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COMPRESSION-IGNITION ENGINE FUEL

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This invention relates to an improvement in fuels for compression-ignition engines, and particularly to improvements in the ignition quality and lubricity of fuels to be employed in high speed Diesel type engines.

The beneficial action of certain addition agents in shortening the delay period or ignition lag between the injection of the fuel oil into the combustion zone of a Diesel engine and the point at which ignition of the fuel sets in has already been pointed out in this art. Also, some materails have been recommended as oiliness agents for conferring on the fuel desirable lubricity to provide lubrication to pumps and valves in the positive injection means. However, not all oiliness agents have been beneficial for a properly timed injection and combustion of the fuels.

It is an object of this invention to improve compression-ignition engine fuels with respect to both their engine performance and their lubricating qualities by the addition of an ingredient capable of making both improvements.

Other more detailed objects of this invention will become apparent from the following description.

More recently, in the preparation of fuels suitable for the high speed Diesel type of compression-ignition engines which operate at about 1,000 revolutions per minute or more, it has been found preferable to use fuels having relatively narrow and lower boiling ranges, and, in some instances, chemically refined to a high degree since such fuels have better ignition qualities than the more viscous and unrefined hydrocarbon fuels, but unfortunately many of these fuels with superior ignition qualities lack the desirable lubricating function. While some lubricating quality is desirable in the fuel to lessen the wear of parts which must necessarily be lubricated by the fuel, a more serious problem is to eliminate fuel leakage around plungers and valves and dribbling from the atomizing or injecting nozzles, because correction of these latter defects is is very essential for properly timed burning of the fuel in the engine. In accordance with the present invention, these fuels are provided with an agent which corrects their lubricating deficiency and, moreover, enhances their ignition qualities.

The ignition qualities and engine performance of Diesel fuels may be determined appropriately by the method more recently recommended by the S. A. E. Volunteer Group for Compression Ignition Fuel Research and described in the S. A. E. Journal of June, 1936, page 225. This consists in matching the performance of a fuel to be tested with a reference fuel having a known cetane number, the cetane number being the percentage of normal cetane by volume in a blend with alpha methyl naphthalene. Normal cetane serves as a standard of high ignition quality hydrocarbon fuel for Diesel engines, because it has a very short ignition lag, and the ignition lag of the reference fuel, consisting of cetane and alpha methyl naphthalene, is shortened very nearly in proportion to the increase in percentage of cetane by volume in the blend. Hence, the cetane number assigned to any Diesel fuel corresponds to the volume percentage of cetane in the reference fuel having equal ignition qualities.

The novel addition agents of this invention are characterized as organic phosphates or esters of phosphoric acid, and more particularly, those containing thio- and alkyl group substituents. The addition to or solution in hydrocarbon fuels of this type of compound for imparting better ignition qualities and injection performance to the fuels constitutes a more specific object of this invention.

Classes of compounds characterized as organic phosphates with proved essential properties for the objects of this invention are exemplified by the following general formula:

$$(RO)_3PO$$

in which a sulfur atom may be substituted for each oxygen atom and where R represents organic groups containing hydrogen and carbon preferably combined as in an alkyl, alkaryl or aralkyl group, the alkyl group being such as a methyl or an ethyl group, but preferably propyl, isopropyl, amyl, and such higher homologous groups, their isomers and their olefinic or naphthenic analogues, the alkaryl or aralkyl group being such as a benzyl, cresyl, and analogous groups. The presence of inorganic substituents, such as halogens, nitrate groups, and active metals in some of the organic groups, particularly the alkyl groups, may add to their effectiveness in accelerating ignition.

For the purpose of illustration, the phosphate esters are divided into the following sub-groups, each sub-group being exemplified by specific compounds with their assigned structural formulae:

1. Alkyl or alkaryl phosphates, for example, triamyl phosphate $(C_5H_{11}O)_3P=O$ tricresyl phosphate $(CH_3.C_6H_4O)_3P=O$
2. Dithiophosphates, for example, triamyl dithiophosphate

$$C_5H_{11}S-\overset{\overset{S}{\|}}{P}(OC_5H_{11})_2$$

tricresyl dithiophosphate

$$CH_3C_6H_4S-\overset{\overset{S}{\|}}{P}(OC_6H_4.CH_3)_2$$

3. Trithiophosphates, for example, triamyl trithiophosphate,

$$C_5H_{11}O-\overset{\overset{S}{\|}}{P}(SC_5H_{11})_2$$

4. Tetrathiophosphates, for example, triamyl tetrathiophosphate $(C_5H_{11}S)_3P=S$ tri-para-cresyl tetrathiophosphate

$$(CH_3.C_6H_4S)_3P=S$$

These phosphates and thiophosphates may be prepared by reacting alcohols or phenols containing the desired alkyl groups with a pentavalent phosphorus compound capable of undergoing a condensation reaction with the alcohol or phenol to produce the desired ester. The phosphates may be produced by the action of phosphoric acid directly on the alcohol or phenol, or, if desired, phosphorus oxychloride or phosphorus pentachloride may be substituted for phosphoric acid. The thiophosphates may be prepared by the reaction of phosphorus pentasulfide with the alcohol or phenol, or by condensation of ortho phosphoric acid with a mercaptan or thio alcohol.

