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2,763,537

DIESEL FUEL OIL

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6 Claims. (Cl. 44—57)

This invention relates to an improved diesel fuel oil, and more particularly to improved diesel fuel-oil compositions having high cetane numbers.

Diesel engines depend upon the heat developed by compressing a charge of air to ignite the fuel injected into the engine cylinder after the air is compressed. A high compression ratio is necessary because most known diesel fuels require a relatively high compression ratio in order to ignite. A factor of major importance in regard to the performance of a diesel fuel oil is the delay in ignition from the beginning of the injection of the fuel to the beginning of its combustion. This property is commonly termed the "ignition-delay characteristic" of the fuel and may be expressed in terms of cetane numbers. If ignition delay is too long, the motor fuel will accumulate in the cylinder until it reaches ignition conditions and then will burn rapidly, causing a sudden pressure increase which may result in engine knocking. In addition, too long an ignition delay may result in a smoky exhaust, a decrease in engine efficiency, and possibly crankcase-oil dilution.

One of the more important difficulties that arises through the use of diesel engines is the problem of starting the engine when it is cold. It is quite common, when using many presently known diesel fuels, to employ special starting procedures wherein various starting fuels, such as ether, are employed. During the warm-up period of the diesel engines, considerable uneven ignition of the fuel may occur in the engine.

An object of the present invention is to provide a diesel fuel-oil composition having a high cetane number that ignites readily and functions smoothly under operating conditions.

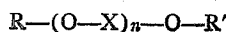
Another object of this invention is to provide a diesel fuel-oil composition that is readily adaptable for starting cold diesel engines.

Still another object of this invention is to provide a high cetane number diesel fuel-oil composition whose base has a low cetane number.

A further object of this invention is to provide a diesel fuel-oil composition that may be used as a reference fuel for fuels having cetane numbers in excess of 100.

In order to meet the increasing demand for diesel fuel oils having high cetane numbers, various cetane-improving materials have been added to the petroleum fuel oil base. The use of cetane-improving materials has also permitted the employment of base fuels having relatively low cetane numbers and has thereby increased, in many instances, the usefulness of "middle-of-the-barrel" stock to the refiners. The cetane-improving materials have been generally of an additive or blend type. The characteristics and properties of these are described below.

We have discovered that when normally liquid oil-soluble aliphatic polyethers, especially those having molecular weights below about 700 with a general formula:



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wherein R and R' are alkyl groups, X is a hydrocarbon group of the alkylene type having at least two carbon atoms, and n is an integer, are blended with a diesel fuel oil containing a cetane-improving additive there is an unexpected synergistic cetane improvement.

The term "cetane-improving additive" as used herein and in the appended claims is a material that produces a relatively large cetane improvement when added in a small concentration to a diesel fuel oil. The improvement is independent of the cetane number of the additive and does not produce a corresponding cetane improvement when added in additional incremental amounts. Generally the amount of a "cetane-improving additive" added to a diesel fuel oil is in the range of about .001 per cent to about 10 per cent.

