

## UNITED STATES PATENT OFFICE

2,575,003

## FUEL OIL COMPOSITION

John B. R. Caron, North Plainfield, and Everett B. Glendenning, Cranford, N. J., and Calmy Wies, New York, N. Y., assignors to Shell Development Company, San Francisco, Calif., a corporation of Delaware

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This invention pertains to hydrocarbon fuels, and more particularly to fuel oil compositions capable of preventing or inhibiting the sludging and/or clogging tendencies generally exhibited by hydrocarbon fuels, such as those utilized in burner systems, diesel and combustion engines, and various other industrial and domestic equipment. In addition, this invention relates to fuel oil compositions capable of removing preformed deleterious matter from filters, screens, and the like, which deleterious matter is formed by deterioration and/or the presence of foreign bodies (e. g. water) in the fuel oils.

Hydrocarbons, such as distillate fuels, for example, those having a normal distillation range of from about 300° F. to about 750° F., and particularly from about 340° F. to about 640° F., generally have a marked tendency to deteriorate under oxidizing conditions, and to form sludge. Also, the presence of impurities in such fuels, such as the presence of moisture, dispersed water, organic and/or inorganic foreign matter, and the like, causes the formation of insoluble products, which tend to settle out and adhere to surfaces with which they come in contact, thereby, in turn, causing clogging or plugging of filters, strainers, screens, conduit lines, and the like, of the equipment in which they are used. This necessitates frequent cleaning and even replacement of parts, thereby markedly decreasing the performance efficiency of various equipment which utilizes such fuel oils.

The problem of screen clogging is common, particularly in domestic fuel oil systems employing distillate fuel oils produced by distilling or cracking of petroleum which fuels are characterized by their relatively low viscosity. Fuel oils of this type generally conform to the specifications set forth in Commercial Standards C. S. 12—40 for Nos. 1, 2 and 3, Fuel Oils. Petroleum distillates within the ranges specified and which generally do not boil above 750° F., and preferably are below 675° F., which distillates are used as diesel fuels, are further examples of oils which under conditions described have a tendency toward screen or filter clogging, particularly when such fuels contain minor amounts of water dispersed therein.

Another place where screen clogging and plugging of conduit lines is encountered is in storage

tanks for fuel oils, which tanks may be connected to the burner systems or engines, etc. The stored fuel generally comes in contact with air, moisture, water, etc. which causes formation and precipitation of sludge material, which, in turn, deposit on and clog the screens or filters used for protecting the burners or engines which use such oils as the fuel.

It is an object of this invention to inhibit sludging tendencies of hydrocarbon fuel oils. It is another object to inhibit sludging and precipitation of contaminants in hydrocarbon distillate fuel oils, and particularly in cracked hydrocarbon fuels. It is still another object to provide distillate fuel oils, particularly fuel oils obtained by cracking of hydrocarbons, which fuels have excellent performance characteristics with respect to freedom from screen clogging, even after extensive storage under oxidizing conditions and in the presence of water. Still another object is to provide a distillate fuel oil composition which is effective in removing preformed sludge deposits produced in fuel oil systems. Still another object is to provide distillate fuel oil compositions, and blends thereof, which are non-corrosive and stable, and which are effective for cleaning and removing sludge.

The above and other objects of this invention may be attained by dispersing or dissolving in hydrocarbon distillate fuel oils (which normally have a tendency to cause clogging or plugging of screens, filters, conduit lines and the like), a minor amount, which amount, however, is sufficient to inhibit said tendencies, of a surface-active agent which is a salt of an organic alicyclic acid (or mixtures thereof) and a detergent salt of the type more fully disclosed hereinafter. If desired, a minor amount of a solutizer or drying agent may also be added to the composition.

The hydrocarbon distillate fuel oils in which the active ingredient and/or ingredients of this invention are dispersed or dissolved may be treated or untreated catalytically cracked fuel oils, or mixtures of cracked fuels with straight-run fuel oils, which have an initial distillation point of about 300° F. and an end distillation point not exceeding 750° F. Generally, these fuels have a boiling range of from about 340° F. to about 700° F., and preferably a boiling range of from about 400° F. to about 675° F.

