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DIESEL FUEL OILS

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This invention relates to improved Diesel fuel oils and more particularly to Diesel fuel oils which contain small amounts of addition agents which improve the performance characteristics of Diesel engines that burn said improved Diesel fuel oils.

Diesel engines are generally operated with fuel oils that have a boiling range above that of gasoline and below that of a motor lubricant. They may for instance have initial boiling points of about 400° F. and end boiling points of about 700° F. In the operation of Diesel engines with such petroleum fuel oils various difficulties arise. Often varnish or gum is formed on the piston surfaces, cylinder walls, valves, and atomizing apparatus of Diesel engines operating on such fuel oils, and the piston rings become stuck. Gum formation on the close fitting pintle valve of the fuel injection equipment results in a rapid drop in power and fluctuating combustion pressure due to inconsistent fuel injection. After several days of operation on ordinary Diesel fuel oils power output and engine efficiency decrease and there is a noticeable amount of knocking when the speed of the engine is increased. The engine must frequently be overhauled, cleaned and adjusted to restore its operating efficiency. Diesel fuel oils used in operating marine Diesel engines often become contaminated with water. As little as 0.1 per cent of water in a Diesel fuel oil can cause corrosion of fuel injectors so serious that the injectors must necessarily be replaced. With certain straight-run light Pennsylvania type fuel oils the wear on the injectors and plungers is sufficient to render them inaccurate after a few days operation thereby causing erratic engine performance. Small and medium size Diesel engines which usually operate on rather light fuel oils in particular operate with lessened efficiency because of insufficient lubrication and corrosion of parts. Corrosion, wear and gum formation on the high pressure injection pumps, interior cylinder surfaces and piston rings appear to be the major causes for the lessened efficiency with which Diesel engines perform when they are operated on ordinary Diesel fuel oils.

It is an object of this invention to manufacture fuel oils for Diesel engines which will improve the power output and performance characteristics of such engines. A further object is to produce Diesel fuel oils which will deposit very little varnish or gum on the engine parts. A still further object is to provide Diesel fuel oils which will not corrode engine parts if said oils become contaminated with water. Another object is to

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provide Diesel fuel oils which will tend to lessen the wear on the engine parts. Other objects will appear hereinafter.

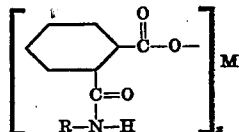
These objects are accomplished in accordance with the present invention by making improved Diesel fuel oils which contain a small proportion of an aliphatic amine soap made from a long chain primary aliphatic amine that has at least 10 carbon atoms and a long chain aliphatic monocarboxylic acid that has at least 10 carbon atoms and which also contain a small proportion of a polyvalent metal salt of an N-alkenyl phthalamidic acid, said aliphatic amine soap and polyvalent metal salt being present in sufficient quantities to improve the performance characteristics of Diesel engines burning said Diesel fuel oils.

The aliphatic amine soaps used in our improved Diesel fuel oils are made from primary aliphatic amines having at least 10 carbon atoms and straight chain aliphatic monocarboxylic acids that have at least 10 carbon atoms. The normal straight chain primary aliphatic amines used in preparing the amine soaps used in the present invention preferably contain from 10 to 20 carbon atoms. Usually normal straight chain primary alkyl amines such as decyl amine, undecyl amine, dodecyl amine, tetradecyl amine, cetyl amine, octadecyl amine and eicosyl amine are employed, but it is also permissible to use unsaturated straight chain primary aliphatic amines such as undecenyl amine and 9,10-octadecenyl amine (also called oleyl amine). Mixtures of the straight chain primary alkyl amines, such as cocoamine, are often used because of their relative cheapness. Cocoamine is a commercial mixture of higher alkyl amines prepared from coconut oil fatty acids. It contains a major amount of primary dodecyl amine, and typical samples thereof have been found to have average molecular weights ranging from 200 to 210.

