Patented July 10, 1945 2,380,341

UNITED STATES PATENT OFFICE

2,380,341

DIESEL FUELS

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No Drawing. Application April 24, 1942, Serial No. 440,346

11 Claims. (Cl. 44—57)

This invention relates to liquid fuels for internal combustion engines and has to do particularly with the modification of fuels for compression ignition engines such as those of Diesel or semi-Diesel type by the addition of characterizing ingredients for the purpose of modifying or controlling the combustion characteristics of the fuels.

In internal combustion engines of the Diesel type where the fuel is injected into a combustion chamber, it is important to the attainment of maximum efficiency, that the delay period between fuel injection and fuel ignition be short. It is thus seen that enhancing the speed of ignition is a desirable characteristic. When fuels are employed in such engines which unduly delay ignition, a "knocking' occurs due to improper coordination of combustion and piston position thereby causing power losses. By decreasing the ignition delay period of Diesel fuels, it is possible to lower the compression pressure which will insure spontaneous ignition without combustion shock or "knock" thereby increasing the ease of starting and improving the coordination between combustion and engine operation with resultant improvement in operating efficiency.

It is well known in this art that the ignition quality of hydrocarbon fuels for compression ignition engines can be improved with respect to the ignition delay periods by incorporating in the fuels small amounts of certain compounds which act as ignition accelerators. This offers a means of improving the better grades of Diesel fuels and a means of widening the range of available fuels by raising the ignition quality of lower grades to a point where they can satisfactorily be used. Among the various compounds which have been proposed as ignition accelerators are amyl thio nitrite, ethyl thio nitrite, amyl nitrate, ethyl nitrate, tetralin peroxide, acetone peroxide, aniline disulfide and diamyl amine disulfide. Of these various ignition accelerators, amyl nitrate appears to be the only one which has experienced commercial development. The ignition quality of Diesel fuels is ordinarily evaluated by comparison with a standard reference fuel in a converted C. F. R. engine using the ignition delay method. The result is expressed as a cetane number or cetane rating which is the per cent by volume of cetane in a blend of cetane and alpha methyl naphthalene which has the same combustion characteristics as the sample tested. This method is known as A. S. T. M. method D613–41T.

While the efficacy of the foregoing ignition accelerators for reducing the ignition delay period, as measured by cetane rating, is satisfactory, many of such additives have the undesirable property of lowering the flash test of the fuels in which they are incorporated. This increases the hazard in handling such fuels and if reduced below statutory requirements, usually 150° F., restrictions are imposed on the shipment thereof.

It is an object of this invention to improve the combustion characteristics of fuels for compression ignition engines.

It is a further object of this invention to reduce the ignition lag of fuels for compression ignition engines without causing concomitant lowering of the flash test of the blended fuels.

It is a still further object of this invention to provide Diesel fuels of high cetane rating and of high flash test.

These and other objects of the invention will become apparent from a consideration of the following detailed description of the invention.

Small quantities, i. e. about 0.5% to 10% of ignition accelerators such as various organic nitrites, thio nitrites and nitrates will produce substantial improvement in the combustion characteristics of Diesel fuels as measured by the cetane ratings of the fuels, but at the same time these ignition accelerators produce an undesirable lowering of the flash tests of the fuels. Examples of ignition accelerators which are effective for improving cetane rating, but which in small amounts will cause an accompanying material lowering of the flash test of otherwise commercially acceptable fuels to below commercial standards, are amyl nitrite, ethyl nitrate, amyl nitrate, isoamyl nitrate, ethyl thio nitrite, butyl thio nitrite and amyl thio nitrite. 0.5% by weight of some of these ignition accelerators will lower the flash test of a straight petroleum Diesel fuel by as much as 17° F. It has now been found that the beneficial effect of such materials in improving the cetane rating of Diesel fuels may be retained and at the same time the undesirable lowering of flash test avoided by incorporating in Diesel fuels containing such ignition accelerators, relatively small amounts of non-inflammable halogen substituted low molecular weight aliphatic hydrocarbons, the boiling points of which are approximately the same as the flash test required on the final fuel blend. The chlorine substituted hydrocarbons are generally preferred. For example, when a flash test of 150° F. (the present commercial standard) as determined by A. S. T. M. method D93–40 is required, the boiling points of the preferred chlorine substituted hydrocarbons fall within the approximate range of 100–200° F. The chlorine compounds which are so used are preferably those which do not materially diminish the cetane rating of the fuel in which they are incorporated. Suitable chlorine-containing compounds are trichlorethylene and carbon tetrachloride. Of these materials, carbon tetrachloride is preferred because of its effectiveness in increasing the flash test of Diesel fuels and because of the fact that this material

causes little or no loss in cetane rating when it is incorporated in the fuels.

