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UNITED STATES PATENT OFFICE

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IGNITION PROMOTOR FOR DIESEL FUELS

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No Drawing. Application July 21, 1938, Serial No. 220,500

10 Claims. (Cl. 44—9)

This invention has as its chief object the improvement of fuels for use in compression-ignition engines and relates particularly to the use of novel addition agents for improving the ignition qualities of hydrocarbon fuels when they undergo combustion in such engines of the high speed Diesel type.

In consideration of increasing the power and fuel economy in the operation of compression-ignition engines, principally when the hydrocarbon fuel contains insufficient amounts of hydrocarbon compounds recognizable as serving these ends by virtue of their suitable ignition qualities, the additions of various oxygen-, nitrogen-, and sulfur-containing organic compounds have been proposed. Hydrocarbon compounds characterized by aromatic hydrocarbons have poor ignition qualities which give rise to the vibrations manifested by "knocking" and result in a loss of power. A poor ignition quality in a fuel is most frequently exhibited by an excessive ignition lag, in other words, an excessive delay between the beginning of fuel injection into the combustion chamber of an engine and the point at which ignition of the injected fuel sets in.

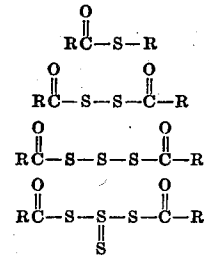
On the other hand, normal aliphatic hydrocarbons have good ignition qualities. Normal cetane, in particular, which serves as a standard of high ignition quality in Diesel fuel rating by recommendation of the S. A. E. Volunteer Group for Compression-Ignition Fuel Research, has a very short ignition lag. The ignition lag of a fuel consisting of cetane and alphamethyl-naphthalene is shortened very nearly in proportion to the increase in the percentage of cetane by volume in such a blend, and when small amounts of addition agents improve the performance of a fuel in the same respect comparable to the improvement made by an increase of about 5% or more of cetane in a blend with alphamethyl-naphthalene, such addition agents have been considered as having commercial significance.

The novel addition agents of this invention are characterized by organic compounds containing a thiocarboxylic acid radical, particularly a dithio-carboxylic acid or thiolic acid radical, and those also containing nitrogen. The solution in liquid hydrocarbon fuels of this type of compounds in small amounts for imparting better ignition qualities to the fuels constitutes a more specific object of this invention.

Classes of compounds which characteristically contain thiocarboxylic acid radicals are: acyl sulfides, xanthates, xanthogenyl sulfides, thiocarbamates, and thiurams.

To these classes of compounds, have been assigned some of the following structural formulae in which R represents generally organic groups containing hydrogen and carbon, but preferably an alkyl group such as ethyl, propyl, and higher homologous groups, their isomers, and olefinic analogues.

I. Monothiocarboxylic Acid or Thiolic Acid Derivatives, i. e., Acyl Sulfides



for example:

Ethyl thioacetate, $CH_3C(=O)-S-C_2H_5$

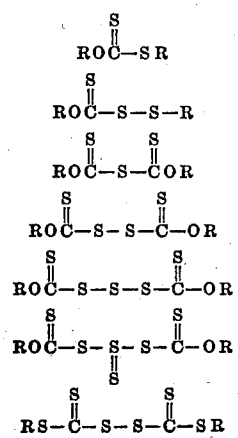
Diacetyl disulfide, $CH_3C(=O)-S-S-C(=O)CH_3$

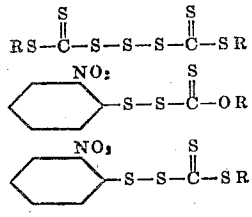
Bismethanecarbothiol sulfide, $CH_3C(=O)-S-S-S-C(=O)CH_3$

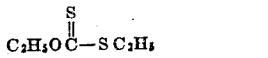
Bismethanecarbothiol disulfide, $CH_3C(=O)-S-S(=S)-S-C(=O)CH_3$

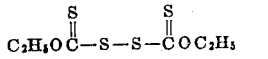
II. Dithiocarboxylic Acid Derivatives

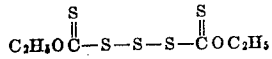
(a) *Xanthogenyl and thioxanthogenyl compounds*

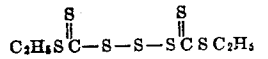




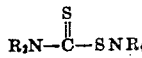
Ethyl S-ethyl xanthate, 

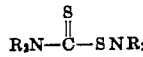
Sulfocaroxylethyl disulfide, 

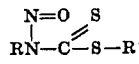
Bisethylxanthogenyl sulfide, 

Bisethylthioxanthogenyl sulfide, 

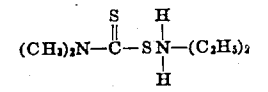
(b) Dithiocarbamates

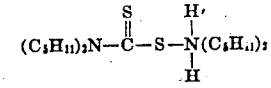


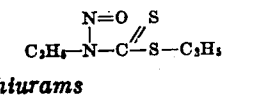




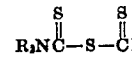
for example:

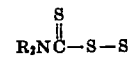
Diethyl-ammonium-dimethyl-dithiocarbamate. 

Diamyl-ammonium-diamyl-dithiocarbamate. 

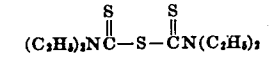
Ethyl-N-nitroso-dithio-ethyl carbamate. 

