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# UNITED STATES PATENT OFFICE

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## DIESEL FUEL

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3 Claims. (Cl. 44—57)

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This invention relates to liquid fuels for compression ignition engines and more particularly to liquid fuels containing novel addition agents for improving their combustion characteristics in compression ignition engines.

For the satisfactory operation of compression ignition engines it is necessary that the fuel employed have the property of igniting readily when introduced into the compression chamber. In order to obtain a sufficiently short ignition delay period it is customary to add to the fuel a compound which will function as an ignition accelerator. Compounds which have been employed for this purpose include certain peroxides, aldehydes, organic sulfides and the lower alkyl nitrates. Many of these compounds are unsatisfactory for reasons such as instability, the undesirable lowering of the flash point and the considerable increase in carbon residue which they impart, or their tendency to form corrosive gases in storage or in operation.

In accordance with my invention an improved fuel for compression ignition engines of the diesel type is obtained by blending with a suitable diesel oil stock a small amount of an ignition accelerating compound comprising an oil-soluble selenium compound of an alkyl substituted dithiocarbamic acid. The compound may be that of di-, tetra-, or hexavalent selenium and a mono- or dialkyl substituted dithiocarbamic acid, or mixed compound of both mono- and dialkyl substituted dithiocarbamic acids, containing sufficient alkyl carbon atoms to impart oil solubility to the molecule. The compounds may be represented by the general formula:

$$Se\left(S-\overset{S}{\overset{\|}{C}}-N\begin{matrix}R\\R'\end{matrix}\right)_x$$

in which $x$ is an integer of the series 2, 4, and 6, R is an alkyl group and R' is an alkyl group or hydrogen. As examples of such compounds may be mentioned the di-, tetra-, and hexavalent selenium compounds of monoctyl-, monodecyl-, monocetyl-, dibutyl-, diamyl- or dihexyl-substituted dithiocarbamic acid. My preferred compounds comprise the compounds of tetravalent selenium and a dialkyl dithiocarbamic acid, represented by the formula:

$$Se(S-\overset{S}{\overset{\|}{C}}-NR_2)_4$$

in which R is an alkyl group containing at least 4 carbon atoms. In general, R may represent an alkyl group having from 4 to about 20 carbon atoms, and preferably 4 to about 16 carbon atoms.

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The compound is preferably the diamyl dithiocarbamic acid derivative of tetravalent selenium.

By the term diesel oil stock is meant such hydrocarbon oil fractions heavier than gasoline usually employed as fuels for compression ignition engines, ordinarily having an initial boiling point in the upper part of the kerosine boiling range and an end boiling point in the heavy fuel oil range, or boiling from about 400° F. to about 750° F. Various other additives such as pour depressants, viscosity improvers and other agents for improving combustion characteristics may be added to the oil in addition to my novel addition agents in order to obtain a finished product of the desired characteristics.

So far as I am aware no use has been made of organic selenium compounds heretofore as ignition accelerators in diesel fuels. Selenium hydrocarbon compounds, such as diethyl and diphenyl selenide, have been suggested as antiknock agents in gasoline, and such compounds have also been proposed to increase the heating value of fuel oils such as burner oils and diesel oils. It has been proposed to employ the nonmetallic organic derivatives or ammonium salts of thiocarbamic or dithiocarbamic acids as additives to increase the cetane number of diesel fuels, but these compounds have the disadvantages of having in general a considerable solubility in water and of requiring relatively large proportions, e. g., 1 to 5 per cent, to effect the desired increase in the cetane number of the fuel. The addition agents of my invention, on the other hand, are highly insoluble in water and effect a substantial improvement in cetane number when employed even in very small amounts. The greater effectiveness of the selenium dithiocarbamates as cetane improvers, that is, as proknock agents, is entirely unexpected in view of the activity of other selenium compounds as antiknock agents.

These selenium compounds have also been found to be effective corrosion inhibitors; and, due to the normal fuel leakage past the piston rings in diesel engine operation, these compounds gain access to the lubricating oil in the crankcase and perform the additional function of preventing bearing corrosion. It is frequently advantageous to use these novel addition agents in conjunction with other additives which are effective for various purposes such as improving viscosity or combustion characteristics but which are ordinarily unsuitable because of their corrosiveness.

The preparation of the selenium dithiocar-

bamates may be carried out by the well-known process which comprises acidifying an aqueous solution of an alkaline dithiocarbamate and of an alkali metal salt of a selenium acid. The dialkyl substituted compounds which constitute the preferred compounds of my invention may also conveniently be prepared by the method described in U. S. 2,347,128, whereby a secondary amine and carbon disulfide are reacted with selenium dioxide in an alcohol solution.

The amount of these addition agents employed depends upon the character of the base stock and upon the effect desired. In general, the amount of these compounds employed will range from about 0.1 per cent to about 1 per cent, and preferably from about 0.25 per cent to about 0.75 per cent by weight, although larger or smaller amounts may be used if desired.

The following table summarizes the results obtained by the addition of various amounts of selenium diamyl dithiocarbamate,

$$Se(SSCN(C_5H_{11})_2)_4$$

to an untreated diesel stock having a flash point of 198° F., an API gravity of 34.2 and a boiling range of 408° F. to 696° F., and to an acid treated diesel stock having a flash point of 202° F., and API gravity of 36.3 and a boiling range of 419° F. to 696° F.

*Table I*

| Weight percent $Se(SSCN(C_5H_{11})_2)_4$ added | Cetane Number | |
|---|---|---|
| | Untreated diesel stock | Acid treated diesel stock |
| 0 | 46.4 | 51.8 |
| 0.25 | 52.5 | 55.2 |
| 0.50 | 54.4 | 57.8 |
| 0.75 | 55.4 | 59.6 |
| 1.00 | 57.6 | 59.2 |

Additions of small amounts of selenium diamyl dithiocarbamate to an asphalt base stock of low cetane number gave the results shown in Table II below.

*Table II*

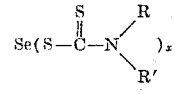
| Weight percent $Se(SSCN(C_5H_{11})_2)_4$ added | Cetane Number |
|---|---|
| 0 | 30 |
| 0.1 | 32 |
| 0.25 | 34 |
| 0.50 | 34 |
| 1.00 | 35 |
| 2.00 | 36 |

The above results were obtained with a standard diesel test engine in which the ignition delay was measured. The cetane number designates the percentage by volume of cetane in a mixture of cetane and alpha methyl naphthalene which gives the same ignition lag as the fuel under test.

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.

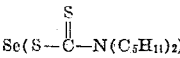
I claim:

1. A fuel for compression ignition engines comprising a diesel hydrocarbon oil stock containing a minor amount effective to substantially improve the cetane number of said diesel hydrocarbon oil stock of an oil-soluble compound having the formula



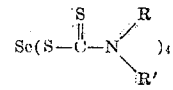
wherein $x$ is an integer of the series 2, 4, and 6, R is an alkyl group containing 4 to 20 carbon atoms and R′ is selected from the group consisting of hydrogen and alkyl groups having 4 to 20 carbon atoms.

2. A fuel for compression ignition engines comprising a diesel hydrocarbon oil stock containing about 0.1 per cent to about 1 per cent by weight of the compound



to substantially improve the cetane number of said diesel hydrocarbon oil stock.

3. A fuel for compression ignition engines comprising a diesel hydrocarbon oil stock containing about 0.1 per cent to about 1 per cent by weight of a compound having the formula



wherein R and R′ are alkyl groups containing from 4 to 20 carbon atoms, to substantially improve the cetane number of said diesel hydrocarbon oil stock.

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