United States Patent Office

3,146,203

Patented Aug. 25, 1964

1

3,146,203
OCTANE REQUIREMENT INCREASE REDUCING FUEL AND LUBRICANT COMPOSITIONS

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No Drawing. Filed Nov. 20, 1961, Ser. No. 153,756
8 Claims. (Cl. 252—49.9)

This invention relates to improved hydrocarbon fuels and motor lubricants containing a mixture of nitrogen-containing additives which reduce or suppress deposit formation in internal combustion engines. More specifically, this invention discloses novel fuels and lubricating oils having improved characteristics with respect to octane requirement reduction and spark plug cleanliness.

In recent years combustion chamber deposits have caused increased problems particularly with respect to octane requirement increase, surface ignition and spark plug life. Various gasoline additives, chiefly organic phosphorus compounds and boron compounds, have been introduced commercially to combat the latter two problems. However, the search for effective deposit modifiers and deposit removers to combat octane requirement increase has not been as fruitful, and the formation of deposits on combustion chamber surfaces still poses a knotty problem to gasoline manufacturers. While these deposits also cause increased engine wear, preignition knocking and spark plug fouling, one of the most deleterious effects is the increase in octane requirement at engine deposit equilibrium. Moreover, the formation of deposits on various other parts of an internal combustion engine, i.e., fuel and air intake system, presents additional problems affecting efficient engine operation. The formation of deposits in a carburetor, for example, can cause sticking of the automatic choke, fouling of the venturi, restriction of idle air flow around the throttle blades, and other conditions which adversely affect engine operating efficiency.

Deposit formation is usually the result of a heat-induced polymerization of various hydrocarbon constituents and/or decomposition products of the gasoline fuel and the crank case lubricating oil. This polymerization reaction is coupled with incomplete combustion of the fuel/air mixture in the engine to produce a non-volatile gum, impregnated with carbon and other combustion residues of the gasoline, e.g., lead salts. These materials become hard and flint-like and adhere to the interior surfaces of a combustion chamber as an agglomerate deposit. Initially, these deposits are present as a thin, varnish-like material which is soluble in organic solvents. However, on continued operation of the engine, the deposits accumulate and become a thick, insoluble thermo-insulating layer with the hardest flint-like deposits formed at high operating temperatures.

It is well known that as these deposits collect in the combustion chamber the octane requirement of the engine gradually rises until a deposit equilibrium level is reached. Generally, it takes on the order of 50 to 100 hours of operation for an originally clean engine to reach an equilibrium octane requirement. The difference between the clean engine octane requirement and the equilibrium octane rquirement is called the octane requirement increase or increment, usually abbreviated ORI, and is a function of both the fuel and the lubricant. Generally, certain fuel and lubricant characteristics and engine-operation conditions determine the amount and character of the combustion chamber deposits formed. Additives which either remove formed deposits or serve to prevent the deposition of materials on the various areas of the combustion chamber are referred to as octane requirement reduction agents (abbreviated ORR).

2

Some materials have been proposed as deposit modifiers or preventers. Boron compounds, metal chelates and various combustion catalysts, for example, have been proposed to remove deposits and clean combustion chamber surfaces. In general, these materials have not been too satisfactory. In fact, there is a long and unsuccessful history of attempts to develop a deposit removal or preventative additive which could be directly incorporated in the fuel or lubricant for spark ignition engines. Only very limited success has been achieved although numerous additives have been tried.

Essentially all commercially available motor gasolines contain additives of various types. The most common of these are the tetraalkyllead antiknock compound such as tetraethyllead and tetramethyllead, which are added in concentrations up to 4 cc. per U.S. gallon in motor gasoline and up to 6 cc. per U.S. gallon in aviation gasoline. Other organo-metallic antiknock additives which may be used are such materials as cyclopentadienyl nickel nitrosyl, methylcyclopentadienyl manganese tricarbonyl, iron pentacarbonyl, tris(acetylacetonate) iron, nickel 2-ethyl salicylate, bis(n-butyl salicylaldimine) nickel, vanadium acetylacetonate, ferrocenes and the like. However, because of the rise in criticality of ignition control problems such as pre-ignition, wild ping, and rumble or pounding, in modern automotive engines, most gasolines today also contain certain ignition control additives. The most effective of the ignition control additives in use currently, and those with which the invention is concerned, are compounds of phosphorus and, to a lesser extent, compounds of boron. Phosphorus compounds which are useful as ignition control additives in leaded gasolines containing halohydrocarbon scavengers are alkaryl phosphates or phosphites as in Yust et al., U.S. 2,899,212, issued June 2, 1959; alicyclic phosphates as shown in Yust et al., U.S. 2,765,220, issued October 2, 1956; carbocyclic phosphorus compounds containing a direct carbon-to-phosphorus bond as in Yust, et al., U. S. 2,828,195, issued March 25, 1958; esterified thiophosphates and thiophosphites containing at least one alkaryl ester group as in Yust et al., U.S. 2,843,465, issued July 15, 1958; tri-heterocyclic phosphates as in Yust et al., U.S. 2,841,480, issued July 1, 1958; tri(beta-haloaliphatic) phosphites and phosphates as in Kolka, U.S. 2,866,808, issued December 30, 1950; dimethyl monophenyl phosphates as in Orloff et al. U.S. 2,911,431, issued November 3, 1959; dimethyl monophenyl phosphates as in Orloff et al., U.S. 2,870,186 issued January 20, 1959; and alkyl phosphates and phosphites.