Suitable additives which may be employed as the "cetane-improving additive" are: alkyl nitrate and nitrites; nitroso compounds; di-azo compounds; di-sulfides; and hydrocarbon peroxides such as di-alkyl peroxides and alkyl hydroperoxides, including peroxides of the tertiary type and corresponding alicyclic peroxides, and acyl peroxides. The alkyl peroxides and hydroperoxides include the following specific compounds: ethyl peroxide and hydroperoxide; isobutene peroxides and hydroperoxides; isopentene peroxides and hydroperoxides; 2-methylpentane peroxides and hydroperoxides; 2-ethyl butene peroxide and hydroperoxide; 2-methylpentane peroxides and hydroperoxides; 3-methylpentane peroxide and hydroperoxide; 2,3-dimethyl butane peroxide and hydroperoxide; and 2,4-dimethylbutane peroxide and hydroperoxide. Peroxides of the di(tertiary alkyl) type include: di(tertiary butyl) peroxide; di(tertiary amyl) peroxide; di(2-methyl, 2-pentyl) peroxides; di(3-methyl, 3-pentyl) peroxide; di(2-ethyl, 2-butyl) peroxide; di(1-halo, 2-methyl, 2-propyl) peroxide; di(1-halo, 2-ethyl, 2-propyl) peroxide; di(1-halo, 2-methyl, 2-butyl) peroxide; di(1-halo, 3-methyl, 3-butyl) peroxide; di(2-halo, 3-methyl, 3-butyl) peroxide; di(1-phenyl, 1-methyl, 1-propyl) peroxide, and di(1-phenyl, 2-methyl, 2-propyl) peroxide. Cyclic hydrocarbon peroxides include: cyclopentyl hydroperoxide; methylcyclopentyl hydroperoxides; the isomeric dimethylcyclopentyl hydroperoxides; ethylcyclopentyl peroxides; the isomeric diethylcyclopentyl hydroperoxides; the isomeric methylethylcyclopentyl hydroperoxides, cyclohexyl hydroperoxide, methylcyclohexyl hydroperoxides; the isomeric dimethylcyclohexyl hydroperoxides; ethylcyclohexyl hydroperoxides; the isomeric diethylcyclohexyl hydroperoxides; 1-4-methyl isopropylcyclohexyl hydroperoxide; hydroperoxides of cyclopentane, cycloheptane, etc., and higher molecular-weight substituted cycloparaffins. Asymmetrical dialkyl peroxides may also be used.

Peroxides especially suitable for the composition of our invention are non-benzenoid hydrocarbon peroxides which include the aliphatic and alicyclic peroxides. An example of these non-benzenoid peroxides is illustrated by the cetane-improving additive disclosed in Schultz et al. Patent No. 2,317,968 and is prepared by partially oxidizing a petroleum distillate relatively free from asphaltic and resinous materials and from large proportions of aromatic ring compounds, and of a higher volatility than kerosene with an oxygen-containing gas under liquid-phase conditions at a temperature of 275 to 310° F. for a sufficient length of time to produce an oil having an oxygen factor (obtained by dissolving an oil sample in 10 cc. of chloroform and 25 cc. of acetic acid and then adding 2 cc. of saturated KI to the solution, agitating for 3 minutes, followed by titrating liberated iodine with Na₂S₂O₃ and calculating the results according to the equation: titer in ml. × normality of the thiosulfate × 1120 / volume of sample in ml.) higher than 800, but insufficient to increase the neutralization number of

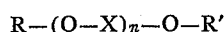
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the oil by more than 20, then arresting said treatment before the oxygen factor of the produced oil decreases to below 800 and then removing the acidic reaction products from the produced oil without reducing the oxygen factor to below about 800.

Patent to Denison et al., No. 2,521,698, discloses another especially desirable non-benzenoid hydrocarbon peroxide for the composition of our invention which may be used as a cetane-improving material and that is prepared by subjecting a petroleum distillate having a boiling range between 200 and 450 and relatively free from asphaltic and resinous materials and from large proportions of aromatic ring compounds to a liquid-phase oxidation treatment with an oxygen-containing gas at a temperature within the range of 200 to 400° F. for a period of time sufficient to produce an oil having an oxygen factor higher than 250; contacting the resulting oxygenated oil with 0.1 to 0.75 pound of 50-90 per cent H_2SO_4 per gallon of oil at a temperature of 50 to 85° F. for less than 90 minutes, thereby producing a more stable and less corrosion-producing oil having a substantially lowered oxygen factor, treating this oil with controlled amounts of weak caustic solution to remove acidic material, and concentrating the caustic-treated oil by fractional distillation to a temperature below 350° F. and a pressure between 10 mm. of mercury and atmospheric to volatilize between 60 and 95 per cent of said oxygenated oil to obtain a concentrate of relatively stable cetane-improving oxygenated oil.

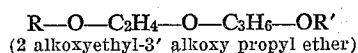
The term "blending agent" as used herein and in the appended claims is a material which produces a cetane improvement in diesel fuel oils corresponding to the amount of blending agent added and the cetane number of the blending agent. The amount of "blending agent" generally added to diesel fuel oils is above about 5 per cent.