An idea of the changes in cetane ratings and flash tests of hydrocarbon Diesel fuels which may be effected by the incorporation therein of small amounts of ethyl nitrate or isoamyl nitrate may be obtained by an inspection of the data presented in Table 5 of a paper entitled "Ignition accelerators for compression-ignition engine fuels," presented before the Society of Automotive Engineers in Detroit, Michigan, January 12–16, 1942, by J. S. Bogen. In this table it is shown that 4% by weight of ethyl nitrate improved the cetane rating of a Mid-Continent cracked Diesel fuel from 33 to 56 but that at the same time the flash test was lowered from 182° F. to 115° F. Similarly, 4% by weight of isoamyl nitrate in the same hydrocarbon stock produced a blended fuel having a cetane rating of 60 and a flash test of 160° F. This lowering of the flash test is especially undesirable when the flash test on the final blended fuel becomes less than the accepted commercial standard of 150° F.

In order to demonstrate the effectiveness of compositions within the scope of this invention, Diesel fuels were prepared and the flash tests and cetane ratings determined. This data is shown in the table.

Table

Fuel	Cetane number	Flash (A. S. T. M. D93-40)
		° F.
Blank	50.7	166
Blank plus 2% by vol. amyl nitrate	82.1	154
Blank plus 2% by vol. carbontetrachloride	50.8	184
Blank {plus 2% by vol. amyl nitrate	78.3	168
Blank {plus 2% by vol. carbon tetrachloride		

In the foregoing table of data, the blank is a straight petroleum Diesel fuel obtained from a Gulf Coast crude oil. It will be seen from an inspection of the data that 2% by volume of amyl nitrate improved the cetane number from 50.7 to 82.1, but at the same time reduced the flash test from 166° F. to 154° F. The use of 2% by volume, each of amyl nitrate and carbon tetrachloride in a separate sample of the same fuel, produced a cetane number of 78.3 which is almost as good as the fuel containing the amyl nitrate alone and at the same time produced a blended fuel having a flash test of 168° F. or 2° F. higher than the original hydrocarbon fuel. It will thus be seen that the cetane rating of petroleum Diesel fuels may be materially improved by the use of amyl nitrate as an ignition accelerator and at the same time a final blended fuel obtained which is much safer to handle than the fuel that results without the use of the non-inflammable chlorine substituted low molecular weight aliphatic hydrocarbon. The avoidance of flash test lowering when incorporating ignition accelerators is particularly important when the flash test of the original unblended Diesel fuel is at, or near, 150° F. since any reduction of flash test below this figure materially detracts from the marketability of the fuel. The amount of non-inflammable chlorinated hydrocarbon required to produce the desired flash test is subject to variation depending on such factors as the nature of the particular hydrocarbon stock employed, the specific material used as an ignition accelerator and the flash test desired on the final blend. Ordinarily the amount used will be between approximately 0.25% to 5% or possibly as much as 10% by volume based on the original fuel.

Obviously, modifications and variations of the invention as hereinbefore described, may be made without departing from the spirit and scope thereof, and therefore, only such limitations are to be imposed as are indicated in the following claims.

What is claimed is:

1. An improved Diesel fuel comprising hydrocarbon distillate, an effective amount of ignition accelerator which when added to the fuel in effective amounts causes a lowering of the flash test of the distillate below a predetermined standard of approximately 150° F. and sufficient non-inflammable halogenated hydrocarbon to raise the flash test on the final blended fuel to at least the predetermined standard, the boiling point of the halogenated hydrocarbon being approximately the same as the predetermined standard.

2. A fuel in accordance with claim 1 in which the non-inflammable halogenated hydrocarbon is carbon tetrachloride.

3. An improved Diesel fuel comprising hydrocarbon distillate, approximately 0.5% to 10% by volume of ignition accelerator, which when present in said amounts causes a lowering of the flash test of the distillate below a predetermined standard of approximately 150° F. and sufficient, about 0.25% to 10% by volume of non-inflammable chlorinated hydrocarbon, to produce the predetermined flash test on the final blended fuel, the boiling point of the chlorinated hydrocarbon being approximately the same as the predetermined standard.

4. A fuel in accordance with claim 3 in which the chlorinated hydrocarbon is carbon tetrachloride.

5. A fuel in accordance with claim 3 in which the ignition accelerator is amyl nitrate and the chlorinated hydrocarbon is carbon tetrachloride.

6. An improved Diesel fuel comprising hydrocarbon distillate having a flash test of approximately 150° F., approximately 0.5% to 10% by volume of ignition accelerator which when present in said amounts cause a lowering of the flash test of the distillate to below 150° F. and sufficient carbon tetrachloride to produce a flash test on the final blended fuel of at least 150° F.

7. The method of improving the operation of compression ignition engines comprising injecting into the combustion zone of such engines the composition of claim 1.

8. The method of improving the operation of compression ignition engines comprising injecting into the combustion zone of such engines the composition of claim 3.

9. The method of improving the operation of compression ignition engines comprising injecting into the combustion zone of such engines the composition of claim 4.

10. The method of improving the operation of compression ignition engines comprising injecting into the combustion zone of such engines the composition of claim 5.

11. The method of improving the operation of compression ignition engines comprising injecting into the combustion zone of such engines the composition of claim 6.

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