Patented Nov. 18, 1941

2,263,234

UNITED STATES PATENT OFFICE

2,263,234

DIESEL FUEL

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No Drawing. Application March 1, 1940, Serial No. 321,718

8 Claims. (Cl. 44—9)

This invention relates to improvements in fuels for high speed compression-ignition engines of the Diesel type and pertains particularly to certain organic sulfur compounds as addition agents for improving ignition qualities without imparting substantial corrosion tendencies.

The ignition quality of a Diesel fuel is appropriately measured in terms of cetane number according to the general method discussed in the S. A. E. Journal of June, 1936, page 225. The corrosion tendencies of the fuels are commonly determined by the A. S. T. M. copper strip corrosion test.

It is well known that organic disulfides, tetrasulfides, and higher polysulfides have been proposed as ignition accelerators or primers for Diesel fuels. The disulfides have been found, in general, to be relatively ineffectual as ignition accelerators in recent tests with high speed C. F. R. Diesel engines while the higher polysulfides, in general, have been found too corrosive for general utilization.

The novel addition agents provided in accordance with the objects of the present invention are organic trisulfides having the following formula:

$$R—S—S—S—R'$$

wherein R and R' represent the organic or hydrocarbon groups, either alike or unlike, and, more particularly, alkyl groups containing at least 3 carbon atoms in a group. The preferred dialkyl trisulfides have relatively high stability, oil solubility, cetane number improving effectiveness, low corrosion tendencies, and freedom from offensive odors.

The addition agents of this invention have the advantage of being easily and efficiently prepared, as for example, by the following method:

Two mols of the mercaptan are reacted with one mol of sulfur dihalide in the presence of an inert solvent such as ethylene dichloride, naphtha, carbon disulfide, carbon tetrachloride, chloroform, etc., the solvent preferably having a low boiling point to facilitate its removal from the reaction product. The reaction proceeds in accordance with the following equation:

$$2RSH+SCl_2 \rightarrow R—S—S—S—R+2HCl$$

To prevent formation of free sulfur in the product, a slight excess of the mercaptan over the theoretical amount is used.

Example

A slight excess of two mols of amyl mercaptan dissolved in about an equal volume of inert solvent is placed in a reaction flask fitted with a dropping funnel, a stirrer, and a reflux condenser, and one mol of sulfur dichloride diluted with an equal volume of the solvent is added slowly through the dropping funnel. The reaction mixture is stirred and maintained substantially at room temperature. After the reaction is completed, the product is washed with water, then with dilute caustic solution to remove remaining amounts of hydrogen chloride and excess mercaptan. It is to be noted that if excess sulfur dichloride is present in the product, it is hydrolyzed by water and deposits free sulfur, and this is preferably avoided. After the product has been washed, the solvent is separated by distillation with the aid of vacuum or by blowing the mixture with air as it is heated on a steam bath. If a Diesel fuel distillate is used as the solvent, the distillation step may be omitted.

It is important to note that for the best results in accordance with the objects of obtaining a non-corrosive addition agent, the formation of the trisulfide is obtained without the presence of sulfur monohalide or free sulfur in substantial amounts, and that the trisulfide product should be substantially free of corrosive sulfur, such as might be present in mercaptans, in unstable polysulfides, or as free sulfur.

The ignition quality promoting effectiveness of the addition agents was evaluated in terms of cetane number increase with a high degree of accuracy by comparison with standard reference fuels and other organic sulfides in a C. F. R. Diesel engine. In these tests a 40 cetane number reference fuel was used as the control.

Agent added to reference fuel	Percent by volume of agent added	Cetane number increase
Ethyl disulfide	5.0	2
Propyl disulfide	3.0	2
Amyl disulphide	1.0	1
Benzyl disulphide	1.0	1
Diamyl trisulfide	0.25	6
Do	0.50	8
Do	1.00	11
Do	2.00	15.5
Trisulfides of refinery mercaptans	1.0	8

The approximate composition of the trisulfides of the refinery mercaptans was 15% methyl tri-

sulfide, 50% ethyl trisulfide, 30% isopropyl trisulfide, 5% trisulfides of alkyl groups containing more than 3 carbon atoms.

The foregoing results, in contrast to data comparably obtained on analogous organic disulfides, show that the trisulfides are many times more effective for increasing the cetane number of a Diesel fuel.

Although the trisulfides, in general, are not more potent than tetrasulfides and higher polysulfides for accelerating ignition of fuel in Diesel engines, they have been found to be definitely more advantageous in their other properties, particularly in stability and avoidance of corrosiveness. In the handling and use of the internal combustion engine fuels, the A. S. T. M. corrosion test is regarded as very significant for determining the safety of metals in the storage and supply systems of the engines from attack by corrosive substances. This method of test is very simply made by exposing a bright copper strip to the fuel tested and kept at 122° F. for a period of three hours. The fuel is reported as passing the test when the exposed copper strip shows not more than extremely slight discoloration in comparison with a fresh copper strip.