The aliphatic polyether blending agents especially suitable for the composition of this invention are normally liquid oil-soluble aliphatic polyethers especially alkyl polyethers having a molecular weight below about 700 with a general formula:

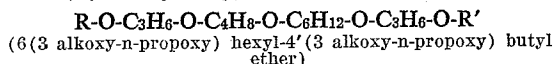
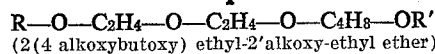


wherein R and R' are like or unlike alkyl groups, X is a hydrocarbon group of the alkylene type having at least two carbon atoms, n is an integer, and when n is more than one, X may be represented by like or unlike alkylene groups. The R and R' radicals may be like or unlike and have from 1 to 18 or more carbon atoms in each radical. The alkylene group X is a group having at least two carbon atoms and is preferably straight chained. Examples of X wherein the nomenclature of alkylene glycols is adopted, in which a C_2H_4 radical with two terminal bonds is considered to be an ethylene group, follow with the numbers indicating substitution points: ethylene; 1,2 propylene; 1,3 propylene; 1,2 butylene; 1,3 butylene; 1,4 butylene; 2,3 butylene; 1,2 pentylene; 1,3 pentylene; 1,4 pentylene; 1,5 pentylene; 2,3 pentylene; 2,4 pentylene; 1,2 hexylene; 1,3 hexylene; 1,4 hexylene; 1,5 hexylene; 1,6 hexylene; 2,3 hexylene; 2,4 hexylene; 2,5 hexylene; 3,4 hexylene; 1,2 heptylene; 1,3 heptylene; 1,4 heptylene; 1,5 heptylene; 1,6 heptylene; 1,7 heptylene; 2,3 heptylene; 2,4 heptylene; 2,5 heptylene; 2,6 heptylene; 3,4 heptylene; 3,5 heptylene; 1,2 octylene; 1,3 octylene; 1,4 octylene; 1,5 octylene; 1,6 octylene; 1,7 octylene; 1,8 octylene; 2,3 octylene; 2,4 octylene; 2,5 octylene; 2,6 octylene; 2,7 octylene; 3,4 octylene; 3,5 octylene; 4,5 octylene; 3 ethyl, -2,4 hexylene; 1,3 dimethyl-2 ethyl-1,4 butylene, etc.

As explained above, X may be presented by unlike alkylene groups. Compounds having unlike X groups, for example, follow:



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The blending agents also include alkylated polyalkylene oxides such as diethyl poly 1,2-propylene oxide and diisopropyl poly ethylene oxide, etc.

The following examples illustrate cetane improvement obtained with compositions of this invention.

The base fuel used in the examples below had the following inspection:

Source	Straight-run California crude.
A. P. I.°	37.6.
Viscosity at 100° F.	1.952 centistokes.
A. S. T. M. color	1—.
Lovibond color (through a 500 series glass using 1" cell).	0.75.
Flash point (Pensky-Martin)	152° F.
Carbon (Conradson 10% bottoms).	0.01.
Aniline point	138° F.
A. S. T. M. distillation:	
Initial	358° F.
5%	399° F.
10%	404° F.
20%	416° F.
30%	428° F.
40%	440° F.
50%	452° F.
60%	468° F.
70%	484° F.
80%	504° F.
90%	532° F.
95%	554° F.
End point	594° F.
Cetane No.	43.

The method of determining the cetane numbers of fuels given in the tables below was A. S. T. M. Test No. D613-47T.

The symbol "ACN" is used to denote cetane number improvement over the base fuel. The cetane-improving additive used in Table I is the material disclosed in Patent No. 2,521,698 to Denison et al. and described above. The numbers reported in the following tables are calculated from the cetane numbers obtained by the average of at least three different tests on the same fuel.

