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DIESEL FUEL

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This invention relates to a composition of matter comprising diesel fuel, a hydrocarbon fuel used in compression ignition engines, and a synergistic mixture of additives for improving properties of the fuel.

One of the fundamental advantages of the early form of the diesel engine was its ability to satisfactorily burn almost any type of liquid fuel. However, the intensive development which has led to the modern high-speed diesel engine has narrowed the range of suitable fuels to such a degree that present day fuels must meet many specifications. One of the most important specifications is ignition quality, or the ease with which the fuel is ignited after it is injected into the cylinders of a diesel engine. This quality is measured in terms of cetane number, which is defined as the percentage of n-cetane in a blend of n-cetane and α-methylnaphthylene which has an ignition quality comparable to the fuel in question. The use of fuels of poor quality results in starting difficulty and detonation, knocking, or rough running. The latter results in (1) increased engine maintenance, (2) reduced engine life, and (3) excessive vibration and noise.

Straight-run distillates from paraffin-base crude oils are generally of high ignition quality. Cracked distillates, or distillates from aromatic crudes, are of inferior quality. Although most refiners have been and are able to supply adequate volumes of straight-run distillate or blends of straight-run with cracked distillate having a satisfactory ignition quality to meet the demand for diesel fuel, it is becoming increasingly difficult for them to do so. Furthermore, the rapidly expanding market for such fuels indicates that it will not be possible to continue to supply future demands without recourse to radically different refining techniques or the use of fuel additives.

The use of cheap fuel additives to improve ignition quality: (1) is more economical than the use of refining techniques, (2) permits refinery operation for low pour point and other desirable qualities, and (3) permits the use of more dense, higher heat content stocks than could otherwise be utilized due to thier low ignition quality. The use of such less expensive stocks permits greater economy of operation by decreasing both fuel cost and fuel consumption. However, expensive additives will not accomplish these results.

While the use of certain additives enhances the cetane value of diesel fuels, an increase in cetane number at any great cost does not justify the use of an additive. Insofar as increasing the cetane value of a diesel fuel is concerned, certain additives have been used with some success, but they are expensive to make and possess other undesirable properties. Besides having the ability to improve the cetane number of a fuel, an additive should be stable; should have good blending properties; should not increase engine deposits, wear, or corrosion; and must not materially increase the cost of the fuel.

It is an object of this invention to provide an additive which conforms to the specifications outlined above and

provides a given cetane number increase at a lower additive concentration and, consequently, at a lower cost.

We have made the surprising discovery that a mixture of a peroxide or a hydroperoxide with a dihalonitro compound, in which the halogen, chlorine or bromine, and nitro groups are attached to a terminal carbon atom, is syngeristic in that the effectiveness of the mixture is greater than the sum of the effectiveness of each of the two compounds taken separately. Thus, either considerable savings or greater effectiveness can be obtained through the use of our mixtures.

Outstanding examples of peroxides and hydroperoxides of this invention are cumene hydroperoxide and peroxidized distillate fuel. The latter is a product which is prepared from a distillate petroleum hydrocarbon fuel of higher than kerosene volatility by treating the fuel with oxygen under controlled conditions. Ordinarily, the fuel is first pretreated with sulfuric acid, liquid sulfur dioxide, aqueous phase or the equivalent to remove sludge and is then contacted with air or an oxygen-containing gas under such conditions that the treated fuel will attain an "oxygen factor" of about 800 or more and usually between 800 and about 1450, usually without increase in neutralization number of more than about 20. The progress of the oxidation treatment is arrested before the "oxygen factor" of the oil has decreased to below about 800 after passing through a maximum. Acidic and other oxidation products are then removed by conventional means. Ordinarily, such peroxidized distillate fuels contain from about 4 percent to about 14 percent of chemically combined oxygen.

The "oxygen factor" of an oil is determined as follows. A 2 to 10 ml. sample of the oil, at approximately 68° F., is accurately pipetted into a 250 ml. glass-stoppered flask. 20 ml. of a mixture consisting of 60 volume percent of C.P. glacial acetic acid and 40 volume percent of chloroform are added to the oil, followed by 2.0 ml. of a saturated aqueous solution of potassium iodide. The mixture is shaken vigorously for three minutes and then diluted with about 50 ml. of distilled water. The liberated iodine is titrated with 0.1 normal standardized sodium thiosulfate solution, adding starch indicator just before the end point is reached. Considerable shaking is necessary near the end of the titration. Oxygen factor=(titer in ml.×normality of thiosulfate × 1120)/(volume of sample in ml.).

