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MODIFIED FUEL

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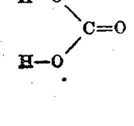
This invention relates to liquid fuels of the type employed in oil furnaces and those used in internal combustion automotive engines, particularly to high flash point spark-ignition engine fuels adapted for injection type engines. It involves the addition to liquid fuels of certain modifying agents which favorably alter the surface tension thereof for efficient dispersion, also, of agents which are effective detonation suppressors in spark-ignition engines.

For economy, higher heating value, and reduction of fire hazards, there has been a trend toward the use of higher boiling fuels which have to be supplied to the combustion chambers of internal combustion engines as liquids by injection through nozzles under high pressures. The injection devices commonly used include pumps which depend upon the fuels for lubrication; for this reason, it is found desirable to employ fuels of sufficiently high viscosity for lubricating action, while on the other hand increased viscosity of a fuel interferes with efficiency of the delivery device and dispersion of the fuel into the combustion chamber. Further difficulty in the injection of fuels arises from their tendency to form deposits in spray nozzles, thereby clogging extremely small fuel channels and orifices in the atomizing spray nozzles.

An object of this invention is to confer on hydrocarbon fuels properties which permit them to pass readily through the injection device and become efficiently atomized thereby, while they act satisfactorily as lubricants and keep the injection in a satisfactory condition. A more specific object is to improve spark-ignition engine fuels in these respects by addition agents which are of substantial benefit to the anti-knock value of the fuels. Further objects and advantages will become apparent from the following description.

Broadly, the objects of this invention are obtained by blending with a liquid hydrocarbon fuel base minor amounts of certain substances found to possess a remarkable ability for making the oil blends spread over metal surfaces and for weakening cohesive forces of the oil molecules so that the oil can be more efficiently atomized. The substances which affect fuel compositions in these respects belong to the class of compounds known as ester derivatives of carbonic acid. Carbonic acid as itself, H_2CO_3, with the theoretical structural formula:



is believed to be too unstable to exist as such, but the radical of this acid is present in a series of ester derivatives in which at least one of the hydrogen atoms in the carboxyl groups is replaced by a hydrocarbon group, such as an alkyl group, an aryl group, or substituted groups of these types which form esters of carbonic acid. A variety of closely related derivatives include esters in which a halogen, such as chlorine, replaces one of the hydroxy groups and esters in which a nitrogen-containing group is present.

The carbonate ester blending agents used according to the present invention are preferably selected to have boiling points which come within the range of the desired fuel composition. They are easily and economically prepared from by-products of petroleum refining, as for example, by known basic methods which involve the reaction of carbon monoxide and chlorine, or carbonyl chloride, with an alcohol, also, of carbonic and chloro-carbonic esters with amines. The following examples will serve to illustrate modes of formation of the carbonate esters used in the practice of this invention:

Example 1

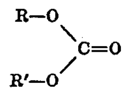
Equimolar proportions of carbon monoxide and chlorine are made to combine in sunlight to form carbonyl chloride known by the common name "phosgene." The phosgene reacted with ethyl alcohol produces ethyl chloro-carbonate, with splitting out of hydrogen chloride. Ethyl chlorocarbonate, which has an ester and an acid chloride, reacts directly with an equimolecular proportion of ethyl alcohol to form diethyl carbonate.

Example 2

In place of reacting the ethyl chloro-carbonate with alcohol, it is reacted with an amine in an equimolecular proportion to form a derivative of carbonic acid which is an ester and an amide.

It is of no consequence which hydrocarbon radical is present in reactants used in synthesizing the carbonate esters.