Cracked fuels may be obtained by thermal or catalytic cracking of certain petroleum hydrocarbon feed stocks. Both types of cracked fuels, as well as blends of cracked and straight-run fuels, may be acid and/or caustic-treated to improve their stability. Specifically, hydrocarbon distillates which are utilized as bases in compositions of this invention are cracked gas oils, fuel oils, furnace oils, burner oils, diesel fuel oils, kerosene, etc., and mixtures of said cracked fuels with the corresponding or like straight-run hydrocarbon fractions. These fuel oils generally have the following properties:

Gravity, °API	29-35	15
ASTM dist., °F.:		
IBP	400-500	
EBP	600-750	
Sulfur per cent W	0.5-1.05	
Carbon residue (10% Btms) per cent W	0.1-0.4	20
Pour point, °F.	0-15	

The surface active agents which possess the property of inhibiting sludge formation and/or of removing preformed deposits from surfaces (thereby preventing clogging of systems utilizing fuels normally susceptible of causing such deterioration) are salts of organic cyclic acids and mixtures thereof.

The preferred salts are the alkali, alkaline earth and heavy metal salts of the organic cyclic acids. The cation portion of said salts may be Na, K, Cs, Ca, Ba, Sr, Mg, Al, Zn, Pb, Sn, Ge, Zr, Cr, Cd, Co, Fe, Mo, Ni, Bi, and the like. The anion portion of the salt of these metals is an organic cyclic acid and may be represented by the formula



wherein R is an alicyclic radical; each X is O, S, Se or Te; Y is a polar group; Z is an organic radical, such as an alkyl, alkylene, alkylaryl, arylalkyl, alkoxy, aroxyl, aryl and like radical; a and b may be zero or an integer of 1 or 2, and c is an integer of 1 or 2. The acid radical (CXXH) is linked directly or indirectly to R. The substituent group represented by Y in the formula may be a hydroxyl, amine, nitro, nitroso, sulfo, mercapto, and the like group. The polar group or groups may be attached directly or indirectly to the R radical.

Specifically alicyclic acids may include: naphthenic acid (derived from petroleum hydrocarbon), phenyl naphthenic acid, hydroxy-phenyl naphthenic acids, benzyl naphthenic acids, benzoyl naphthenic acids, naphthyl naphthenic acids, xenyl naphthenic acids, phenyl-vinaconic acid, phenyl-caronic acid, truxillic acid, phenyl-norpinic acid, phenyl-pinic acid, phenyl-camphoric acid, phenyl camphenic acid, phenyl 2,3,4-trimethyl cyclopentane-3 carboxylic acid, phenyl hexahydrobenzoic acids, hydrophenyl hexahydrobenzoic acid, benzyl hexahydrobenzoic acid, phenyl hexahydrophthalic acid, phenyl quinic acid, hexahydrobenzoic acid, tetrahydrophthalic acid, hexahydrophthalic acid, alkyl hexahydrophthalic acid, alkylene cyclohexadiene carboxylic acid, cyclohexane carboxylic acid, cyclohexyl acetic acid, cyclohexylbutyric acid, cyclohexylcaproic acid, cyclohexylpropionic acid, cyclohexylvaleric acid, fencholic acid, cholic acid, abietic acid and their homologues and analogues.

Some specific salts of organic cyclic acids are listed below in which any of the cations listed

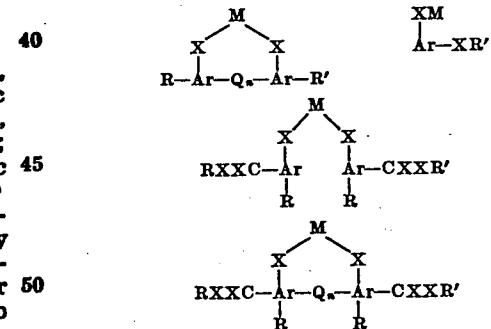
5 may be combined with any of the anion parts listed to form the salts:

Cation	Anion
Sodium	petroleum naphthenic acid
Calcium	phenyl naphthenic acid
Barium	hydrophenyl naphthenic acid
Strontium	naphthyl naphthenic acid
Lead	phenylpinic acid
Tin	phenyl hexahydrobenzoic acid
Aluminum	phenyl hexahydrophthalic acid
Zinc	cyclo hexadiene carboxylic acid
Cadmium	cyclo hexylcaproic acid
Cobalt	abietic acid
Germanium	
Zirconium	
Chromium	
Magnesium	

The second additive, namely a detergent salt, functions in compositions of this invention as a peptizer and aids in inhibiting or preventing the settling and adhering of impurities and sludge to surfaces, thus allowing any impurities present or formed to pass through the screen or filter system.

Detergents which may be used are alkali, alkaline earth and heavy metal and organic nitrogen base salts of various organic acids. The acidic portion of such detergents may be sulfonic acids, aromatic and hydroxy aromatic carboxylic acids, aliphatic acids, said acids containing, if desired, substituent groups, e. g., an amino, hydroxyl, mercapto, halo and/or sulfur and the like groups. Also phenates, alcoholates, carbamates, thiocarbamates, xanthates, etc. may be used.

Particularly preferred class of detergents are 35 the salts of alkyl substituted phenol sulfides or its selenide and/or its telluride equivalent. These phenolic salts may be represented by the general formulas:



wherein M is a metal; R and R' represent at 55 least one alkyl radical attached to the aromatic ring, Ar, the total number of carbon atoms in all of such radicals being at least 5; X is O and/or S; Q is S, Se, or Te and n is an integer of from 1 to 4.

To form the salts of these phenolic compounds 60 they may be treated with such metal compounds as Li, Na, K, Cu, Hg, Fe, Mn, Mg, Ca, Ba, Sr, Pb, Ni, Co, Cr, Sn, Fe, etc. Alkaline earth metals are particularly preferred because of their solubility in hydrocarbons and potent detergent properties.

In addition to the normal salts of phenolic compounds, basic salts may be used and can be represented by the formula



wherein the symbols are the same as referred to in the previous formulas. These basic salts may 75 be formed by reacting the aromatic acidic com-

pounds with more than the amount of metal oxide or hydroxide necessary to form the normal salt.

Some specific compounds as represented by the above formulas are: barium tertiary octyl phenol sulfide and disulfide, barium tertiary amyl phenol sulfide, calcium iso-hexadecyl phenol sulfide, magnesium tertiary amyl phenol sulfide, cobalt tertiary amyl phenol sulfide, barium dodecyl salicylate sulfide, sulfide of the barium salt of the ethyl ester of p-hydroxy dithiobenzoic acid, calcium octyl phenol selenide, etc. The amount of detergent salt used may vary between about 5 and 15% and preferably is kept below 10%.

Another preferred class of detergents is the alkali (e. g. Na, K, Li), and/or alkaline earth metal (e. g. Ca, Sr, Ba, Mg) salts of petroleum sulfonic acids, preferably of high molecular weight, derived from petroleum hydrocarbon crudes and fractions thereof which are of the so-called mixed type, i. e. containing naphthenic type hydrocarbons.

These oil-soluble petroleum sulfonates may be obtained by processes, such as those disclosed in the U. S. patents, 2,388,677, 2,395,713, 2,413,713, 2,413,311, 2,414,773, 2,416,397, and if desired purified by such means as those disclosed in U. S. patents, 2,236,933, 2,334,532, 2,357,866, 2,368,452, and 2,406,763.

In systems wherein substantial amounts of moisture are present a drying agent may be added which is compatible with the active ingredients of this invention. By tying up most of the free moisture in this manner, the amount which would normally combine with sludge forming materials is diminished, thus alleviating a most aggravating clogging problem.

