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FUEL HAVING IMPROVED KNOCK QUALITIES

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5 Claims. (Cl. 44—69)

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The present invention relates to a liquid hydrocarbon fuel having superior performance characteristics.

Heretofore, liquid hydrocarbon fuels such as gasoline, and the like, have been rated by assigning to them an octane number. The octane number of a fuel is stated as the whole number nearest to the percentage by volume of iso-octane (2,2,4-trimethyl pentane) in a blend of iso-octane and n-heptane that matches the knock characteristics in a standard engine under the same conditions. Thus, for example, a gasoline is given an octane rating of 70 if, on running it in the standard engine under the same conditions, it knocks with the same intensity as a mixture of 70 parts of iso-octane and 30 parts of normal heptane.

It has also been known that it is possible to raise the octane rating of a gasoline by adding thereto an anti-knock compound, such as tetraethyl lead. Thus, for example, a given quantity of tetraethyl lead can be added to a gasoline having an octane rating of 60, and the gasoline with the tetraethyl lead will knock with the same intensity in a standard engine as a mixture of 70 parts of iso-octane and 30 parts of normal heptane. The gasoline with the tetraethyl lead therefore has an octane rating of 70 and the addition of the tetraethyl lead increased the octane number by 10.

It has also been known to the oil and automotive trades that a dirty engine, that is, one that has been in sufficient use to form deposits on the piston head, valves and walls of the combustion chamber, requires a gasoline of higher octane rating in order not to knock than is required by a new or a clean engine. This means, in other words, that the octane value of a gasoline demanded by such a dirty engine in order not to knock (referred to as "octane demand") is higher than the octane demand of a clean engine. For example, a clean engine which requires a gasoline having an octane rating of 60 in order not to knock is said to have an octane demand of 60. If the same engine when dirty requires a gasoline having an octane rating of 75 in order not to knock, such a dirty engine is said to have an "octane demand" of 75, or an "octane demand increase" of 15. As a clean engine starts to get dirty the octane demand rises with continued use. Finally there is no more octane demand increase with continued use. Apparently the motor has then become as dirty as it is ever going to with continued use or, if it becomes dirtier after a certain point, it does not requires a gasoline of greater octane value in order not to knock.

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Since the development of tetraethyl lead as an anti-knock compound, a great deal of effort has been made to develop other anti-knock compounds. Iron carbonyl is used in some parts of the world as an anti-knock compound but it has not come into general use for the reason that it requires frequent cleaning of the spark plugs because of the formation of magnetic oxide in the spark gap. It has also been proposed, as disclosed in U. S. Patent No. 2,212,992, issued August 23, 1940, to add to gasoline monomeric silicols and silicyl ethers in quantities that are substantially the same by weight as tetraethyl lead for the purpose of raising the octane rating of the fuel.

Efforts in the past have been directed primarily to the development of compounds that can be added to gasoline in order to raise the octane value of the gasoline and in this way to satisfy the higher octane demands of dirty engines. By way of contrast, the present invention is concerned with the development of a fuel containing compounds that do not raise the octane rating of the fuel but have the effect of preventing increase in the octane demand of an engine on prolonged operation. In other words, whereas the addition of tetraethyl lead and other prior art additives decrease the tendency of the fuel to knock, the addition of compounds in accordance with our invention decreases the tendency of the engine to cause fuels to knock.

To illustrate this difference, the present invention contemplates treating, for example, a 72 octane gasoline without raising its octane rating so that an internal combustion engine, having an octane demand of 70 when clean and an octane demand of 85 when dirty, can run indefinitely on the treated gasoline without knocking because the treatment of the gasoline in accordance with the present invention reduces the increase in the octane demand for an engine without raising the octane rating of the fuel. By the same token, however, a gasoline having an octane rating of 60, when treated in accordance with the present invention, does not have its octane rating raised by the treatment, and therefore cannot be used to run the same engine without knocking whether it is clean or dirty. As contrasted with this, a gasoline having an octane rating of 60 can, however, have sufficient tetraethyl lead added to it in accordance with the prior art to bring its octane rating to 85 and thus be made to satisfy the greatly increased octane demand of the dirty engine.

