5

15

Patented Aug. 15, 1961

1

## 2,996,364

2,996,364 FUEL OIL COMPOSITION Raymond Gay and Emanuel Siganos, Notre-Dame-de-Gravenchon, France, assignors to Esso Research and Engineering Company, a corporation of Delaware No Drawing. Filed June 17, 1958, Ser. No. 742,494 Claims priority, application France June 20, 1957 7 Claims. (Cl. 44-62)

The present invention relates to an improved fuel oil. 10 The words "fuel oil" are herein defined as a normally liquid hydrocarbon for example a petroleum distillate boiling above about 400° F. and including light fuel oils, gas oils, used as fuels for diesel engines, and heavy oils used in furnaces.

To increase the power output of an internal combustion engine, for example, a diesel engine, it is common practice to inject an increased quantity of fuel into the combustion chamber. However, in the case of diesel engines, when the quantity of injected fuel exceeds certain critical 20limits, then a copious liberation of smoke occurs in the exhaust gases due to incomplete combustion of the fuel. Further, the increased power output which is obtained as a result of an increased injection of fuel is not directly proportional to the amount of fuel used. Consequently 25the specific consumption of the engine increases with increasing fuel injection.

It has previously been proposed to add oil-soluble lead salts to fuel oil particularly diesel oils to improve the anti-corrosive properties of the oils. Whilst these additives lessen the anti-corrosive properties of fuel oils having a high sulphur content, they have no effect on the combustion properties of the oil particularly the tendency to form smoke.

It has now been discovered that it is possible to substan- 35 tially improve the properties of the fuel oil, particularly the tendency to smoke by adding to the fuel oil a small proportion of a composition comprising an ashless detergent and the oil-soluble salt of a metal of group IV of the periodic table.

Lead salts are particularly preferred in the composition of the present invention. A mixture of the salts of the aforesaid metals may be used instead of the salt of one metal.

The oil-soluble metallic salts used in accordance with 45 characteristics: the present invention may be salts of fatty acids, for example, palmitic, stearic, erucic, oleic or ricinoleic acids, or salts of naphthenic abietic or sulphonic acids, or salts of any organic acid having more than 6 carbon atoms per molecule. 50

Any ashless detergent may be used in the present invention. It is preferred to use polymeric or copolymeric products containing an active detergent group, which may be obtained by incorporating in the polymeric or copolymeric chain sulphurised or phosphosulphurised groups, or 55 nitrogen- or oxygen-containing groups, and which may of may not contain alkoxy groups.

Suitable detergents may be built up of copolymerisable unsaturated mono- and/or dibasic acids, or alkoxy derivatives thereof, including ester derivatives. Such prod- 60 ucts may be derived from  $C_4$  to  $C_{20}$  alcohols and maleic and/or fumaric acids, or mixtures of said esters including alkoxylated partial esters, and vinyl esters of  $C_2$  to  $C_6$ monobasic acids, e.g., vinyl acetate.

Other copolymeric compounds may be derived from alkyl-substituted acrylic acid and aliphatic alcohols, including amino alcohols.

Condensation products of an oil-soluble sulphonate and

an alkyl polyamine such as ethylene diamine and triethylamine may be also used as the ashless detergent in the composition of the present invention.

2

A mixture of the above detergents may be used instead of any particular detergent.

The total additive composition incorporated in the oils according to the present invention preferably comprises from 25 to 90% by weight of the oil-soluble salt of the said group IV metal and from 10 to 75% by weight of the said ashless detergent, and more particularly from 40 to 60% by weight of the oil-soluble salt of the group IV metal and from 60 to 40% by weight of the ashless detergent, the percentage being based on the total additive compound.

The total quantity of detergent additive added to the fuel oil is preferably within the range of 0.001 to 0.5% and more particularly 0.005 to 0.1% by weight of fuel oil.

Fuel oil compositions prepared according to the present invention were tested on a General Motors diesel engine (G.M. 371) having the following characteristics:

No. of cylinders	3
Bore (4¼")mm	108
Stroke (5")mm	127
Cylinder capacity (212 cu. ins.)ccs	3490
Temperature of water° C	80
Temperature of oil° C	

The smoke measurements at the exhaust were carried out with the smoke indicator known by the name of "Von 30 Brand Smoke-Meter." This apparatus makes it possible to measure the smoke in the exhaust gases by causing them to pass through a paper screen which unwinds con-tinuously at constant speed. The intensity of the spot obtained is measured by interpolation between two standards (one white, the other black); this determination is effected by comparison with a datum scale, or more accurately by measuring the percentage of light reflected by means of a photo-reflectometer.

