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FUELS FOR INTERNAL COMBUSTION ENGINES

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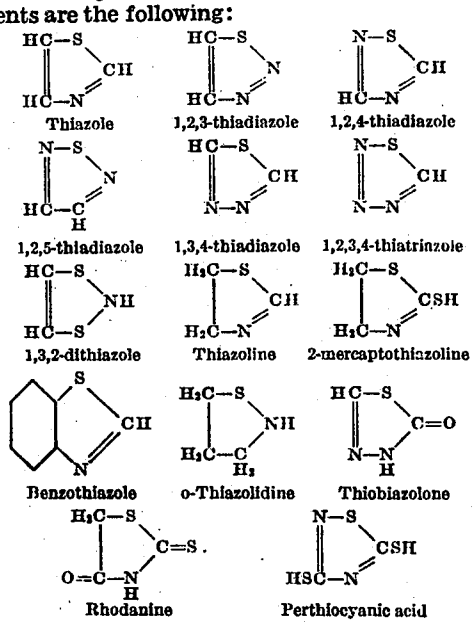
10 Claims. (Cl. 44—57)

This invention relates to compression-ignition engine fuels and is concerned particularly with the use of addition compounds which enhance the ignition qualities and other properties of fuels used in high speed engines of the Diesel type.

In most instances, addition compounds which have been recommended for accelerating ignition of hydrocarbon oils in Diesel engines have characteristically contained oxygen, nitrogen and sulfur in highly unstable groupings. While it is true that many of these proposed compounds are very effective in shortening the delay period between injection and spontaneous ignition of the fuel, particularly when the fuel is freshly made up, a reduction in their effectiveness tends to occur during storage owing to their inherent instability. Not only do these unstable compounds tend to deteriorate, but on deteriorating they tend to induce oxidation of hydrocarbons in the fuel which results in gum formation, and, further, they tend to develop corrosive decomposition products in storage and in operation of the engines.

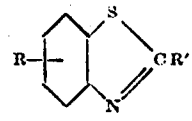
An object of this invention is to provide an improved Diesel fuel composition with a novel stabilizing agent, which, added to the fuel by itself or in combination with unstable types of ignition promoters, has a definite and substantially beneficial influence on the ignition quality of the fuel. It is a further object of the invention, also accomplished by adding the said novel stabilizing agent, to provide a fuel which is stable from the standpoint of gum formation and the formation of acidic materials, and is not corrosive to metals, even when such fuel contains sulfur or sulfur compounds as additional ignition promoting agents. It is a further object of the invention to provide an addition agent which does not diminish the ignition promoting qualities of other such agents present in the fuel.

The new class of ignition promoting and stabilizing addition compounds, which have been found to accomplish all of the objects above set forth when compounded in petroleum Diesel fuels, includes the organic compounds containing a five-membered heterocyclic ring structure containing both nitrogen and sulfur. The class includes compounds of a very wide variety, and comprises such well known types of compounds as the thiazoles, thiadiazoles, thiazolines, benzothiazoles, mercaptobenzothiazoles, etc. A number of examples of the preferred class of addition agents are the following:



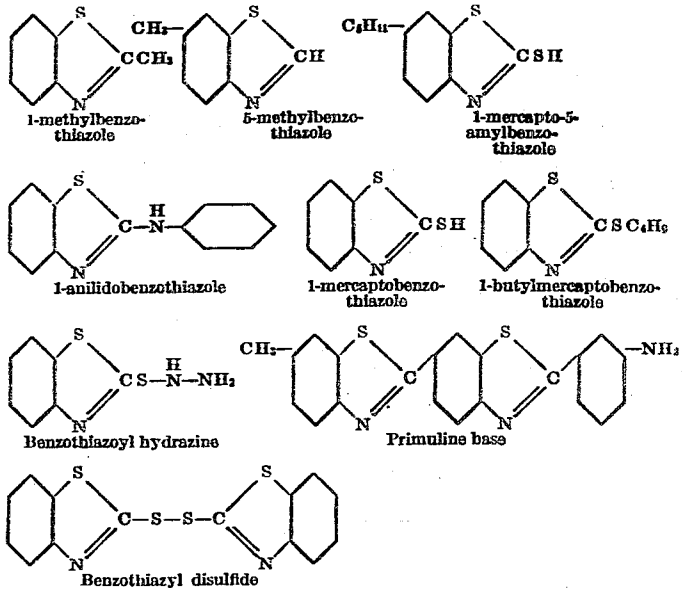
Further examples of the preferred class of compounds may be found by substituting one or more hydrogen atoms of the above or similar compounds with halogen, amino, mercapto, hydroxyl or organic groups such as alkyl, aryl, -NH-alkyl, -NH-aryl, -N-alkyl, -N-aryl, -S-alkyl, -S-aryl, or organic groups containing heterocyclic ring structures.