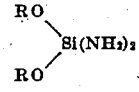
It has now been found that the increase in octane demand of an engine can be prevented or reduced materially by adding to a motor fuel

which also contains tetraethyl lead, relatively small quantities by weight of organic silicon compounds which are soluble or dispersible in the fuel and remain in this state in the fuel.

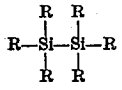
The silicon compounds found to be extremely useful for this purpose are monomeric and polymeric organic silicon compounds such as, for example, hydrocarbon silicates, silanes including amine silanes, silanols and siloxanes including polysiloxanes, which contain hydrocarbon or other organic radicals. The polysiloxanes are more commonly known in the trade as silicones, are polymers containing siloxane linkages, and are available commercially in a considerable number of viscosity grades. Examples of organic silicon compounds useful in accordance with the invention are compounds of the general formulae:

(1) $SiH_{(4-x)}R_x$

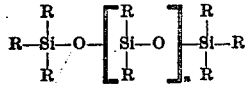
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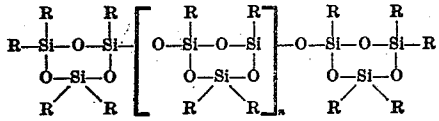
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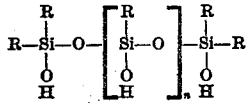
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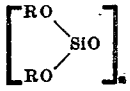
(6)



(7) $SiO_x(OR)_y$

and

(8)



wherein the R's stand for the same or different alkyl, aryl, alkaryl or heterocyclic radicals, n is a whole number equal to at least 2, x is an integer from 1 to 4, y is either 2 or 4, and z is 1 when y is 2, and z is zero when y is 4.

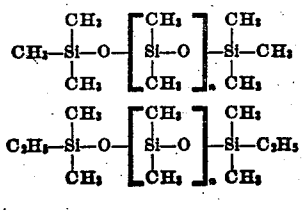
More specific examples of such compounds are:

(1) $(CH_3)_2Si(C_2H_5)(C_3H_7)$
$(CH_3)_2Si(C_5H_{11})$
$(CH_3)_2Si(C_2H_5)(C_4H_9)$
$(C_2H_5)_4Si$
$(CH_3)_2Si(C_6H_5)$
$(CH_3)_2Si(C_2H_5)(C_6H_5)$
$(C_2H_5)_2Si(C_6H_5)$

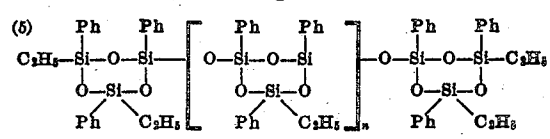
(2) $(C_2H_5O)_2Si(NH_2)_2$

(3) $(CH_3)_2Si—Si(CH_3)_3$

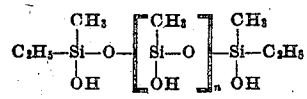
(4)



(5)



(6)



(7) $Si(OC_2H_5)_4$

(8) $[(OC_2H_5)_2SiO]_n$

It has been found that for the purpose of the present invention, the polysiloxanes having viscosities ranging from about 3 to about 1000 centistokes at 25° C. are particularly useful. These organic silicon compounds should not have so low a boiling point as not to be retainable in the fuel and may be dissolved or colloidally dispersed in the liquid hydrocarbon fuel.

The quantities of organic silicon compound required to be added to the untreated fuel, in order effectively to prevent or minimize an increase in the octane demand of an engine, are extremely small and are less than the quantities of metallic derivative anti-knock compounds such as tetraethyl lead required to be added to untreated fuel. Amounts are less than about 0.5 cc. of the silicon compound to one gallon of fuel, and amounts in the range of 0.1 to 0.2 cc. per gallon give good results. Much lower amounts result in a significant improvement in lowering the octane demand increase of an engine. The addition of up to about 0.5 cc. of silicon compound to leaded gasoline has been found to be especially effective and forms a preferred embodiment of this invention. Tetraethyl lead is also included in the gasoline, and it may be present in the usual amounts, i. e., 0.5 to 5.0 cc. per gallon.