Comparative corrosion tests were made on a fuel base (Colombian gas oil) as a blank and on samples of this base stock each blended with one per cent of the organic sulfide to be tested. In each instance the fuel satisfactorily passed when containing the trisulfides in ignition quality improving amounts, but failed to pass when blended with the higher sulfides as illustrated in the following tabulation:

A. S. T. M. copper strip corrosion test, 3 hrs./122° F.

Fuel composition	Percent by volume of addition agent	Result
Fuel base alone	0	Passed.
Fuel base+tert butyl-trisulfide	1	Do.
Fuel base+diamyl-trisulfide	1	Do.
Fuel base+mixed dialkyl-trisulfides	1	Do.
Fuel base+mixed dialkyl-tetrasulfides	1	Failed.
Fuel base+mixed dialkyl-pentasulfides	1	Do.

In the foregoing tests, the mixed dialkyl sulfides were obtained by treatment of refinery mercaptans. Even with the amounts of addition agents decreased or increased, the results on corrosiveness were substantially as indicated, the branched and the higher dialkyl trisulfides being found to be exceptionally good in leaving the exposed copper strip without discoloration and in being free of offensive odor. The low molecular weight trisulfides in which the alkyl groups contain only 3 to 5 carbon atoms were found most satisfactory when the alkyl groups were branched, as for example, in an isopropyl or tert butyl radical.

The amount of the agent added to the fuel may vary from that given in the foregoing test. In general, about 0.1% to 5% by volume is sufficient, although greater amounts may be used if desired, preferably from 0.25% to 4% is ordinarily used. Thus, small amounts of these agents may be used for improving hydrocarbon oils boiling above gasoline or kerosene range, such as the gas oil fraction used in the test. The fuel base is ordinarily best suited for high speed Diesel engines when it has a viscosity of about 30 to 65 Saybolt seconds at 100° F. and boils within the range of 375° F. to 700° F.

As indicated by the tests, the addition agents provided by the present invention are useful for improving low quality base stocks, therefore, they may be used advantageously with any variety of fuel whether it be paraffinic, aromatic, or naphthenic and regardless of the method of refining. They may be used with other addition agents, e. g., other ignition quality promoters, pour point depressants, viscosity improvers, oiliness agents, corrosion inhibitors, etc., as needed or desired.

While the invention has been described mainly with reference to dialkyl trisulfides, it is to be understood that the scope of the invention is intended to include various isomers or analogous organic trisulfides, particularly, organic sulfur-containing compounds in which the sulfur atoms form a linear linkage between the carbon atoms of the organic groups, such as, cyclic hydrocarbon radicals, and hydrocarbon radicals having substituents which may include oxygen, nitrogen, phosphorus, or a halogen. Also, it is to be understood that the methods of producing and incorporating the organic trisulfides into the hydrocarbon fuels may be varied; for example, the organic trisulfides may be formed from mercaptans in the Diesel fuel oil, the oil acting as the solvent medium, or the organic trisulfide may be admixed with the fuel oil as it is being supplied to the engine or be separately supplied to the engine during the compression stroke but prior to ignition of injected fuel.

It can be well appreciated that the novel agents of the present invention have many advantages over agents hitherto proposed. They are cheaply manufactured, safe to handle, highly soluble in Diesel fuel oil, and efficient for the purpose intended. The preferred alkyl trisulfides in which the alkyl groups contain at least 3 carbon atoms, and more particularly in which the alkyl groups are branched, are exceptionally beneficial in these respects, and furthermore, are free from objectionable physiological properties.

Obviously, many modifications and variations of the invention, as hereinbefore set forth, may be made without departing from the spirit and scope thereof.

I claim:

1. A high speed Diesel fuel comprising a hydrocarbon Diesel fuel blended with a minor quantity of an alkyl trisulfide in sufficient amount to improve the ignition quality of the fuel.

2. A high speed Diesel fuel comprising a hydrocarbon Diesel fuel blended with a cetane number improving amount of an organic compound having the general formula:

$$R—S—S—S—R'$$

in which R and R' represent hydrocarbon radicals.

3. A high speed Diesel fuel comprising a hydrocarbon Diesel fuel and 0.25% to 5% by volume of alkyl trisulfides, wherein alkyl groups contain 3 to 5 carbon atoms and are branched.

4. A Diesel fuel comprising a hydrocarbon Diesel fuel and a dialkyl trisulfide having at least 3 carbon atoms in each alkyl group added in a proportion from about 0.25% to about 5% by volume of the fuel.

5. A high speed Diesel fuel comprising a hydrocarbon Diesel fuel and from 0.25% to about 5% by volume of diamyl trisulfide.

6. A high speed Diesel fuel comprising a hydrocarbon Diesel fuel and from 0.25% to about 5% by volume of tertiary butyl trisulfide.

7. A high speed Diesel fuel comprising a hydrocarbon Diesel fuel and from 0.25% to about 5% by volume of isopropyl trisulfide.

8. The method of preparing a high speed Diesel engine fuel of improved ignition qualities and capable of successfully passing a copper strip corrosion test which comprises blending a hydrocarbon Diesel fuel which is satisfactorily noncorrosive to copper with a minor proportion of a dialkyl trisulfide in a quantity sufficient to substantially raise the cetane number of the fuel.

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