Patented Dec. 30, 1941 2,268,383

UNITED STATES PATENT OFFICE

2,268,383

FUEL FOR COMBUSTION

Pharis Miller and Gould H. Cloud, Elizabeth, N. J., assignors to Standard Oil Development Company, a corporation of Delaware

No Drawing. Application October 1, 1938, Serial No. 232,799

11 Claims. (Cl. 44—9)

This invention relates, in general, to improvement of hydrocarbon fuels for efficient combustion in combustion engines. More specifically, this invention relates to economical fuels with suitable ignition qualities for efficient combustion in high speed compression-ignition engines and methods for the preparation of these fuels by addition, in small proportions, of inexpensive chemical substances, such as elemental sulfur, to hydrocarbon fuels.

Combustion engines, more particularly, high speed compression-ignition engines, are generally referred to by the name of their prototype, the Diesel engine. Hydrocarbon fuels which have been found most suitable for these engines are crude oil distillates which are highly paraffinic, but these fuels are limited in supply and relatively expensive.

In consideration of increasing power and fuel economy with elimination of vibration harmful to the mechanism in the operation of compression-ignition engines, principally when the hydrocarbon fuel contains insufficient amounts of hydrocarbon compounds recognized as serving these ends by virtue of their suitable ignition qualities, the addition of various chemical substances to the fuels has been proposed.

Hydrocarbon compounds characterized by aromatic, other cyclic, and highly unsaturated hydrocarbons have poor ignition qualities as Diesel engine fuel ingredients, following from the fact that hydrocarbon fuels containing a large proportion of these compounds fail to undergo prompt and smooth combustion in representative types of engines in which unsuitable combustion is manifested by engine vibrations and annoying "knocking" sounds. A poor ignition quality in a compression-ignition engine fuel is most frequently exhibited by an excessive ignition lag, in other words, an excessive delay between the beginning of fuel injection into the combustion chamber of the engine and the point at which ignition of the fuel sets in. In contrast, the normal paraffin hydrocarbon cetane, which serves as a standard of high ignition quality in Diesel fuel rating by recommendation of the S. A. E. Volunteer Group for Compression-Ignition Fuel Research, has a desirable minimum ignition lag. Since the ignition lag of a blend consisting of normal cetane and the aromatic compound alpha-methyl naphthalene is shortened very nearly in proportion to the increase in percentage of cetane by volume, the ignition quality of a fuel can be measured in terms of the cetane content of such a blend. Accordingly, when the improvement in a fuel by a small amount of addition agent corresponds to an improvement by an increase of about 5% or more of cetane by volume in a blend with alpha-methyl naphthalene, such an addition agent is considered to have commercially significant effectiveness, provided the addition agent used is not very costly in comparison with the value of the fuel.

Various attempts have been made to find substances effective for reducing knocking properties of Diesel fuels, but substances which have been found effective for this purpose are not altogether satisfactory from all points of view for commercial use. For example, ethyl nitrate is suitably effective for promoting the ignition qualities of a Diesel fuel, but it has to be used in relatively expensive quantities, it lowers the flasn point of the fuel, and is not stable in an undiluted state.

An object of this invention is to improve Diesel fuels by the addition of an agent which is very inexpensive, is stable in an undiluted state, and which does not lower the flash point of the fuel. A further object is to provide for the addition of an agent which can be efficiently incorporated into the fuel where the fuel is being used so that the fuel can be improved for any particular engine. Another related object is to provide for a method of adding and modifying the ignition improving agents of the class herein described so that corrosive action of the agent is satisfactorily reduced.

The novel addition agents of this invention are characterized as containing sulfur principally in a free or elemental form and with modifications for diminishing any undesired corrosive action which might accompany the use of sulfur. Although it might seem that the increasing of the sulfur content of a fuel is harmful, it has become more recently recognized that no relation exists between the sulfur content of the fuel and the amount of cylinder wear which takes place in engines operating at high temperatures, and that no harm would result in many types of Diesel engines, even if the sulfur content of the fuel used in such engines were as high as about 2% by weight. The percentages of added agents hereinafter referred to are also on a weight basis.