The aliphatic amine soaps used in our improved Diesel fuel oils are made by reacting amines such as those mentioned in the preceding paragraph with straight chain aliphatic monocarboxylic acids containing at least 10 carbon atoms such as capric acid, lauric acid, myristic acid, palmitic acid, stearic acid, oleic acid, ricinoleic acid, linoleic acid and arachidic acid. Technical mixtures of these acids such as may be obtained by hydrolyzing fats or oils such as castor oil, tallow, lard, olive oil, cottonseed oil, linseed oil, palm oil, coconut oil, peanut oil, palm kernel oil, rape oil, etc., may be utilized in preparing the amine soaps employed in the Diesel fuel oils of this invention.

One of the amine soaps which has been found to be a very desirable addition agent to Diesel fuel oils is the cocoamine salt of oleic acid. Cocoamine oleate is prepared by neutralizing 282 parts by weight of oleic acid with 200 parts by weight of cocoamine which has an average molecular weight of 200.

The Diesel fuels of the present invention also contain a small proportion of a polyvalent metal salt of an N-alkenyl phthalamidic acid which has the following general formula:



wherein α denotes the numeral 2 or 3, R stands for an alkenyl group and M stands for a divalent or trivalent metal. These divalent and trivalent metal salts of N-alkenyl phthalamidic acids are prepared by reacting equimolecular quantities of alkenyl amines and phthalic anhydride to form N-alkenyl phthalamidic acids, followed by conversion of said acids to the desired divalent or trivalent metal salts thereof. Preferably the alkenyl group contains a long chain of 8 or more carbon atoms and is derived from a long chain alkenyl amine such as octenyl amine, decenyl amine, undecenyl amine, dodecenyl amine, tetradecenyl amine, hexadecenyl amine, 9,10-octadecenyl amine, eicosenyl amine, etc. M preferably stands for calcium, but it may also denote other divalent metals such as magnesium, strontium, barium, zinc, cadmium, lead, tin, copper, nickel or cobalt, or trivalent metals such as aluminum or bismuth.

One of the most readily prepared polyvalent metal salts used in the Diesel fuels of the present invention is the calcium salt of N-9,10-octadecenyl phthalamidic acid. This compound is prepared by reacting equimolecular quantities of phthalic anhydride and 9,10-octadecenyl amine (also called oleyl amine) to form N-9,10-octadecenyl phthalamidic acid, which is then converted to its calcium salt by neutralization with calcium hydroxide. A more detailed description of the preparation of this compound is given in the following paragraph.

Into a suitable reaction vessel were placed 267 parts by weight of 9,10-octadecenyl amine (also called oleyl amine) and 148 parts by weight of phthalic anhydride. This mixture was agitated and heated to from 180 to 220° F. While maintaining the temperature and continuing the agitation, 37 parts by weight of hydrated lime were added, and the reaction mixture was held at this temperature for a period of 10 hours. The reaction product thus obtained was the calcium salt of N-9,10-octadecenyl phthalamidic acid.

Suitable Diesel fuel oils of the present invention may be made by adding to an ordinary Diesel fuel oil as little as 0.004 per cent by weight of one of the aliphatic amine soaps mentioned hereinabove and 0.004 per cent by weight of one of the polyvalent metal salts of N-alkenyl phthalamidic acids, which are hereinbefore described. In adding these compounds to a Diesel fuel oil we find it convenient to blend 92 parts by weight of a Texas oil having a viscosity of 1200 SUV at 100° F. with 4 parts by weight of an aliphatic amine soap made from a long chain primary aliphatic amine that has at least 10 carbon atoms and a long chain aliphatic monocarboxylic acid that has at least 10 carbon atoms and with 4 parts by