## EXAMPLE I

A gas oil containing an additive in accordance with the present invention was used in a diesel engine of the type described above. The gas oil used had the following

	Density at 15° C	0.868
	Engler Viscosity at 20° C	1.48
	Sulphur, percent	1.08
_	Cetane index	43

The additive contained 50% by weight of an ashless detergent "A" and was added to the gas oil in quantities such that 1 kilogram of the oil contained 0.0005 gram atoms of metal.

The ashless detergent "A" was prepared as follows. Maleic anhydride was reacted with a C<sub>9</sub> Oxo alcohol at 70° C., in the presence of a boron trifluoride/ether complex. One mole of the monoester obtained was then condensed with 3 moles of ethylene oxide. 8% by weight of the ethoxylated monoester was then copolymerised with 37% by weight of a C<sub>9</sub> Oxo alcohol maleofumarate, 35%by weight of a C<sub>16-17</sub> Oxo alcohol maleofumarate, and 20% by weight of vinyl acetate, at 70-75° C., for 5 hours in the presence of benzoyl peroxide as catalyst.

The smoke index (I); consumption in litres per hour (C); specific consumption in gms./H.P./hour (Cs) and mean temperature of exhaust gases (t) were measured and the results obtained are summarised in Table I.

It will be seen from Table I that the gain in power,

30

35

40

55

60

65

**3** at a specific smoke index, resulting from the incorporation of an oil-soluble salt of a group IV metal plus an ashless dispersant is substantially greater than without the dis-

persant, and corresponding improvements are obtained in specific consumption (taken at a given smoke index). 5 The variations in the output of a diesel engine of the type previously described and the specific consumption of such an engine were investigated as a function of the

of such an engine were investigated as a function of the smoke index when the engine was supplied with a fuel oil with or without the addition of additive compositions 10 according to the present invention.

The gas oil used had the following characteristics.

Density at 15° C	0.857	
Engler Viscosity at 20° C	1.43	1
Sulphur, percent	0.5	
Cetane number	42	

The additive composition comprised 60% by weight of an ashless detergent and lead naphthenate and was added to the gas oil in quantities such that 1 kmg. of the gas oil contained 0.001 gm. atoms of lead.

The results of the experiment are summarised in Table II.

From the results it can be seen that for a given smoke 25 index, for example, 6, the addition of the additive composition of the present invention to the gas oil results in:

(1) A gain in output of from 6% to 12%.

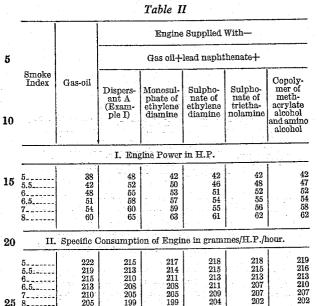
(2) A decrease in specific consumption of from 2 to 3%.