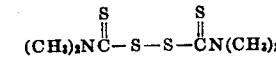
(c) Thiurams



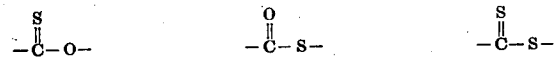


for example:

Tetraethyl thiuram sulfide, 

Tetramethyl thiuram disulfide, 

It is readily apparent that a common characteristic of all the foregoing active compounds is the thiocarboxylic acid group, and particularly such a group with one or more sulfur atoms attached to a carbon atom which has a double bond linkage to sulfur or oxygen as in dithiocarboxylic acid, thiolic acid, or their derivatives. Accordingly, the monothio- and dithio-carboxylic radicals which may be depicted as occurring in the three configurations:



are considered essential active parts of the compounds which are suitable for the purposes of the present invention, and preferably the compounds should contain only 2 to 3 sulfur atoms in a straight chain linkage, except when sulfur is interlinked between carbon and nitrogen as in the thiocarbamates.

The effectiveness of compounds containing an active thiocarboxylic acid radical in raising the cetane number of a hydrocarbon fuel is illustrated by the following tabulated results from comparative tests on a sample of an unmodified fuel oil and on samples of the same fuel oil modified by small amounts of these compounds.

Fuel tests

Compound blended with a 40 cetane Columbian gas oil	Percent of compound in fuel	Cetane number increase
Bismethanecarbothiol sulfide	1.0	+5
Bismethanecarbothiol disulfide	1.0	+9
Bisamylthioxanthogenyl sulfide	3.0	+6
Sulfocarboxylethyl disulfide	3.0	+8
Bisethylxanthogenyl sulfide	3.0	+15
Dimethyl ammonium dimethyl dithiocarbamate	<3.0	+5
Diethyl ammonium diethyl dithiocarbamate	1.0	+10
Tetramethyl thiuram disulfide	1.0	+6
Sodium N-dibutyl dithiocarbamate	<3.0	+6

The proportion of the ignition quality improving agent to be added to the hydrocarbon fuel may range from a fraction of one percent to the limit of solubility in the fuel, but preferably from about .025 to 5%. A gas oil boiling from about 400° F. to 700° F., or 750° F., or, in general, having a suitable boiling range for use as a fuel in Diesel type engines may be used as the hydrocarbon fuel. Under some circumstances, a more narrowly cut fraction such as one distilling from about 400° F. to 600° F. or from 500° F. to 700° F. may be used. Ordinarily, the hydrocarbon fuel may be said to have a boiling range above that of gasoline.

This invention makes commercially feasible the preparation of Diesel fuels giving satisfactory engine performance from crude oils, gas oils, and residual fuels having low pour points, low A. P. I. gravities, and high heat values, such as those procured from naphthene base, asphalt base, or mixed base stocks by the addition of active compounds, described, in small quantities. The burning qualities of gas oils from paraffin crudes are also enhanced by these novel addition agents.

Small quantities of the novel addition agents of this invention may be used for adapting various mixtures of hydrocarbons for use as Diesel fuels, including recycle stock from a cracking operation, non-paraffinic extracts, oils from destructive distillations of pyrobituminous and asphaltic materials, mixtures of these with one another or with crude petroleum fractions. Other agents for enhancing various other qualities without detracting substantially from the ignition qualities of the fuel may be admixed, such as, oiliness agents, sludge dispersers, dyes, corrosion inhibitors, anti-oxidants, viscosity improvers, pour depressants, and gum solvents. Also, other promoters of ignition qualities may be admixed.

It is not intended that this invention be limited to the specific examples which are given merely for the sake of illustration. It is desired to claim all the novelty inherent in the invention in the appended claims as broadly as the prior art permits.

We claim:

1. A fuel for compression-ignition engines of the Diesel type, comprising essentially a hydrocarbon fuel and a small amount of about 1% to about 5% of an organic compound containing a thiocarboxylic acid radical for imparting better ignition qualities to the fuel.

2. A fuel for compression-ignition engines of the Diesel type, comprising essentially a hydro-

carbon fuel and a small amount of about 1% to about 5% of an organic compound containing a monothiocarboxylic acid radical for imparting better ignition qualities to the fuel.

3. A fuel for compression-ignition engines of the Diesel type, comprising essentially a hydrocarbon fuel and a small amount of about 1% to about 5% of an acyl sulfide for imparting better ignition qualities to the fuel.

4. A fuel for compression-ignition engines of the Diesel type, comprising essentially a hydrocarbon fuel and a small amount of bismethanecarbothiol disulfide for imparting better ignition qualities to the fuel.

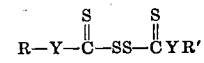
5. A fuel for compression-ignition engines of the Diesel type, comprising essentially a hydrocarbon fuel and a small amount of about 1% to about 5% of an organic compound containing a dithiocarboxylic acid radical for imparting better ignition qualities to the fuel.

6. A fuel for compression-ignition engines of the Diesel type, comprising essentially a hydrocarbon fuel and a small amount of a compound containing a xanthogenyl group imparting better ignition qualities to the fuel.

7. A fuel for compression-ignition engines of the Diesel type, comprising essentially a hydrocarbon fuel and a small amount of bisethylxanthogenyl sulfide for imparting better ignition qualities to the fuel.

8. A fuel for compression-ignition engines of the Diesel type, comprising essentially a hydrocarbon fuel and a small amount of an organic compound containing an active thiocarboxylic acid radical with 2 to 3 sulfur atoms in a straight chain linkage to impart better ignition qualities to the fuel.

9. An improved diesel fuel oil containing, in sufficient amount to raise the cetane number of the oil, a compound having the formula



wherein R and R' are hydrocarbon radicles and Y is sulfur or oxygen.

10. An improved Diesel fuel comprising a hydrocarbon Diesel fuel oil and in admixture therewith sulfocarboxylethyl disulfide in an amount sufficient to decrease the ignition delay period of the fuel.

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