weight of a polyvalent metal salt of an N-alkenyl phthalamidic acid. We denote this blend of a Texas oil with an aliphatic amine soap and a polyvalent metal salt of an N-alkenyl phthalamidic acid as a concentrate of Diesel fuel addition agents. We add from 0.10 per cent to 1 per cent by volume of this concentrate of Diesel fuel addition agents to a Diesel fuel oil in preparing the improved Diesel fuel oils comprehended by the present invention. It is therefore obvious that the improved Diesel fuel oils of the present invention contain from about 0.004 per cent to about 0.04 per cent by weight of one of the aliphatic amine soaps hereinbefore described and from about 0.004 per cent to about 0.04 per cent by weight of one of the polyvalent metal salts hereinbefore described. If desired we may dispense with the Texas oil of 1200 SUV at 100° F. and add the aliphatic amine soap and the polyvalent metal salt directly to the Diesel oil in the desired proportions. We generally find it practical to add 0.5 per cent by volume of the concentrate of Diesel fuel addition agents to an ordinary Diesel fuel oil which means that the Diesel fuel oils of the present invention generally contain about 0.02 per cent by weight of one of the aliphatic amine soaps described hereinbefore and about 0.02 per cent by weight of one of the polyvalent metal salts described hereinabove.

A preferred concentrate of Diesel fuel addition agents which has been used in preparing some of the improved Diesel fuel oils of the present invention is prepared by blending 4 per cent by weight of the cocoamine salt of oleic acid and 4 per cent by weight of the calcium salt of N-9,10-octadecenyl phthalamidic acid with 92 per cent by weight of a Texas oil having a viscosity of 1200 SUV at 100° F. This concentrate of Diesel fuel addition agents has the following properties:

Gravity	-----°API	21.9
Viscosity, SUV:		
100° F.	-----	1482
210° F.	-----	84.3
Flash, OC	-----°F	460
Fire, OC	-----°F	510
Pour	-----	+10

The following table gives the comparative properties of a heavy Diesel fuel oil and an improved heavy Diesel fuel oil of the present invention which was made therefrom by blending 0.5 per cent by volume of the concentrate of Diesel fuel addition agents described in the preceding paragraph with 99.5 per cent by volume of the heavy Diesel fuel oil.

Table I

	With Concentrate	Without Concentrate
Gravity	24.6	24.5
Viscosity, SUV:		
100° F.	165	162
210° F.	44	44
Flash, P-M ASTM D93-42	230	230
Flash, OC	230	230
Fire, OC	320	320
Pour	+40	+40
Sulfur	0.40	0.40
Water and Sediment	0.10	0.10
Sediment ASTM D473-38T	0.01	0.01
Carbon Residue	1.50	1.50
Precipitation No.	trace	trace
Ash	0.01	0.01
B. t. u./Lb. (gross)	19,188	19,188
Corrosion Test No. 1 of Patent No. 2,371,833	bright	rust
Corrosion Test:		
ASTM D665-44T—		
Steel Strip, Appearance	bright	rust
Area Rusted	nil	100

The following table gives the comparative properties of a light Diesel fuel oil and an improved light Diesel fuel oil of the present invention which was made therefrom by blending 0.5 per cent by volume of the concentrate of Diesel fuel addition agents described above with 99.5 per cent by volume of the light Diesel fuel oil.

Table II

	With Concentrate	Without Concentrate
Gravity..... ° API..	42.9	43.0
Viscosity, SUV, 100° F.....	35.4	35.2
Flash, P-M ASTM D93-42..... ° F.	164	164
Pour..... ° F..	-5	-5
Color, Saybolt.....	+20	+18
Sulfur, L..... per cent..	0.08	0.06
Water and Sediment..... do..	nil	nil
Carbon Residue..... do..	0.01	0.01
Carbon Residue on 10% Bottoms..... do..	0.04	0.04
Precipitation No.....	nil	nil
Copper Strip Test, 212° F., 3 hrs.....	good	good
Neutralization No.....	0.01	0.01
Acid Heat, ° F.: ASTM D481-39.....	6	6
Unsaturation, per cent. Method 550.2, Gov't.....	3	3
Aniline Point, ° F.: ASTM D611-44T.....	170.0	171.0
Cetane No.: CFR Ignition Delay Method.....	62	62
Diesel Index No.....	74	74
Ash..... per cent..	nil	nil
Distillation, Gas Oil:		
ASTM D158-41—		
Over Point..... ° F..	380	380
End Point..... ° F..	636	630
10% at..... ° F..	440	441
50% at..... ° F..	496	494
90% at..... ° F..	549	545
Corrosion Test No. 1 of Patent No. 2,371,853.....	bright	rust
Corrosion Test:		
ASTM D665-44T—		
Steel Strip, Appearance.....	bright	rust
Area Rusted..... per cent..	nil	100