The following examples illustrate the invention more specifically:

Example I

An initially clean engine which requires a fuel having an octane rating of 70 in order not to knock, i. e., having an octane demand of 70, was run on unleaded gasoline and after about 50 hours operation, equivalent to about 1500 miles, the engine was found to require fuel having an octane rating of 80. The octane demand increase of the engine operated on unleaded fuel was 10.

The same initially clean engine was run on the same gasoline except that it contains 3.0 cc. of tetraethyl lead per gallon. After about 52 hours operation, it was found that the engine required a fuel having an octane rating of 85 in order not to knock. The octane demand increase of the engine when operated on leaded fuel was therefore 15.

When the same initially clean engine was operated in accordance with the invention on the same leaded gasoline containing 0.1 cc. per gallon of a polysiloxane (available from the Dow-Corning Company as a fluid known as Type 200), the octane demand of the engine was 72 after 30 hours of operation and remained constant thereafter for an indefinite period. The octane demand increase of the engine when run with the fuel in accordance with the invention was 2, as compared with an octane demand increase of 15 when the engine is run with leaded gasoline, and an octane demand increase of 10 when the engine was run with untreated gasoline.

Example II

An initially clean, standard F–4 engine, equipped with a standard Waukesha L-head cylinder, was run on 76 octane gasoline containing, in addition, 3.0 cc. tetraethyl lead per gallon. After 34 hours, the octane demand increase of the engine was found to be 14 and no further increases were noted thereafter.

The same engine, when clean, was run under identical conditions with similarly leaded gasoline but containing 0.1 cc. per gallon of a polysiloxane available from Dow-Corning as Fluid type 500. After 34 hours, no perceptible increase in octane demand could be discovered.

Example III

The same initially clean, standard F–4 engine was run on a base gasoline having an octane rating of 76 and containing, in addition, 3.0 cc. of tetraethyl lead and 0.2 cc. of ethyl ortho-silicate per gallon. The octane demand increase of the engine was found to level off at 2 after 13 hours of operation.

Example IV

The same initially clean, standard F–4 engine was run on a base gasoline having an octane rating of 76 and containing, in addition, 3.0 cc. of tetraethyl lead and 0.2 cc. of $(C_2H_5O)_2Si(NH_2)_2$ per gallon. The octane demand increase of the engine was found to level off at 1.6 after 25 hours of operation.

It has been found that the amount of deposits on the walls of the combustion chamber, on the valves and the piston head, when fuel treated in accordance with the present invention is used, is substantially equal in amount to that ordinarily deposited and it is, therefore, believed that the results described are not obtained by reducing the deposits but rather by coating or otherwise affecting the carbon deposits in some manner that effectively minimizes the increase in the octane demand of a dirty engine.

While particular examples have been described in detail, it is not intended that the scope of the invention be limited by the description in said examples or by any theory designed to explain the action of the silicon compounds disclosed as being effective in reducing the increase in the octane demand of an internal combustion engine.

We claim:

1. Gasoline containing tetraethyl lead and an organic silicon compound soluble in the fuel in an amount up to 0.5 cc. per gallon of fuel.

2. Gasoline containing tetraethyl lead and up to about 0.5 cc. of a polysiloxane per gallon of fuel, said polysiloxane having a viscosity of from 3 to about 1000 centistokes at 25° C.

3. Gasoline containing tetraethyl lead and an organic silicon compound soluble in the fuel.

4. Gasoline containing 0.5 to 5.0 cc. of tetraethyl lead per gallon and an organic silicon compound soluble in the fuel in an amount up to 0.5 cc. per gallon of fuel.

5. Gasoline containing tetraethyl lead in an amount to increase substantially the effective octane rating of the gasoline and from about 0.1 to about 0.2 cc. per gallon of an organic silicon compound to depress the octane demand increase of an engine powered by said tetraethyl lead-containing gasoline.

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MILTON H. CAMPBELL.

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