An especially preferred sub-group of compounds, which are particularly effective in promoting ignition in Diesel fuels and in inhibiting oxidation, corrosion, etc., are benzothiazole and its substitution products. These may be defined by the formula



where R' is hydrogen, -NH_2, -SH, -OH, or an organic group, such as alkyl, aryl, -NH-alkyl, -NH-aryl, -N-alkyl, -N-aryl, -S-alkyl, -S-aryl, or an organic group containing a heterocyclic ring

structure. Illustrations of this group of compounds are the following:



Of the above, the most desirable are 1-mercaptobenzothiazole and its substitution products obtained by substituting alkyl groups in the mercapto radical. The alkyl mercaptobenzothiazoles, owing to the presence of the alkyl radical, are unusually soluble in Diesel oils, and they are particularly effective in increasing the cetane number of the fuels. 1-butylmercaptobenzothiazole and 1-mercapto-5-amylbenzothiazole are easily produced and especially valuable members of this class.

The value of the above-described compounds as ignition promoters is determined by dissolving a small amount in a 40 cetane number gas oil, and testing each sample in a high speed Diesel engine according to the method disclosed in the S. A. E. Journal of June, 1936, page 225. Each sample is given a cetane number rating by comparison with blends consisting of cetane and alpha methyl naphthalene. Since the ignition lag of a blend consisting of normal cetane and alpha methyl naphthalene is shortened very nearly in proportion to the increase in percentage of cetane by volume, the ignition quality of the fuel can be evaluated in terms of the cetane content of such a blend giving comparable performance in the test engine. It has been found that even when the proportion of added agent is less than 1%, substantial improvement in cetane number is produced in the treated fuel. The improvement is noted even in the case of compounds containing the amino or imino groups, such as 1-anilidobenzothiazole. This is noteworthy, since the presence of an amino or imino group in the compound has the power to counteract ignition promoting action generally, as in the case of aniline and its derivatives.

The new compounds are useful also in conjunction with other ignition promoters. When, for example, nitrogen tetrasulfide, N_4S_4, is used alone with Diesel fuels, a very considerable increase in the cetane number is produced; but the fuel is notably corrosive to metal tanks, pipes and engine parts with which it comes in contact. A further addition of one of the preferred new compounds, such as 1-mercaptobenzothiazole, inhibits the corrosive action of the nitrogen tetrasulfide, and not only does not interfere with the ignition promoting qualities of this compound, but adds its own ignition promoting effect as well.

The new addition agents will in general stabilize Diesel fuels containing unsaturated hydrocarbons or potentially unstable ignition promoters which tend to induce oxidation, with attendant acid and gum formation, and the development of corrosive decomposition products. Examples of potentially unstable ignition promoters are: aliphatic nitrates, aliphatic nitrites, aliphatic polysulfides, acetone peroxide, aromatic peroxides, nitrogen sulfides, hexasulfamide, nitro compounds, nitrosoamines, and other compounds of similar structure.

To prepare the Diesel fuel compositions of improved ignition qualities, which can be stored for long periods without deterioration, also with reduced acid and sludge formation, the ignition promoting and stabilizing compound need be used only in quantities of 1% or less, whether used alone or together with 0.1% to about 5% of other addition compounds. About 0.2% to 1% of the stabilizing promoter is generally adequate; and even as little as 0.01% is sufficient when it is to be added chiefly as a corrosion inhibiting agent; but in the case of readily oxidizable fuels or when a relatively large amount of unstable addition compounds are present, as much as 3% may be used.

Examples of Diesel fuels containing the new addition agents in advantageous proportions are shown by the following formulas, in which the base oil is a gas oil of 40 cetane number and a viscosity of 37 (Saybolt Universal) at 100° F. When it is desired to form a saturated solution of the ignition promoter, the oil may be passed through a filter containing the compound. The formulas show fuels containing a second ignition promoter and, in one case, an oiliness agent.