tin and the second		Table 1			
Engine output regulated to	Datum fuel oil	Lead oleate dispers- ant A	Tin naph- thenate+ dispers- ant A	Titanium sul- phonate (without dispers- ant A)	Thorium sul- phonate (without dispers- ant A)
$42 \text{ CV} \begin{cases} I_{-} \\ C_{-} \\ C_{s} \\ t_{-} \\ t \end{cases}$	3.510.14207.60242	$2.5 \\ 10.04 \\ 205.60 \\ 237$	$3 \\ 10.01 \\ 204.90 \\ 237$	2.5 10.07 206 237	3, 5 10, 14 207, 60 241
45 OV	3, 510, 82206, 70258	$2.5 \\ 10.76 \\ 205.50 \\ 256$	3 10.69 204,30 254	2.5 10.69 204.30 255	3, 5 10, 81 206, 60 257
$48 \text{ OV} \begin{cases} 1 \\ 0 \\ 0 \\ c_8 \\ t \\ t \end{cases}$	4 11. 52 206. 40 273	3 11.38 203.80 268	$     \begin{array}{r}       3 \\       11.30 \\       202.45 \\       269     \end{array} $	3.5 11.48 204.10 269	3.5 11.40 204.25 272
51 $\operatorname{OV} \begin{cases} T_{0} \\ O_{1} \\ C_{8} \\ t_{-} \end{cases}$	$\begin{array}{r} 4.5 \\ 12.24 \\ 206.40 \\ 288 \end{array}$	$\begin{array}{r} 3.5 \\ 12.02 \\ 202.70 \\ 285 \end{array}$	$\begin{array}{r} 3.5 \\ 11.86 \\ 200 \\ 285 \end{array}$	4 12.09 203.80 286	$\begin{array}{r}4\\12.10\\204\\287\end{array}$
54 $\operatorname{CV} \left\{ \begin{matrix} \mathbf{I} \\ \mathbf{O} \\ \mathbf{O} \\ t \\ t \end{matrix} \right\}$	$5 \\ 12.7 \\ 202.60 \\ 296$	4 12, 50 199, 05 293	4 12.44 198.10 291	$\begin{array}{r} 4.5 \\ 12.55 \\ 200 \\ 292 \end{array}$	4.5 12.58 200.40 296
55.8 {I C C t	5.5 13.13 202.30 307	4.5 12.91 198.90 304	4.5 12.92 198.90 303	5 13 200, 20 305	5 13.01 200.30 307

Table I

Results deduced from this table:

		index	70
Titanium	6½	2.3	
Tin+Dispersant	13, 13	6.7	
Thorium	6. 5, 6½	2.1	
Lead+Dispersant	13, 13	3.7	



4

What is claimed is:

1. A fuel oil containing from 0.001 to 0.5% by weight of a mixture of an oil soluble salt of a metal of group IV and from 10 to 75% by weight of an oil soluble ashless copolymer produced by copolymerizing 8 parts of an ethoxylated monoester of C<sub>9</sub> Oxo maleate with 37 parts of C<sub>9</sub> Oxo maleofumarate, 35 parts of C<sub>16</sub>-C<sub>17</sub> Oxo maleofumarate and 20 parts of vinyl acetate.

 A fuel oil composition as defined in claim 1 wherein said fuel oil is a petroleum distillate boiling above 400° F.
 A fuel oil composition as defined in claim 1 wherein

said group IV metal is lead.4. A fuel oil composition as defined in claim 1 wherein said group IV metal is tin.

5. A fuel oil composition as defined in claim 1 wherein said oil soluble salt has more than 6 carbon atoms per molecule.

6. A fuel oil containing from 0.005 to 0.1% by weight of a mixture of from 40-60% by weight of tin naphthenate and from 40-60% by weight of an oil soluble ashless copolymer produced by copolymerizing 8 parts of an ethoxylated monoester of C<sub>9</sub> Oxo maleate with 37 parts of C<sub>9</sub> Oxo maleofumarate, 35 parts of C<sub>16</sub>-C<sub>17</sub> Oxo maleofumarate and 20 parts of vinyl acetate.

7. A fuel oil containing from 0.005 to 0.1% by weight of a mixture of from 40–60% by weight of lead oleate and from 40–60% by weight of an oil soluble ashless copolymer produced by copolymerizing 8 parts of an ethoxylated monoester of C<sub>9</sub> Oxo maleate with 37 parts of C<sub>9</sub> Oxo maleofumarate, 35 parts of C<sub>16</sub>–C<sub>17</sub> Oxo maleofumarate and 20 parts of vinyl acetate.

## References Cited in the file of this patent

## UNITED STATES PATENTS

2,141,848 2,151,432 2,296,069	Adams et al Dec. 27, 1938 Lyons et al Mar. 21, 1939 Talbert et al Sept. 15, 1942
2,338,578 2,403,267	Downing et al Jan. 4, 1944 Davis July 2, 1946 Dittmar et al June 15, 1948
2,443,378 2,524,864 2,560,542 2,575,003	Wies et al Oct. 10, 1950 Bartleson et al July 17, 1951 Caron et al Nov. 13, 1951
2,684,292	Caron et al July 20, 1954 FOREIGN PATENTS
561,328 776,189	Great Britain May 15, 1944 Great Britain June 5, 1957