In accordance with the present invention, it is also proposed to make modifications in the use of elementary sulfur as an addition agent to eliminate corrosive action when required. The ordinary Diesel fuels obtained as crude distillates contain substantially no free sulfur, and many of the fuels have been subjected to a pretreatment, such as hydrogenation, which lowers their sulfur content to a negligible amount. Hence, the addition of free sulfur in very minor amounts necessary for the improvement of the fuels does not necessarily give the fuels excessive sulfur contents. Free sulfur need be added in amounts varying only from .01 to about 1% to make a marked improvement in the ignition

quality of the oil by reducing the ignition lag or increasing the cetane number of the fuel. Such a small amount of added sulfur will not even prevent many fuels from passing sulfur content specifications, particularly, fuels naturally low in sulfur and fuels which have undergone a desulfurization, such as certain hydrogenated oils. If the total sulfur content of an oil is considered extremely high, organic sulfur compounds may be removed by a suitable treatment and replaced by the more effective free sulfur, which is in some ways less corrosive. The treatment for removing the organic sulfur compounds may even be such as to leave active sulfur in the oil. The crude oil distillate may be treated with sodium plumbite and a certain excess of free sulfur, for example, to eliminate objectionable organic sulfur compounds and leave a certain amount of free sulfur dissolved in the oil. Also, a crude oil fraction may be merely heated in the presence of a certain amount of added free sulfur. Other known methods for reducing the original total sulfur content of a crude fraction may be employed.

The effectiveness of free sulfur in raising the cetane number of a hydrocarbon fuel is illustrated by the following tabulated results in which a crude distillate fuel containing added amounts of free sulfur is compared with the unmodified fuel which has a total sulfur content of 0.44%:

Fuel tests

Percent of free sulfur in a 40 cetane number Colombian gas oil	Cetane number	Cetane number increase
0.00	40	0
0.01	41	1
0.025	42	2
0.05	43	3
0.1	45	5
0.20	46	6
0.50	48	8
1.0	51	11

The method of testing is described in the S. A. E. Journal of June, 1936, page 225, and consists in matching the performance of a test sample with blends of cetane and alpha-methyl naphthalene. The per cent by volume of cetane in the blend with the alpha methyl naphthalene giving the same ignition quality test performance as the fuel in the test sample is taken as the cetane number rating of that fuel.

The cetane number improvement made by adding free sulfur to a hydrogenated fuel having no appreciable sulfur content, i. e., only 0.17% total, is shown in the following table:

Fuel tests

Percent of added free sulfur in a hydrogenated Diesel fuel	Cetane number	Cetane number increase
0.00	50	0
0.05	52	2
0.10	54	4
0.50	56	6
1.0	61	11

In instances when it is desired to maintain the sulfur content of the fuel oil low while adding active sulfur for ignition quality improvement, this may be obtained by partly combining or associating the sulfur with another element, such as phosphorus, or an inorganic radical, such as an amino group. In such combinations or associations, the effectiveness of the sulfur may be increased and corrosiveness diminished. The free sulfur may be used in these combinations by being added to the oil with elementary phosphorus, either of the red or yellow form, or with ammonia, or a suitable ammonium compound, such as ammonium sulfides.

Also, elemental sulfur may be reacted to some extent with a reagent which combines with the sulfur prior to addition to the oil. It has been found that sulfur combines with a small proportion of amino groups as in hexasulfamide which is believed to have a composition represented by the formula S_6NH_2 or $S_{18}N_3H_x$, x being undetermined, and in this composition produces almost the same cetane number increase as does free sulfur when added to a Diesel fuel, while having a much lower copper strip corrosion action and higher solubility. To obtain a combination of sulfur with the amino group, ammonia may be reacted with a sulfur chloride or sulfur may be reacted with ammonia. A convenient method used to prepare hexasulfamide in good yields is one in which ammonia is passed through a solution of sulfur monochloride in chloroform, the reaction mixture being cooled by heat exchange with a freezing mixture in the early part of the reaction to prevent violent reaction, and after darkening of color, being permitted to have an increase in temperature. The admission of ammonia was continued until the reaction mixture color became salmon red. From the resulting reaction products, ammonium chloride was filtered off. Alternatively, the ammonium chloride may be removed by extraction with water. Other low boiling alkyl halide diluents, such as ethylene dichloride, may be used in place of chloroform. With increase of temperature toward the end of the reaction, the yield of hexasulfide, forming a larger part of the reaction products, is increased while the undesired by-product, sulfur nitride, which is unstable and relatively unsoluble in hydrocarbon oils, is reduced to a negligible amount.

It is possible to separate the combined sulfur and amine compound from the other reaction products so that it may be added alone to the Diesel fuel, or the sulfur reaction products, including free sulfur, may be added together to the oil. Hexasulfamide crystals may be recovered from the chloroform solution in which it is prepared by fractional crystallization due to the relatively greater solubility of the hexasulfamide in organic solvents. For example, the chloroform solution is first evaporated down to about a fourth of its original volume, then, upon addition of 95% ethyl alcohol, in excess, a by-product comprising some free sulfur comes out of solution. After filtering off the by-product precipitate, reconcentrating the filtrate, and diluting the concentrate with benzene, hexasulfamide is crystallized out from the benzene by addition of aqueous alcohol. Purified hexasulfamide, obtained by recrystallization, is insoluble in and stable towards water, odorless, non-explosive, and stable to air. Cetane number tests on a Diesel oil composed of a Colombian gas oil and containing only 1.5% of the aminated sulfur show that this addition agent gives the fuel a cetane number increase of +10 or +11.