Of the various carbonic acid derivatives, a type which functions particularly well for the objects of this invention embraces those which behave as true esters. Specific examples of the alkyl esters are the methyl, ethyl, propyl, isopropyl, and butyl carbonates, also, the homologous alkyl carbonates which contain two different alkyl groups. Aryl carbonates, such as creosote carbonate, phenol ethyl carbonate, and the like may be prepared by esterifying phenols rather than aliphatic alcohols. Aryl alcohols such as benzyl alcohol and other cyclic alcohols, e. g., cyclohexanol, may also be esterified in the same manner. Polyhydroxy alcohols such as glycol, substituted glycols, glycerols, etc., may also be employed to prepare such carbonates. In general, these compounds are characterized by the compositional formula:



wherein R and R' represent aliphatic, aromatic, or hydro-aromatic radicals, alike or unlike. In the other useful analogous carbonic ester derivatives, one of the organic groups may contain a halogen substituent, e. g., an alkoxy group may be replaced by a halogen as in chloro-carbonates, or a nitrogen-containing group as in the ester amides of carbonic acid. For the purpose of the present invention, however, the dialkyl carbonates are preferred.

In making an improved motor fuel for high compression spark-ignition engines, a light petroleum distillate, a synthetic fuel or mixtures thereof, obtained by any of the known commercial processes may be used as the hydrocarbon base; for instance, ordinary gasoline having a boiling range within the limits of 100° F. and 450° F. may be used. The present invention, however, is adapted more for the heavy liquid fuels such as those for injection type engines, having the safety advantage of a high flash point, the initial point of the fuel being about 300° F. and the end point approaching even 600° F.; but for aviation motors, the end point should not far exceed 400° F. or 450° F.

To improve high speed compression-ignition engine fuels and heating oils, the hydrocarbon base fuel may have a boiling range within the limits of 400° F. and 700° F. or a still higher boiling range.

The esters of carbonic acid used as the improving agents are blended with the hydrocarbon base in any desired proportions up to the limits (if any) of their solubilities in the fuel, and if desired, solubilizing agents, e. g., ethers, amines, hydroxy esters or ethers, soaps, and the like, may also be incorporated into the fuel composition. For example, it is possible to add with the carbonates the following types of compounds: dioxanes, tert-butyl ether, "Cellosolve" and "Carbitol" type compounds, aluminum, tin, calcium, and other oil-soluble metal soaps, "reverse" soaps such as onium soaps, e. g., cetyl pyridinium chloride, alcohols, ketones, etc.

In practice, the proportion of the carbonic ester is preferably used in a concentration of 1% to 10% by volume of the fuel composition. For obtaining increased improvement in the antiknock or octane blending value of the fuel as well as in the physical characteristics of the composition preferably in the proportion of the carbonic ester should be above 3%, say 5% or 10% or even more. However, in compression-ignition engine fuels, the proportion is preferably more limited to less than about 5% and in some instances 3%, since in higher proportions the carbonic acid derivatives are not knock-suppressors in such fuels, although they do not adversely affect the cetane number of a Diesel fuel to any appreciable extent when used specifically therein to improve the surface tension characteristics of the fuel.

The present invention is highly suited for improving furnace oils and other heavy liquid fuels. Although it is true that mechanical features more or less govern the efficiency of an oil burner, it is possible to improve the tendency for oils to form fine droplets by adding thereto, substances which will affect the surface tension characteristics of the oil. Oil-soluble carbonates of the type described herein considerably lower the surface tension of liquid fuels causing the oil to spread and break up into small particles readily. By the addition of a fraction of a percent or more of such a substance, it is possible to improve a fuel to such an extent that it will atomize readily even under adverse mechanical conditions.

The effectiveness of the carbonic ester derivatives for lowering the surface and interfacial tension of a fuel oil, thereby giving better injection delivery and spray penetration is visibly demonstrated by a spread measurement test. In this test, a minor amount of the agent is blended with a refined mineral oil such as one which may be used as a fuel and precisely measured drops are allowed to spread on a polished metal plate under fixed conditions. The area of spread for each sample tested is measured and expressed in percentage of the spread area for the hydrocarbon base oil containing no addition agent, the hydrocarbon base oil being referred to as the blank. Typical comparative tests are shown in the following table:

Composition	Percent area of spread
Blank	100
Blank + 3.0% di-n-butyl carbonate	180
Blank + 3.0% diethyl carbonate	130

The foregoing tests illustrate how the carbonic esters in a very unique manner are valuable aids for delivering the fuel through the injection system and for breaking up the fuel into numerous uniformly small droplets at the nozzle orifice. By the aid of this factor, good distribution can be obtained even in fuels of high viscosity and low volatility to promote efficient ignition and combustion. Improvement of the injection system condition is also believed accountable to the tendency of the fuels containing the spreading blending agent to more readily pass through the narrow channels in the nozzle and thereby avoid stationary oil layers which tend to form clogging deposits.