The phenols to be used according to the present invention are obtainable as by-products in the liquefaction of coal, from cracked petroleum oils, from tar acids, by hydroxylation of aromatic hydrocarbons, and by alkylation of phenols.

While the phosphate esters, in general, have been found effective for increasing the oiliness of Diesel fuels without any impairment to the ignition qualities of the fuels, the alkyl group and sulfur-containing phosphate esters have been found to be superior in improving the lubrication and proper atomization under extremely high pressure and in effectively increasing the ignition qualities of the fuel. The effectiveness of these compounds in raising the cetane number of a hydrocarbon fuel is illustrated by the following tabulated results from comparative tests on samples of an unmodified hydrocarbon fuel with samples of the same fuel modified by a small amount of an added phosphate ester.

Modifying agent in a 40 cetane number Colombian gas oil	Weight per-cent used	Increase in cetane number
N-butyl phosphate	1.00	0 to +1
Triphenyl phosphate	1.00	0 to +1
Triphenyl tetrathiophosphate	3.00	0 to +1
Trithiophenyl phosphate	1.00	0 to +1
Triamyl trithiophosphate	Less than 1.00	+1 to +2
Triparacresyl tetrathiophosphate	0.25	+3 to +4

From pertinent data as illustrated in the foregoing table, it may be seen that the alkyl group containing thiophosphates are definitely superior to other phosphate esters. Evidently, the sulfur and alkyl group constituents in the phosphate esters not only aid in increasing the lubricity of a hydrocarbon fuel but also in imparting to the fuel an improved engine performance.

The hydrocarbon fuel to be used in conjunction with these novel addition agents may be any of the prevalently used hydrocarbon fractions such as a gas oil fraction boiling within the range of 400° F. to 700° F., regardless of whether such a fraction be obtained from a naphthenic base, paraffinic base, or a mixed base crude oil. Since the new and preferred types of addition agents are chiefly advantageous for increasing lubricity of a fuel, they may be employed most valuably with light gas oil cuts having A. P. I. gravities above 30° and viscosities in the range of about 30 to 40 Saybolt seconds at 100° F., and particularly those which have been chemically refined for the removal of aromatic and asphaltic compounds. The narrow boiling range cuts having a 10% distillation between 475° F. and 580° F. and a 90% distillation point between 600° F. and 675° F., exhibit in common superior ignition qualities regardless of the crude source, provided their aniline miscibility points are substantially above 140° F., and to impart this property of aniline miscibility to the oil may require an amount of chemical refining which tends to remove oiliness components. To derive the full benefits of high ignition qualities from these improved narrow fractions, it is important to provide them with an agent which is highly effective for imparting the desired lubricity without detriment to their ignition qualities, or better yet, with more highly effective agents such as the alkaryl thiophosphates, capable of enhancing their ignition qualities. When blended with agents of this type, these less viscous fuels are improved more than a gas oil fraction and can thus have cetane numbers of about 60 to 80.

In preparing the improved fuels according to the present invention, the phosphate ester is added to the hydrocarbon fuel base in amounts varying generally from 0.1% up to about 5.0% by weight, or to the limit of their solubility in the oil, depending upon the type of fuel and addition agent employed as well as the design of the compression-ignition engine in which the fuel is to be used. Small quantities of these novel addition agents 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, pyrobituminous and asphaltic materials and mixtures of these with one another or straight run petroleum fractions.

Other agents for enhancing various other physical and chemical characteristics of the fuel without detracting from the ignition quality of the fuel may be admixed, such as sludge dispersers, dyes, corrosion inhibitors, anti-oxidants, viscosity improvers, pour point 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 were give 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.

I claim:

1. A fuel composition for compression-ignition engines of the Diesel type comprising a hydro-

carbon Diesel fuel blended with a thiophosphate ester containing in the molecule three to four sulfur atoms and three organic groups each of which has an alkyl group, the hydrocarbon components of said fuel composition boiling below 700° F. and said ester being added in sufficient amount to substantially enhance the ignition quality of said fuel.

2. A fuel composition according to claim 1, in which said thiophosphate ester is a trialkaryl tetrathiophosphate.

3. A fuel composition according to claim 1 in which said thiophosphate ester is triparacresyl tetrathiophosphate.

4. A fuel composition according to claim 1, in which said thiophosphate ester is a trialkyl trithiophosphate.

5. A fuel composition for compression-ignition engines of the Diesel type comprising a hydrocarbon Diesel fuel blended with a sufficient amount of a trialkaryl tetrathiophosphate to substantially enhance the ignition quality of said fuel, the hydrocarbon components of said fuel composition boiling within the range of 400 to 700° F., having a 10% distillation point between about 475° F. and 580° F. and a 90% distillation point between about 600 and 650° F.

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