Fuel #1

	Per cent
1-butylmercaptobenzothiazole	0.5
Lower alkyl esters of wax oxidation acids	0.25
Base oil—to make	100

Fuel #2

Acetone peroxide	1.0
1-mercaptobenzothiazole—to give saturated sol	(<0.5)
Base oil—to make	100

Fuel #3

Amyl nitrate	1.0
1-mercaptobenzothiazole—to give saturated sol	(<0.5)
Base oil—to make	100

Every hydrocarbon oil suitable as a fuel for Diesel engines may be improved in the described manner. Ordinarily the hydrocarbon fuel to be used may be said to have a boiling range above that of gasoline, and, more particularly, the boiling range and viscosity of hydrocarbons present in a gas oil which boils from 400° to 700° F. Under some circumstances, a more narrowly cut fraction such as one distilling from about 400° or 450° to 600° F. may be used. Considerable benefit may be obtained in improving lower cost fuels by the stabilizing promoters in that the lower cost fuels contain larger quantities of hydrocarbons unstable toward oxidation.

Small quantities of the novel addition agents of this invention are useful for adapting various mixtures of hydrocarbons for use as Diesel fuels, including recycle stocks from cracking operations, non-paraffinic extracts, distillates from the destructive distillations of coal and asphaltic materials, and 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, dyes, pour point depressants, viscosity modifiers, oxidation inhibitors and knock suppressing agents.

Practical advantages obtained in using the stabilizing promoters are:

1. Economy in the use of more potent ignition promoters which are subject to degradation when used without a stabilizing agent;

2. Protection of storage tanks and engine parts from corrosive decomposition products of the more potent ignition promoters;

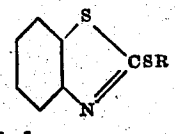
3. Stabilization of the fuel against the development of insoluble gums and resins which tend to clog fuel lines and atomizers; and

4. Substantial improvement in the ignition of the Diesel engines due to the increase in cetane number of the blended fuel.

The above description and examples are to be taken as illustrative only and not as limiting the scope of the invention. Any modification or variation therefrom which conforms to the spirit of the invention is intended to be included within the scope of the claims.

We claim:

1. A compression-ignition engine fuel comprising a hydrocarbon Diesel fuel oil and 0.2% to 3% of a compound of the formula

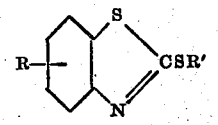


where R is an alkyl group.

2. A compression-ignition engine fuel comprising a hydrocarbon Diesel fuel oil and 0.2% to 3% of 1-butylmercaptobenzothiazole.

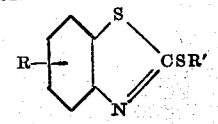
3. A compression-ignition engine fuel comprising a hydrocarbon Diesel fuel oil and 0.2% to 3% of 1-mercaptobenzothiazole sufficient to substantially decrease the ignition delay period of said fuel.

4. A compression-ignition engine fuel comprising a hydrocarbon oil boiling above the gasoline range and 0.2% to 3% of a compound of the formula



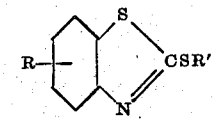
where R and R' are members of the group consisting of hydrogen, halogen, —NH_2, —SH, —OH and organic groups.

5. The method of increasing the ignition quality of a compression-ignition engine fuel which comprises adding to said fuel 0.2% to 3% of a compound of the formula



where R and R' are members of the group consisting of hydrogen, halogen, —H_2, —SH, —OH and organic groups.

6. The method of improving the combustion of a compression-ignition engine which comprises igniting a hydrocarbon Diesel fuel oil in the cylinder of said engine in the presence of 0.2% to 3% of a compound of the formula

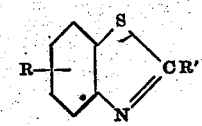


where R and R' are members of the group consisting of hydrogen, halogen, —NH_2, —SH, —OH and organic groups.

7. A compression-ignition engine fuel comprising a hydrocarbon oil boiling above the gasoline range and 0.2 to 3% of a thiazole.

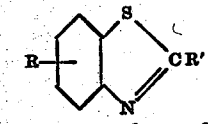
8. The method of improving the combustion of a compression-ignition engine which comprises igniting a hydrocarbon Diesel fuel oil in the cylinder of said engine in the presence of 0.2 to 3% of a thiazole.

9. The compression-ignition engine fuel comprising a hydrocarbon oil boiling above the gasoline range and 0.2 to 3% of a compound of the formula



where R and R' are members of the group consisting of hydrogen, —NH_2, —SH, —OH, and organic groups.

10. The method of improving the combustion of a compression-ignition engine which comprises igniting a hydrocarbon Diesel fuel oil in the cylinder of said engine in the presence of 0.2 to 3% of a compound of the formula



where R and R' are members of the group consisting of hydrogen, —NH_2, —SH, —OH, and organic groups.

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