It can be readily appreciated that the blending agent serves more advantageously if it is not detrimental to the combustion qualities of the fuel. The preferred blending agents of the present invention have been found to have excellent anti-knock values for spark-ignition or Otto cycle engines as shown by A. S. T. M. determinations of their effects on hydrocarbon fuels. For example, diethyl carbonate, $(C_2H_5O)_2C{:}O$, which boils at 260° F., has an A. S. T. M. octane blending value of 96 in a 78.7 octane number (A. S. T. M.) gasoline reference fuel when employed therein in a 5% by volume concentration. These results were checked with other reference fuels containing similar proportions of the alkyl carbonate. A 73.9 (A. S. T. M.) octane number fuel was improved to an octane number of 75 by 5% of the alkyl carbonate, indicating that the alkyl carbonate has a blending value of 98. The corresponding amide ester, $(C_2H_5O)CO{\cdot}NHC_2H_5$, tested in the same manner was found to have an A. S. T. M. blending value of 100. When blended in a 6% by volume concentration with a Diesel fuel, the alkyl carbonate showed no appreciable alteration in the cetane number of the fuel, thus indicating the blending agent can properly be used to such an extent in compression-ignition engine fuels without detriment to their ignition qualities. Moreover, they can be used in larger proportions in a Diesel fuel together with ignition quality promoters if it is considered necessary to compensate for any lowering of the cetane number which might be found to arise from the carbonate ester. A number of analogous carbonate esters were tested and similar advantageous results were obtained.

From the foregoing, it will be seen that the carbonate ester blending agents may serve very usefully in very viscous fuel oils or be used together with thickeners that increase the viscosity of the fuel since the spreading effect of the ester carbonates diminishes the cohesion tendencies of thickened or viscous oils. Accordingly, a non-viscous fuel base may be improved in viscosity, lubricity, and other characteristics, by a thickener or V. I. improver such as iso-olefin polymers, soaps, fatty oils, and the like, and still be made to flow properly and be efficiently atomized by the injection system. Likewise, the modification by the carbonate esters adapts ordinarily less desirable heavy fuel oils for use in compression-ignition engines. Other addition agents may also be incorporated into the fuels with improvement by the ester carbonates, for example, lubricants, high boiling gum flux oils, oxidation inhibitors, pour point depressants, etc.

Other variations of the invention will be apparent to those skilled in the art, and the invention is not to be limited by the specific examples nor by the theory of the mechanism through which the desired improvements are obtained.

This application is a division of copending application Serial No. 302,689, filed November 3, 1939.

I claim:

1. An improved liquid fuel composition comprising a major proportion of a hydrocarbon liquid fuel base blended with a minor proportion of a soluble ester amide of carbonic acid in sufficient amounts above 1% to substantially lower the surface tension of the fuel.

2. A composition as described in claim 1, in which the liquid fuel base is a heavy petroleum oil.

3. An improved fuel for injection type internal combustion engines comprising a major proportion of a hydrocarbon fuel base stock boiling between about 300° F. and about 700° F. and a minor proportion of a soluble carbonate ester amide in an amount sufficient above 1% to improve spreading characteristics of the fuel.

4. A fuel composition as described in claim 3, in which said carbonate ester amide has the formula $(C_2H_5O)CO \cdot NHC_2H_5$.

5. An improved spark-ignition engine fuel comprising in a major proportion a naphtha fraction boiling in the range of about 300° F. to 600° F. and from about 3% to 10% by volume of a soluble carbonate ester amide.

6. A liquid motor fuel for high-compression spark-ignition engines comprising a hydrocarbon fuel containing gasoline hydrocarbons and a minor proportion of a soluble alkyl carbonate amide in sufficient amount of at least about 5% to improve the anti-knock value of the fuel.

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