As starting material for this peroxidation treatment it is preferred to use distillate fuels which are relatively low in aromatic content and which are also low in asphalt and resin content. Straight petroleum distillates are preferred especially those with an initial boiling point above 200° F. and an end point below 600° F.

The following specific examples illustrate the preparation of a peroxidized distillate fuel of this invention.

EXAMPLE I

A straight run petroleum distillate fraction having the following characteristics:

Gravity, ° API	46.6
Initial boiling point	312
50% boiling point	327
End boiling point	369

was treated at ordinary temperature with about 0.5 pound of 98 percent H_2SO_4 per gallon. The sludge was settled and removed and the treated oil was washed with water, neutralized with caustic soda solution and again washed with water in a usual gasoline- or petroleum solvent-type of treatment. About 10 gallons of this preliminarily treated oil was heated to a temperature of 300–310° F. and transferred to a vertical cylindrical vessel or "still" about 8 inches internal diameter and 96 inches in height,

of chrome-nickel steel and equipped with a horizontal porous plate partition about 1 inch from its bottom (Filtros plate, grade R, manufactured by Filtros Inc., East Rochester, New York) and provided with a heating and cooling jacket and with a vapor condenser. The designated volume of oil filled the vessel, above the plate, to a depth of about 48 inches. About 2 percent volume of a "seed stock" (a completely modified, partially oxidized oil of the invention, from an earlier preparation) was added to the treated distillate introduced to the vessel. During the charging of the vessel, air was passed upwardly through the porous plate partition at a rate of about 0.3 volume per volume of oil to be charged, per minute, to prevent the charged oil from passing downwardly through the plate. The air rate was increased as rapidly as possible, following the completion of the charging operation, without decreasing the temperature appreciably below about 300° F.; this rate should be 2 or more volumes per volume of oil per minute, and may be as high as 3 or more volumes per volume of oil per minute, depending somewhat upon the tendency of the material to foam into the condenser. Blowing was continued for 5 hours at an oil temperature of 295–305° F. (it may advantageously be held between 290 and 295° F. for the latter half of the operation). During the first part of the reaction heat was supplied to compensate for the cooling caused by evaporation; during the latter part of the reaction less heat was needed (and cooling is indeed sometimes required), as the reaction is exothermic. Such oil as evaporated was liquefied in a stainless steel condenser, condensed water was trapped out, and the condensed oil was returned directly to the main reaction mixture. After 5 hours of blowing under these conditions, the oil had an oxygen factor of 1210, a neutralization number of 11 and a saponification number of 30.5.

The partially oxidized oil was cooled as rapidly as possible to a temperature of 100° F., while discharging from the treating vessel, by circulating cool water through the coils and passage of the treated stock through heat exchanger; the air rate through the porous plate was reduced to about 0.3 volume per volume of charged oil per minute at the end of the discharging operation (and may be maintained at this rate during the charging of the next batch of oil to be treated).

The modified oil was washed at atmospheric temperature with 5 percent aqueous caustic soda solution to remove such acidic products as were present in the oil; the caustic soda solution was added in only small excess of that calculated to be required, from the neutralization number. Finally, the oil was washed with water and settled bright in the usual manner. The characteristics of this peroxidized distillate fuel were as follows:

Gravity, ° API	42.8
Oxygen factor	985
Saponification number	19.4
Neutralization number	0.1

EXAMPLE II

A clean straight run gas oil distillate of California origin having the following characteristics:

Gravity, ° API	38.2
Pour point, ° F	−30
Cetane number	44
Initial boiling point, ° F	355
50% boiling point, ° F	455
End boiling point, ° F	565

was blended with the finished modified oil prepared as described in Example I, the proportions of the blend being 80 volume percent of the clean gas oil distillate and 20 volume percent of the 985 oxygen factor oil prepared in accordance with Example I. This mixture was carefully washed with 3 percent of its volume of 5 percent aqueous caustic soda solution, then washed with water and allowed to settle bright, such final treatment being desirable to enhance the storage stability of the blend. The characteristics of this peroxidized distillate fuel were as follows:

Gravity, ° API	39.0
Pour point, ° F	−30
Cetane number	63
Oxygen factor	148

EXAMPLE III

A raffinate from an SO_2-treated petroleum distillate of California origin having the following characteristics:

Gravity, ° API	43.8
Pour point, ° F	−30
Cetane number	53
Initial boiling point, ° F	350
50% boiling point, ° F	435
End boiling point, ° F	580

was blended with the finished modified oil as described in Example I, the proportions of the blend being 97.5 percent by volume of the SO_2 raffinate and 2.5 percent by volume of the 985 oxygen factor oil prepared in accordance with Example I. This blend was washed with 3 percent of its volume of 5 percent aqueous caustic soda solution, washed with water and settled bright. The characteristics of this peroxidized distillate fuel were as follows:

Gravity, ° API	43.8
Pour point, ° F	−30
Cetane number	60
Oxygen factor	19

Di-tert-butyl peroxide, acetyl peroxide, tolyl and benzoyl peroxide are also suitable, as are hydrocarbon peroxides in general containing 4 to 14 carbon atoms. Likewise, we can successfully use alkyl hydroperoxides; especially hydroperoxides containing alkyl groups possessing from between 4 to about 8 carbon atoms inclusive, such as, for example, tert-butyl hydroperoxide, isooctyl hydroperoxide, and the like.

The dihalonitro compounds which can be successfully employed in the synergistic compositions of the present invention comprise aliphatic dihalonitro compounds; that is, compounds wherein the organic portion of the molecule is of an aliphatic nature. In one embodiment of our invention we prefer the lower alkyl dihalonitro compounds which, in general, contain alkyl groups possessing from about 1 to about 12 carbon atoms inclusive. Examples of such dihalonitro compounds which we employ are: 1,1-dichloro-1-nitroethane; 1,1-dibromo-1-nitroethane; dichloronitromethane; 1,1-dibromo-1-nitropropane; 1,1-dichloro-1-nitrobutane; 1,1-dibromo-1-nitropentane; 1-chloro-1-bromo-1-nitropentane; 1,1-dichloro-1-nitrohexane; 1,1-dibromo-1-nitroheptane; 1-chloro-1-bromo-1-nitroheptane; 1,1-dichloro-1-nitrooctane; 1,1-dichloro-1-nitrononane; 1,1-dibromo-1-nitrodecane; 1,1-dichloro-1-nitroundecane; 1,1-dibromo-1-nitrododecane; and the like. The halo and nitro groups should be on terminal carbon atoms.

A facet of our invention consists of the discovery of important proportions of the aforesaid ingredients, which produces the unexpected synergistic effect. The weight ratio of the two components of our synergistic mixtures, that is, the peroxide or hydroperoxide and the dihalonitro compound, used in obtaining this important effect is contingent upon: first, the fuel type; second, the particular composition of the mixture employed; third, the total amount of combined additive used; and fourth, the desired increase in cetane rating to be produced. In general, however, the total amount of additive used should be within the range of 0.1 and 2.0 percent by weight of the base fuel. The ratio of the additives should be between about 2 to 3 and 3 to 2, with the best results being at about 1 to 1.

The effectiveness of our mixture of additives over that obtained by using the additives separately in improving the ignition qualities of a diesel fuel is shown by comparison with a standard reference fuel in a C.F.R. engine using the ignition delay method according to the method described in American Society for Testing Materials, volume 36, I, 418 (1936).

Table I, given below, illustrates the cetane improvement obtained when the additives are used separately.

Table I

	Fuel			Increase in Cetane Number			
	Refining Process	Crude Source	Cetane Number	Additive	Concentration, Wt. Percent		
					0.25	0.50	1.0
1	Catalytically cracked	Gulf Coast	26.5	1,1-dichloro-1-nitroethane	2.6	4.6	7.5
2	do	do	26.5	peroxidized distillate fuel	2.4	4.0	5.8
3	do	do	26.5	cumene hydroperoxide	2.6	4.3	6.6
4	Straight run	do	33.0	1,1-dichloro-1-nitroethane	2.5	4.5	8.2
5	do	do	33.0	peroxidized distillate fuel	2.1	3.7	5.8
6	do	do	33.0	cumene hydroperoxide	1.9	3.7	6.6

The peroxidized distillate fuel in Items 2 and 5 of Table I was prepared by the procedure of Example I.

The following Table II illustrates the improved results obtained by our synergistic mixtures when blended with dlifferent fuels.

Table II

	Fuel			Increase in Cetane Number				
	Refining Process	Crude Source	Cetane Number	Mixture	Ratio Used By Weight	Total Concentration, Wt., Percent		
						0.25	0.5	1.0
1	Catalytic cracked	Gulf Coast	26.5	peroxidized distillate fuel and 1,1-dichloro-1-nitroethane.	1 to 1	3.2	5.5	8.9
2	Straight run	do	33.0	do	1 to 1	3.5	5.8	8.8
3	do	do	33.0	cumene hydroperoxide and 1,1-dichloro-1-nitroethane.	1 to 1	4.0	6.5	10.3
4	Catalytic cracked	do	26.5	do	1 to 1	4.1	6.8	10.6
5	do	do	26.5	do	2 to 3	3.6	5.8	9.0

The peroxidized distillate fuel of Items 1 and 2 in Table II was prepared by the procedure of Example I.