Table I

Percent Cetane-Improving Additive	Percent Diethylene Glycol Di-Ethyl Ether	ACN produced by the Cetane-Improving Additive (Alone)	ACN produced by Diethylene Glycol Diethyl Ether (Alone)	ACN Total Calculated	ACN Observed
1	10	7	8	15	17
1	20	7	15	22	27
1	30	7	25	32	38
2	10	10	8	18	22
2	20	10	15	25	30
2	30	10	25	35	42
10	10	23	8	31	35
10	20	23	15	38	46
10	30	23	25	48	57

From the foregoing table, it is apparent that the ACN observed in all cases was substantially above the expected improvement which would be the summation of the cetane improvement obtained separately from the cetane-improving additive and from the diethylene glycol diethyl ether. Since cetane number can only be obtained up to 100, cetane numbers in excess of this are expressed in terms of cetane (n-hexadecane) plus the number of cubic centimeters of amyl nitrate per gallon of fuel required to match the fuel being tested. Cetane number

above 100 is merely a relative term, and determinations of such numbers generally do not have a particularly significant meaning, and therefore, no report has been included of a fuel having a cetane number above 100. However, as can be seen from the above table, a fuel having a cetane number above 100 is compounded by merely increasing the amount of blending agent. For example, it is apparent from Table I that a base fuel containing 40 per cent diethylene glycol diethyl ether and 10 per cent of the cetane-improving additive would result in a fuel having a cetane number substantially above 100.

Table II, below, is a tabulation of results obtained when amyl nitrate was used as the cetane-improving additive and when dimethoxy tetraglycol was used as the blending agent.

Table II

Percent Amyl Nitrate	Percent Dimethoxy Tetraglycol	ΔCN produced by Amyl Nitrate (Alone)	ΔCN produced by Dimethoxy Tetraglycol (Alone)	ΔCN Total Calculated	ΔCN Observed
1	10	11	7	18	28
1	20	11	19	30	52
5	10	44	7	51	54

The results of Table II augment the results obtained in Table I and further show the synergistic improvement of different additive plus different blending agents. An outstanding example of the improvement obtained by our invention is the above-compounded diesel fuel oil containing one per cent amyl nitrate, 20 per cent dimethoxy tetraglycol, wherein the difference between the calculated improvement and the improvement obtained by actual test engine results was greater than 20 cetane numbers.

A further test was made to indicate the improvement obtainable with a composition of our invention. In this test, a diesel fuel oil of the base given above, was compounded with one per cent each of the cetane-improving additives of Tables I and II and additionally contained 20 per cent of dimethoxy tetraglycol. The calculated cetane improvement was 37, but the measured improvement from actual test engine results showed an improvement of 50. Thus again this shows the cetane improvement obtainable with compositions of our invention.

To further illustrate the advantage obtainable by employing a diesel fuel oil composition of our invention, an addition of 10 per cent dimethoxy tetraglycol was made to the base fuel and caused an increase of 7 cetane numbers. To another sample of the base fuel was added 0.5 per cent amyl nitrate and this addition caused an increase of 9 numbers. A one-to-one mixture of these two blends produced a fuel which has a 12 number increase above the base stock which is considerably above the expected number improvement. Normally when two fuels of different cetane number are blended in equal proportion, the resulting fuel has a cetane number equal to the average of its components.

In another example, equal portions of a fuel containing 10 per cent of the cetane-improving additive of Table I, which increased the rating of the base fuel 23 numbers, and a fuel containing 35 per cent ethylene glycol dibutyl ether, which caused an increased rating of 20 numbers, were blended in a one-to-one ratio. The resultant fuel rated 32 numbers above the base stock and again above the expected or calculated average of 21.5 numbers.

When ethylene glycol dibutyl ether was added in equal proportions to a petroleum distillate having a cetane number of 43, the resulting fuel had a cetane number of 78. Five per cent of tertiary butyl hydroperoxide increased the cetane number of the petroleum distillate from 43 to 83. A one-to-one mixture of these blended fuels resulted in an increase of 45 cetane numbers over

the base fuel or 7 cetane numbers above the expected value.