A similar cetane number increase is obtained when phosphorized sulfur, which is believed to

have preferably the composition of phosphorus sesquisulfide, P_4S_3, is added in a concentration of less than 1% to a 40 cetane number Colombian gas oil. The free sulfur undergoes reaction with either yellow or red phosphorus when heated together to form various phosphorus polysulfides. The phosphorus polysulfide is somewhat difficult to dissolve in the oil except by heating the oil. Solubilizing methods may be used, for example, boiling of the phosphorus polysulfide in alcohols with which the phosphorus and sulfur are believed to undergo reaction to some extent, forming associations or complex compounds which might be identified as alkoxyphosphopolysulfides, and which dissolve more readily in liquid hydrocarbon fuels at normal temperatures. The phosphorus sesquisulfide, on being dissolved into a heated fuel oil is noted to form an opalescent colloidal suspension which, however, is fairly stable in the fuel oil. Injection of the fuel into the combustion zone of a Diesel engine is not hindered by the colloidally suspended active sulfur which accelerates ignition of the fuel.

It is realized that in using the high sulfur-containing substances of this invention, care must be taken especially with parts of apparatus usually constructed of corrodible metals, such as zinc and copper, to avoid corrosion. Since the apparatus parts which usually contain these metals for flexibility are the fuel supply tanks and feed lines, care might have to be taken to use more expensive non-corrosive metals in these parts. But, in accordance with the present invention, the stable active sulfur addition agents are readily adapted for addition to the fuel at some convenient point just prior to the introduction of the fuel into the combustion chamber, as for example, at the fuel line filter so that the supply tank and fuel line for the most part are not contacted by the high-sulfur containing agent. The promoter in a solid state, such as flowers of sulfur or crushed roll sulfur, may be maintained in a reservoir through which the oil passes for injection into the combustion zone, and the fuel oil will dissolve the promoter to the extent desired. The rate of solution may be increased by the application of heat, which may be readily supplied from the engine, as, for example, from exhaust gases to the fuel or the promoter reservoir. By placing the solid addition agent reservoir in a by-pass of the fuel line near the engine, the amount of hydrocarbon fuel passed into contact with the agent for bringing it into solution can be regulated.

This method of dissolving into the oil or passage to the engine desired amounts of a slightly soluble normally solid Diesel fuel ignition promoter is particularly advantageous for high sulfur-containing promoters which may tend to corrode supply tanks and fuel lines made of metals which do not resist sulfur corrosion. But this method has other advantages in utilizing normally solid and slightly soluble promoters. For instance, it avoids troubles from deterioration and separation of such an agent which might arise from long standing and exposure to air and moisture of fuel containing the agent, and it permits better adaptation of the fuel for any particular engine and at any time of the engine's operation, since engines have different sensitivities to ignition qualities and ignition quality improvement is more necessary when starting a cold engine than in a heated running engine.

Owing to the good stability to heat, air, and moisture of ignition accelerating sulfur in the free and combined forms described, not only are these materials suitable agents for addition to a fuel on its passage through a fuel line to the engine but also to a fuel containing heat received in a processing step. For example, these stable agents may be dissolved into a hot hydrocarbon distillate as the distillate is being condensed in a fractionating tower or be added at some convenient point in a withdrawal line where the distillate is sufficiently hot to aid the solution of the agent. This method of adding the agent to the fuel is advantageous for conserving heat and for efficient handling of materials.

The proportion of ignition quality improving agent to be added to a hydrocarbon fuel ranges from a fraction of 1% to the limit of solubility in the fuel, and, as needed, free sulfur. Although free sulfur dissolves in some hydrocarbon fuels in concentrations as high as about 2 to 3%, is may be preferably used in concentrations of about .025 to 1 or 2%. When combined or associated with phosphorus or amino groups, the thus modified sulfur may be preferably used in concentrations from about .025 to 5%. A gas oil boiling from about 400° F. to 700° F. or 750° F., or, in general, having a suitable boiling range and viscosity for use as a fuel in Diesel type engines, may be used as the hydrocarbon fuel. Under some circumstances, a more narrowly cut fraction, such as one distilling from 400 to 600° F. or from 500 to 700° F. may be used. Ordinarily, the hydrocarbon fuel may be said to have a boiling range above that of gasoline.