The Diesel fuel oils of the present invention such as those described in the preceding tables display many advantages over ordinary Diesel fuel oils. The close fitting pintle valves in the injection equipment of Diesel engines burning our improved fuel oils do not become covered with gum or corroded, and therefore the combustion pressure and power output remain constant even after over 1000 hours of operation. This is an important advantage especially in connection with the operation of marine Diesel engines such as those used in power barges. Our new Diesel fuel oils substantially prevent corrosion and wear of the high pressure injection pumps, interior cylinder surfaces and piston rings, and reduce the tendency for piston rings to stick. Our Diesel fuels thus improve markedly the performance of Diesel engines, particularly those of small and medium size that usually operate on rather light fuel oils. The Diesel oils of the present invention decrease the tendency toward ring sticking and varnish formation on cylinder walls, valves and atomizing apparatus, thereby improving engine performance, power output and engine efficiency. The speed of Diesel engines burning our improved fuel oils may be increased with less knocking, and such engines will operate for a longer running time without having to be overhauled. If our Diesel fuel oils become contaminated with a little water, no serious cor-

rosion of the injectors will ensue, since the addition agents added to our fuel oils increase their water tolerance. The wear on the plungers and injectors decreases considerably when our fuel oils are employed. Our improved Diesel fuel oils successfully counteract many of the factors that decrease the efficiency of Diesel engines operating on ordinary Diesel fuels.

Resort may be had to such modifications and variations as fall within the spirit of the invention and the scope of the appended claims.

What we claim is:

1. An improved Diesel fuel oil which contains a small proportion of an aliphatic amine soap made from a long chain primary aliphatic amine that has at least 10 carbon atoms and a long chain aliphatic monocarboxylic acid that has at least 10 carbon atoms and which also contains a small proportion of a polyvalent metal salt of an N-alkenyl phthalamidic acid, said aliphatic amine soap and polyvalent metal salt being present in sufficient quantities to retard corrosion, wear, gum formation and ring sticking in a Diesel engine burning said Diesel fuel oil.

2. An improved Diesel fuel oil which contains a small proportion of an aliphatic amine soap made from a long chain primary aliphatic amine that has at least 10 carbon atoms and a long chain aliphatic monocarboxylic acid that has at least 10 carbon atoms and which also contains a small proportion of a divalent metal salt of an N-alkenyl phthalamidic acid, said aliphatic amine soap and divalent metal salt being present in sufficient quantities to retard corrosion, wear, gum formation and ring sticking in a Diesel engine burning said Diesel fuel oil.

3. An improved Diesel fuel oil which contains from about 0.004 per cent to about 0.04 per cent by weight of an aliphatic amine soap made from a long chain primary aliphatic amine that has at least 10 carbon atoms and a long chain aliphatic monocarboxylic acid that has at least 10 carbon atoms and which also contains from about 0.004 per cent to about 0.04 per cent by weight of a calcium salt of an N-alkenyl phthalamidic acid wherein said alkenyl group contains at least 8 carbon atoms.

4. An improved Diesel fuel oil which contains about 0.02 per cent by weight of cocoamine oleate and about 0.02 per cent by weight of the calcium salt of N-9, 10-octadecenyl phthalamidic acid.

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