro-toluene is employed as the emission and deposit reducing agent.

EXAMPLE 3

To a blending vessel is added 1000 gallons of a diesel fuel having a boiling range of from 430–572° F., and a cetane number of 47. To this is added 0.3 weight percent amyl nitrate as a cetane improver. There is then added 0.2 weight percent of picryl acetate, resulting in a diesel fuel having reduced exhaust emission properties.

In any of the previous examples, the forementioned emission reducing compounds can be employed, giving fuels having reduced emission properties. Also, the concentrations may be varied from those shown. In general, a concentration of from about 0.05 to 3 weight percent of the emission reducing additive can be employed. A preferred concentration range is from about 0.1 to 1 weight percent, and a most useful range is from about 0.1 to 0.5 weight percent.

Tests have been conducted to demonstrate the useful exhaust emission properties of the present compounds. In these tests, a single cylinder overhead valve engine, having a 10:1 compression ratio and a 36 cubic inch displacement, is operated on a typical commercial gasoline containing 3.17 grams of lead as a commercial tetraethyllead antiknock mixture containing one theory of chlorine as ethylenedichloride and 0.5 theory of bromine as ethylenedibromide. One theory of either bromine or chlorine is two gram atoms of bromine or chlorine per gram atom of lead. The engine is idled for 45 seconds and then run at 50 percent wide open throttle for 135 seconds under the following conditions.

Air/fuel ratio		13
R.p.m.		1370
Ignition timing	°BTC	15

The above cycle is continuously repeated until both deposits and hydrocarbon emissions have stabilized. This usually requires from about 100–145 hours of operation. The hydrocarbon content of the exhaust gas is determined using a Beckman 109–A Flame Isomerization Detector, and the deposits are determined by disassembling the engine, removing and weighing the deposits. The procedure is first carried out using a fuel without the emission reducing additive and then repeated on the same fuel containing an emission reducing additive. This is followed by another test on the fuel, again without the emission additive, to reconfirm the baseline. Using this procedure, the following results in terms of the percent reduction in exhaust hydrocarbon emission and engine deposits were obtained using emission reducing additives of this invention.

Additive	Conc. (wt. percent)	Percent reduction	
		Deposits	Emission
Nitrobenzene	.25	[1] 22	[1] 28
1,4-dimethoxy-2-nitrobenzene	.25	40	25
1-chloro-2,4-dinitrobenzene	.25	29	14
2,4-dinitrotoluene	.25	.22	17

[1] Gain average of two tests.

As these results show, the emission reducing additives of the present invention effectively reduce both exhaust emission and engine deposits. The reduction in deposits and emission was very significant. Deposit reduction ranged from 22–40 percent and emission reduction from 14–25 percent. In contrast, nitrobenzene (not claimed as this invention) gave a sharp increase in both deposit weight and exhaust emission.

We claim:

1. A liquid hydrocarbon fuel of the gasoline boiling range having reduced emission and deposit forming properties when used to operate an internal combustion engine, said fuel comprising a major quantity of a liquid hydrocarbon of the gasoline boiling range and a minor amount sufficient to reduce exhaust emissions and engine deposits of an aromatic nitro compound selected from the group consisting of 1.4-dimethoxy-2-nitrobenzene, 2,4-dinitrotoluene, and picryl acetate.

2. The composition of claim 1 containing from 0.5 to 6 grams of lead per gallon as a tetraalkyllead antiknock, from 0.5 to 2 theories of chlorine as ethylene dichloride and from 0.25 to 1.0 theory of bromine as ethylene-bromide.

3. The composition of claim 1 wherein said aromatic nitro compound is 1,4-dimethoxy-2-nitrobenzene.

4. The composition of claim 1 wherein said aromatic nitro compound is 2,4-dinitro toluene.

5. The composition of claim 1 wherein said aromatic nitro compound is picryl acetate.

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U.S. Cl. X.R.

44—57, 74, 75

UNITED STATES PATENT OFFICE

CERTIFICATE OF CORRECTION

March 25, 19

Patent No. 3,434,814

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It is certified that error appears in the above identified patent and that said Letters Patent are hereby corrected as shown below:

Column 4, line 74, "1.4-" should read -- 1,4- --. Column 5, line 5, "bromide." should read -- dibromide. --.

Signed and sealed this 7th day of April 1970.

(SEAL)

Attest:

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