The addition of one per cent ditertiary butyl peroxide gave an increase of 11 cetane numbers to a base fuel having a cetane number of 43. When 15 per cent of diethylene glycol diethyl ether was added to a base fuel having a 43 cetane number, an increase of 12 cetane numbers resulted. However, when a one-to-one blend of these two fuels was made a 17 cetane member over the 43 resulted. This is 5.5 numbers above the expected calculated value.

The amount of cetane-improving additive in diesel fuel oil compositions of our invention varies greatly and is generally preferred to be within the range of 0.01 to 10 per cent by weight. The blending agent, alkyl ethers, of our invention are usually employed in concentrations greater than 10 per cent by weight. However, the amount of aliphatic polyethers may vary from about five per cent to about 95 per cent of the total volume of the fuel of this invention with both the fuel-oil base and the polyethers being present in amounts exceeding five per cent by volume. Ordinarily, fuels suitable for commercial usage contain less than about 50 per cent by volume of the polyethers. Fuels containing greater amounts of the polyethers are suitable for high-cetane number test fuels. These alkyl ethers may be di- or poly-ethers and have straight chain radicals or branched chain radicals, with the former generally being preferred, although either, or mixtures thereof, may be employed in compositions of our invention.

Because of the high cetane numbers available with compositions of our invention, the fuel compositions may be used as cold-engine starting fuels of diesel engines.

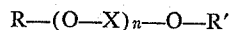
The fuel-oil base of the compounded diesel fuel oil of our invention may be straight-run or cracked petroleum distillates or derived from synthetic processes or be mixtures thereof and boil in the range of from about 325° F. to about 750° F. The compound diesel fuel-oil composition is suitable as a fuel for engines of the diesel type, turbine type, and jet type.

This application is a division of our application, Serial No. 95,146, filed May 24, 1949, now Patent No. 2,655,440 granted Oct. 13, 1953, entitled "Diesel Fuel Oil."

While various specific embodiments of the invention have been illustrated and described, many modifications and adaptations may be made without departing from this invention, and all such changes as are intended to be included within the scope of the claims.

We claim:

1. An improved compression-ignition engine fuel consisting essentially of a major proportion of a mixture of a petroleum hydrocarbon fuel oil base boiling in the range of about 325° F. to about 750° F. and an oil-soluble aliphatic polyether blending agent having a molecular weight below about 700 and the general formula:



wherein R and R' are alkyl groups, X is a hydrocarbon group of the alkylene type having at least two carbon atoms and n is an integer, both components being present in amounts exceeding 5% of the total volume of the fuel and a minor proportion not exceeding 10% of the total volume of the fuel of amyl nitrate.

2. The composition of claim 1 wherein the oil-soluble aliphatic polyether blending agent is dimethoxy tetraglycol.

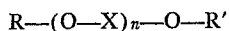
3. The composition of claim 1 wherein the oil-soluble aliphatic polyether blending agent is diethylene glycol dibutyl ether.

4. The composition of claim 1 wherein the oil-soluble aliphatic polyether blending agent is diethylene glycol diethyl ether.

5. An improved compression-ignition engine fuel consisting essentially of a major proportion of a mixture of a petroleum hydrocarbon fuel oil base boiling in the

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range of about 325° F. to about 750° F. and a normally liquid oil-soluble aliphatic polyether blending agent having a molecular weight below about 700 and the general formula:

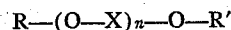


wherein R and R' are alkyl groups containing from 1 to 18 carbon atoms, X is an alkylene group having at least two carbon atoms and *n* is an integer, both components being present in amounts exceeding 5% of the total volume of the fuel and a minor proportion not exceeding 10% of the total volume of the fuel of amyl nitrate.

6 A compounded diesel fuel oil consisting essentially of a major proportion of a mixture of a straight-run California crude distillate boiling in the range of about 325° F. to about 750° F. and normally liquid oil-solu-

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ble blending agents having molecular weights below about 700 and having the general formula:



- 5 wherein R and R' are alkyl groups, X is an alkylene group having at least two carbon atoms and *n* is an integer, both components being present in amounts exceeding 5% of the total volume of the fuel and a minor proportion of at least 0.01% but not exceeding 10% by
10 volume of amyl nitrate.

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