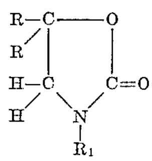
Among the boron compounds useful as additives for abnormal ignition control are oleophilic group-substituted heterocyclic compounds of boron and nitrogen as shown in Scott et al., U.S. 2,821,463, issued January 28, 1958; cyclic esters of boric acid as in Garner, U.S. 2,940,839, issued June 14, 1960; alkyl boronic acids as in Darling, U.S. 2,710,251, issued June 7, 1955; and esters of alkane diols and boronic acids as in Darling U.S. 2,710,252, issued June 7, 1955.

Such ignition control additives do not generally reduce the amount of combustion chamber deposits but rather they modify the deposits in such a manner as to reduce abnormal ignition phenomena, e.g., by lowering the electrical or thermal conductivity of deposits. Furthermore, such additives do not significantly reduce the tendency of the octane number requirement of the engine to increase.

It is accordingly an object of the invention to provide improved internal combustion engine fuels and lubricating compositions having reduced tendencies to form combustion chamber deposits. It is also an object of the invention to provide a fuel which will reduce the quantity of combustion chamber deposits which are laid down in engines. It is an object of the invention to provide an improved lubricating oil which will reduce the quantity of combustion chamber deposits which are laid down in engines. It is a further object of the invention to provide a fuel composition which will have a reduced octane requirement at engine deposit equilibrium. A still further object of the invention is to provide a new method of reducing the octane number requirement of engines already containing substantial quantities of combustion chamber deposits. Another object of the invention is to provide an ORR agent with properties such that it will perform effectively in an internal combustion engine under varying conditions. Still other objects will become apparent in the description of the invention.

Accordingly, it has been found that when certain alkyl substituted 2-oxazolidones are used as gasoline and lubricating oil additives in internal combustion engines, a significant reduction in octane requirement is produced. More particularly, the use of such ORR agents in either the gasoline fuel or the crank case lubricating oil, substantially eliminates engine deposits or at least minimizes deposits to a point where they are no longer a material consideration in engine operation. This outstanding advantage is obtained without deleteriously affecting other necessary characteristics of the fuel or lubricating oil, such as stability, performance ratings, and the like.

The improved hydrocarbon fuels and lubricating oils of the invention contain a mixture of from about 0.01% v. to about 5.0% v. of an alkyl-substituted 2-oxazolidone having the structural formula:

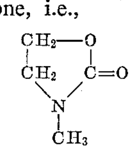


(I)

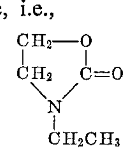
These alkyl-substituted 2-oxazolidones are oil- and gasoline-soluble compounds composed solely of carbon, nitrogen, oxygen, and hydrogen wherein R and R_1 represent low-molecular-weight alkyl radicals containing from 1 to 4 carbons atoms and R can also be a hydrogen atom. The above structural formula will be referred to hereinafter as (I).

Specific examples of the ORR agents of the invention include

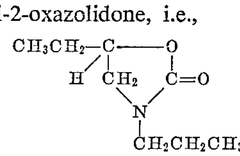
N-methyl-2-oxazolidone, i.e.,



N-ethyl-2-oxazolidone, i.e.,



N-propyl-5-ethyl-2-oxazolidone, i.e.,



Quite unexpectedly, it was discovered that the materials of Formula I produce significant reductions in octane requirement and engine deposit (i.e., one Research Octane number and greater). This result is particularly significant and unexpected when the materials of Formula I are compared to related 2-oxazolidones wherein the nitrogen atom is not alkyl-substituted. For it has been discovered that the 2-oxazolidones are not effective as ORR agents unless the nitrogen atom is substituted with an alkyl radical having from one to four carbon atoms. Further, it has been found that the unexpected ORR properties of the materials of Formula I are limited to nitrogen-substituted 2-oxazolidones wherein the number 4 atom in the ring, that is the carbon atom adjacent to the nitrogen atom, contains only hydrogens. That is, if the number 4 carbon atom is substituted with anything other than hydrogen, the resultant compound is ineffective as an ORR agent.