A comparison of the results obtained in Tables I and II clearly shows the synergism which our mixtures exhibit. For example, Item 3 in Table II shows that a 1 to 1 mixture of cumene hydroperoxide and 1,1-dichloro-1-nitroethane in straight run Gulf Coast hydrocarbon diesel fuel gives a cetane number increase of 4.0 numbers at a total additive concentration of 0.25 percent. Referring back to Table I, it is seen that the expected increase in cetane number would be 1.3 cetane numbers contributed by the 1,1-dichloro-1-nitroethane (half of the increase obtained by use of 0.25 percent of this additive) and 1.0 cetane numbers by the cumene hydroperoxide (half of the increase obtained by use of 0.25 percent of this additive) or a total cetane number increase of 2.3. Due to synergism of this mixture of compounds the cetane number increase actually obtained was 174 percent of the expected value. Similarly, use of a 1 to 1 mixture of cumene hydroperoxide and 1,1-dichloro-1-nitroethane at a total additive concentration of 0.25 percent in catalytically cracked Gulf Coast hydrocarbon diesel fuel gave a cetane number which was 158 percent of the expected value. Inspection of Tables I and II shows that similar unexpected synergistic effects were obtained with every mixture thereon.

Thus, a comparison of the results given in Tables I and II shows that an exceptional improvement can be

obtained by using our synergistic mixture over the expected use of such a mixture.

Other synergistic mixtures of our invention which will also give similar results when tested as above are: di-tert-butyl peroxide and 1,1-dibromo-1-nitroethane; acetyl peroxide and dichloronitromethane; tert-butyl hydroperoxide and 1,1-dibromo-1-nitropropane; cumene hydroperoxide and 1,1-dibromo-1-nitroethane; di-tert-butyl peroxide and 1,1-dichloro-1-nitrobutane; acetyl peroxide and 1,1-dibromo-1-nitrohexane; tert-butyl hydroperoxide and 1,1-dibromo-1-nitrooctane; cumene hydroperoxide and 1,1-dichloro-1-nitrodecane; and the like.

Many variations within the spirit and scope of the present invention will be apparent to those skilled in the art. We particularly wish to emphasize the fact that we can obtain the important synergistic effects characteristic of this invention by blending a mixture of the peroxide or hydroperoxide and the dihalonitro compound with any hydrocarbon fuel of the diesel fuel boiling range. In addition, we can blend these components with distillate fuel separately; that is, we can blend the peroxide or hydroperoxide with the distillate fuel and subsequently blend therewith the dihalonitro compound. Similarly, the order of blending can be reversed; that is, we can blend with diesel fuel an aliphatic dihalonitro compound and subsequently blend with the resulting mixture a peroxide or hydroperoxide.

Having fully described the nature of the surprising and important compositions of the present invention, we do not intend that our invention be limited except within the spirit and scope of the appended claims.

We claim:

1. Hydrocarbon diesel fuel containing a synergistic cetane improving composition consisting essentially of one member selected from the class consisting of cumene hydroperoxide and peroxidized distillate fuel; and as a second member, 1,1-dichloro-1-nitroethane; the proportion of the members of the synergistic mixture being in the weight ratio of between about 2 to 3 and 3 to 2, said synergistic composition being present in concentration of 0.1–2.0 percent by weight of said fuel.

2. Hydrocarbon diesel fuel containing a synergistic cetane improving composition consisting essentially of

cumene hydroperoxide and 1,1-dichloro-1-nitroethane; the proportion of the members of the synergistic composition being in the weight ratio of between about 2 to 3 and 3 to 2, said synergistic composition being present in concentration of 0.1–2.0 percent by weight in said fuel.

3. A synergistic composition for use as a cetane improver consisting essentially of one member selected from the class consisting of cumene hydroperoxide and peroxidized distillate fuel; and as a second member, 1,1-dichloro-1-nitroethane; the proportion of the members of the synergistic mixture being in the weight ratio of between about 2 to 3 and 3 to 2.

4. As a synergistic composition for use as a cetane improver, a mixture which consists essentially of cumene hydroperoxide and 1,1-dichloro-1-nitroethane; the proportion of the members of the synergistic composition being in the weight ratio of between about 2 to 3 and 3 to 2.

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