This invention makes commercially feasible the preparation of Diesel fuels giving satisfactory engine performance from crude oils, gas oils, and residual fuels having low pour points, low A. P. I. gravities, and high heat values, such oils being procured from naphthene base, asphalt base, or mixed base stocks. Heavier and lower grades of petroleum oil, such as residual oils, are even made more suitable for slow speed engines.

The burning qualities of fractions from paraffin crudes or hydrogenated oils are also enhanced by the novel addition agent of this invention.

Small quantities of these novel addition agents may be used for adapting various mixtures of hydrocarbons for use as Diesel fuels, including recycle stocks from cracking operations, non-paraffinic extracts, oils from destructive distillations of pyro-bituminous and asphaltic materials, and mixtures of these with one another or with crude petroleum fractions. With improvement in the ignition qualities of the hydrocarbon fuels mentioned by addition of inexpensive agents herein disclosed better performance of a Diesel engine operating on the improved fuel is obtained in the way of easier starting, smoother idling, silent running, and absence of shock loading.

It is not intended that this invention be limited to the specific examples which are given merely for the sake of illustration, but it is desired to claim all the novelty inherent in this invention in the appended claims as broadly as the prior art permits.

Other agents for enhancing various other qualities without detracting substantially from the ignition qualities of the fuel may be admixed, such as oiliness agents, sludge dispersers, colloidal suspension dispersers and stabilizers, dyes, antioxidants, viscosity improvers, pour point depressants, solubilizers, gum solvents, and corro-

sion inhibitors. Substances such as olefines, amines, and peroxides may be mentioned as being effective for reducing any corrosive tendencies of active sulfur promoters. Also, other promoters of ignition quality may be admixed, particularly alkyl nitrates, such as amyl nitrate.

We claim:

1. A fuel for compression-ignition engines of the Diesel type comprising a liquid hydrocarbon Diesel fuel boiling above 400° F. and an added small proportion of sulfur in a free and loosely combined form to improve substantially ignition qualities of the fuel, free sulfur being added in an amount above 0.025%.

2. A fuel as described in claim 1 in which added sulfur is loosely combined in substantially molecular additive form with amino groups.

3. A fuel as described in claim 1 in which the sulfur is partly combined with phosphorus.

4. A fuel for compression-ignition engines of the Diesel type comprising a liquid hydrocarbon Diesel fuel boiling above 400° F. and a small amount of added free sulfur above 0.025% to improve substantially ignition qualities of the fuel.

5. A compression-ignition engine fuel comprising a hydrogenated hydrocarbon oil boiling in a Diesel fuel range and from ½% to about 1% of dispersed free sulfur added in small and sufficient amounts for promoting ignition of the fuel to a substantial degree.

6. A fuel for combustion engines of the Diesel type comprising a liquid hydrocarbon Diesel fuel and a small amount of a high sulfur containing ignition promoter in which sulfur is combined with amino groups in the ratio required to form hexasulfamide with which above 0.025% of free sulfur is incorporated in the fuel.

7. A fuel for compression ignition engines of the Diesel type comprising a liquid hydrocarbon Diesel fuel and a small amount of a high sulfur-containing ignition-promoter in which sulfur is combined with phosphorus in the ratio required to form phosphorus sesquisulfide with which at least 0.025% of free sulfur is incorporated in the fuel.

8. Method of preparing a Diesel fuel of improved ignition qualities which comprises treating a crude petroleum oil Diesel fuel distillate, boiling above about 400° F., to disperse therein a sufficient amount of free sulfur to improve substantially ignition qualities of the fuel from ½% to about 1% of free sulfur being incorporated into the treated fuel.

9. A method of accelerating ignition of a fuel for combustion in engines of the Diesel type which comprises incorporating into a liquid hydrocarbon Diesel fuel boiling above about 400° F. prior to ignition a sufficient amount of free sulfur above 0.025% to improve substantially ignition qualities of the fuel.

10. A fuel for compression-ignition engines comprising a major proportion of a liquid hydrocarbon Diesel fuel boiling above about 400° F. and a minor proportion of sulfur partly in the form of free sulfur and partly in the combined form of hexasulfamide, the free sulfur being added in an amount above 0.025% to substantially raise the cetane number of the fuel.

11. A fuel for compression-ignition engines comprising a major proportion of a liquid hydrocarbon Diesel fuel boiling above about 400° F. and a minor proportion of sulfur partly in the form of free sulfur and partly in the combined form of phosphorus sesquisulfide, the free sulfur being added in an amount above 0.025% to substantially raise the cetane number of the fuel.

PHARIS MILLER.
GOULD H. CLOUD.