The mechanism by which the materials of Formula I function is not thoroughly understood; however, it has been determined that the effective ORR agents of the invention are unexpectedly limited to the N alkyl-substituted 2-oxazolidones of Formula I. Moreover, it is preferred that the materials of Formula I contain 10 or less total carbon atoms to insure optimum effectiveness.

In a further preferred embodiment of the invention the materials of Formula I are used in gasoline motor fuel compositions containing phosphorus and boron surface ignition-control additives such as disclosed in U.S. Patents, 2,889,212, 2,765,220, 2,828,195, 2,843,465, 2,841,480, 2,866,808, 2,911,431, 2,870,186, 2,821,463, 2,940,839, 2,710,251 and 2,710,252.

The ORR agents of this invention can be introduced into the combustion zone of the engine in various ways to accomplish a reduction in deposits and to prevent further accumulation of engine deposits. Thus these ORR agents can be injected directly into the intake manifold intermittently or substantially continuously as desired. A preferred method is to incorporate the mixture into the fuel composition. For example, it can be added separately to the fuel or blended with other gasoline additives. Moreover, the additives can also be introduced into the combustion chamber as a separate fuel charge during those periods of engine operation at which the hardest deposits are more likely to form, thereby effecting economy in using the additive. Spark ignition engine fuels, jet engine fuels and also compression engine fuels can be treated in this manner.

Another preferred method of introducing an ORR agent of the invention into the combustion chamber is as an additive to the crank case lubricating oil. Such a lubricating oil is effective in maintaining deposits at a low level with the result that an engine lubricated therewith will show exceptionally clean cylinder head, combustion chamber, intake valve and piston crown and ring areas. Deposits on surfaces contacted by these lubricating oil containing additives, such as piston skirts and cylinder walls, are markedly reduced.

The ORR agents of the invention are effective in motor fuels and lubricating oils in total concentrations as low as about 0.02% by volume but total concentrations of about 0.05 to about 1.0% v. are normally employed. There is no critical upper limit of concentration but economic considerations dictate that the total concentration of the additive be less than about 5% v. in the fuel. In a preferred embodiment the materials of Formula I are employed in concentration of about 0.5% v. It is further understood that mixtures of various materials of Formula I can be employed within the concentration limitations set forth above.

The fuel to which the additive is added is preferably a gasoline boiling in the range of about 30° F. to 450° F. and usually about 30° F. to about 425° F., preferably consisting mainly of hydrocarbons. However, the additives can also be added to diesel engine fuel comprising hydrocarbons boiling in the range of about 400° F. to 750° F. and to jet engine fuels comprising hydrocarbons boiling in the range of about 100° F. to 600° F. The fuels used in this embodiment of the invention can contain in addition to the compounds of Formula I any of the fuel additives commonly used in the art such as organometallic antiknock agents, i.e., tetraalkyllead, and other organo-metallic additives such as iron pentacarbonyl, methylcyclopentadienyl manganese tricarbonyl and halogen scavengers such as ethylene dibromide and dichloride. In addition to the above additives, the fuel composition of the invention can and ordinarily will contain other additives, for example, dyes, spark plug anti-foulants such as tricresyl phosphate, dimethyl xylyl phosphate and diphenyl cresyl phosphate, combustion modifiers such as alkyl boronic acids and lower alkyl phosphates and phosphites, oxidation inhibitors, metal deactivators such as polymerized linoleic acids and N,C-disubstituted imidazolines and the like. The ORR agents of the invention are effective in hydrocarbon fuels which do not contain antiknock and other organo-metallic additives; however, in a preferred embodiment of the invention the ORR agents are used with hydrocarbon fuels containing organo-metallic antiknock additives, preferably a tetra-lower-alkyl lead compound as tetraethyllead, tetramethyllead, methyl triethyl lead and the like.

The lubricating oils to which the ORR additives of the invention are added are preferably mineral oils. They can be paraffin base, naphthene base or mixed paraffin-naphthene base distillate or residual oils. Lubricating oils having an SUS viscosity at 100° F. between about 50 and 1,000 may be used. These lubricating oils will usually contain other additives such as detergents and dispersants. A preferred lubricating oil for use in the invention is a non-ash forming mineral oil within the SAE 10–30W range.

This invention also contemplates the combination of hydrocarbon fuels containing an ORR agent of Formula I used in conjunction with a lubricating oil containing the same or a related ORR additive. In this mode of engine operation the ORR agent is added to the hydrocarbon fuel in a concentration of about 0.01 to 1% by volume and to the lubricating oil in a concentration of about 0.05 to 1% by volume.

The following are examples of compositions suitable for use according to the invention.

Example I

Catalytic reformate	99.9 % v.
N-methyl-2-oxazolidone	0.1% v.
Phenyl discresyl phosphate	0.2 theory.
Methylcyclopentadienyl manganese tricarbonyl	0.5 g. Mn/gal.

Example II

Catalytic reformate	98.75% v.
Mixture of:	
N-n-propyl-2-oxazolidone	1.0% v.
N-isopropyl-2-oxazolidone	0.25% v.
Cresyl diphenyl phosphate	0.4 theory.

Example III

Straight run gasoline	80% v.
Butene-isobutane motor gasoline alkylate	19.5 v.
N-ethyl-5-methyl-2-oxazolidone	0.5% v.
Tricresyl phosphate	0.3 theory.

Example IV

Platformate (containing 3 cc. tetramix/gal.)	99.0% v.
N-butyl-2-oxazolidone	1.0% v.
Tricresyl phosphate	1.0 theory.

Example V

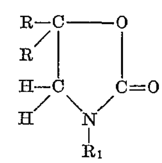
A method of operating an internal combustion engine wherein a catalytic reformate gasoline containing 0.5% v. N-n-butyl-2-oxazolidone and 0.3 theory phosphorus as cresyl diphenyl phosphate is used as a fuel; a mineral oil SAE 10W–30 at 99.5% v. having a viscosity of 120 SSU at 100° F. and containing 0.25% v. N-ethyl-5-isobutyl-2-oxazolidone is used as lubricating oil.

Example VI

Mineral lube oil having a viscosity of 320 SSU at 100° C.	99.9% v.
N-methyl-5-isobutyl-2-oxazolidone	0.1% v.

I claim as my invention:

1. An improved fuel composition for use in internal combustion engines consisting essentially of a stable gasoline boiling between about 30° F. and 425° F. containing an octane number-improving amount of an organometallic primary antiknock agent, a minor amount of an ignition control additive selected from the group consisting of phosphorus and boron compounds and mixtures thereof, and from about 0.01 to about 5.0% by weight of a gasoline-soluble, alkyl-substituted 2-oxazolidone composed solely of carbon, hydrogen, nitrogen and oxygen having the structural formula

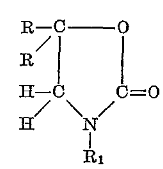


wherein R and R_1 are low-molecular-weight alkyl radicals containing from 1 to 4 carbon atoms, and R can also be a hydrogen atom.

2. The composition of claim 1 which contains from 0.05 to 1.0% by weight of the alkyl-substituted 2-oxazolidone.

3. The composition of claim 1 in which the alkyl-substituted 2-oxazolidone is N-ethyl-2-oxazolidone.

4. An improved lubricating oil composition for use in an internal combustion engine having an SUS viscosity at 100° F. between about 50 and 1000 and consisting essentially of a minor amount of an ignition control additive selected from the group consisting of phosphorus and boron compounds and mixtures thereof and from about 0.01% by weight to about 5.0% by weight of an oil-soluble alkyl-substituted 2-oxazolidone composed solely of carbon, hydrogen nitrogen and oxygen, and having the structural formula



wherein R and R_1 are low-molecular-weight alkyl radicals containing from 1 to 4 carbon atoms, and R can also be a hydrogen atom.

5. The composition of claim 4 in which the alkyl-substituted 2-oxazolidone is N-ethyl-2-oxazolidone.

6. The composition of claim 1 in which the organometallic primary antiknock agent is methylcyclopentadienyl manganese tricarbonyl.

7. The composition of claim 1 in which the organometallic primary antiknock agent is an organolead compound.

8. The composition of claim 1 in which the organometallic primary antiknock agent is tetraethyllead.

References Cited in the fil: of this patent

UNITED STATES PATENTS

1,692,784	Orelup et al.	Nov. 20, 1928
2,932,675	Steele et al.	Apr. 12, 1960