Drying agents which are particularly suited are the glycol-ether type such as diethylene glycol monoethyl, ethyl N- and isopropyl ether, diethylene glycol mono-butyl ether, diethylene glycol mono-decyl ether, etc.; also dipropylene glycol monoethyl ether, dipropylene glycol mono-isopropyl ether, dipropylene glycol mono-isoamyl ether, diisobutylene glycol mono-isopropyl ether, ethylene propylene glycol mono-ethyl ether, ethylene-isobutylene glycol mono-isopropyl ether, etc. Instead of the glycol-ethers, various alcohols may be used such as diols having 6 or more carbon atoms in the molecule such as hexylene glycol, decylene glycol, cetylene glycols, etc.; diglycols such as dipropylene glycols, dibutylene glycol, diamylene glycol, ether alcohols and particularly the glycol mono-alkyl ethers, e. g., the cellosolves such as ethylene glycol mono-ethyl ether, ethylene glycol mono-propyl ether, ethylene glycol mono-tert-butyl ether, ethylene glycol mono-hexyl ether, propylene glycol mono-ether ether, propylene glycol mono-isoamyl ether, etc. Also glycerine and the like may be used.

The following is a general formula of a base (concentrate) composition of this invention:

Per cent

Surface active agents, e. g. aluminum naphthenate	10-20
Detergent, e. g. phenate, sulfonate, etc.	5-15
Drying agent, e. g. glycol-ether	0-50
Hydrocarbon fuel oil, balance	

Specific base compositions may be illustrated by the following examples:

Composition A

Per cent

Aluminum naphthenate	15
Na petroleum sulfonate	10
Fuel oil	75

Composition B

	Per cent
Iron naphthenate	15
Na petroleum sulfonate	10
Fuel oil	75

The following table further illustrates suitable anti-clogging base compositions of this invention.

	Components <sup>1</sup>	1	2	3	4	5	6	7	8	9
<i>Surface Active Agents</i>										
Al petroleum naphthenate	x				x		x	x		
Fe petroleum naphthenate		x				x		x	x	x
Ca petroleum naphthenate				x		x				
Al abietate			x							
Ca abietate										
<i>Detergents</i>										
Na petroleum sulfonate	x			x			x			
Ca petroleum sulfonate		x			x		x	x		
Ba salt of alkyl phenol sulfide	x			x		x				x
Ca alkyl salicylate			x							
<i>Drying Agent</i>										
Diethylene glycol monobutyl ether	x			x			x			
Cetylene glycol		x						x		x

<sup>1</sup> All of the above compositions are diluted with a hydrocarbon distillate fuel oil in amounts indicated above.

Compositions of this invention are generally mixed in amounts of 1 pint or less with from about 250 gallons of fuel oil. Thus for example, on a percentage basis of fuel used, one pint of any one of the compositions described above per 250 gallons of fuel would correspond to approximately the following concentration of the active ingredients in the final fuel compositions:

Salts of organic cyclic acids from about 0.0025% to about 0.0075%; detergent (phenates, sulfonates) from 0.0015 to 0.004%; drying agent (glycol-ether) from zero to about 0.0265%.

To inhibit any corrosive tendencies of fuel compositions of this invention a minute amount of caustic or aromatic nitrogen compounds, such as aniline, may also be added. These compounds act as alkaline reserves and render the fuel compositions substantially non-corrosive to copper, brass and other metals.

The following example illustrates the effectiveness of compositions of this invention:

Example

An undoped fuel oil was first treated by blowing steam therethrough until the fuel oil became clouded. This steam treated oil was then circulated by means of a conventional oil burner pump, for approximately 24 hours through an apparatus containing a 100 mesh screen. The drop in flow, as measured by a rotameter placed in the stream, indicated the extent to which the screen became clogged during this test period. Similar tests were run using a fuel oil doped with Composition A and B. The results are tabulated below:

	Max. decrease in flow rate, percent
Undoped fuel oil <sup>1</sup>	57.4
0.025% Composition A in fuel oil	15.1
0.025% Composition B in fuel oil	10.2

<sup>1</sup> Properties of undoped fuel oil:

Gravity, ° API at 60° F.	33.6
Flash P. M. cc. ° F.	190
Cloud point, ° F.	10
Pour point, ° F.	-5
Sulfur, per cent b. w.	0.85
ASTM dist.:	
IBP, ° F.	380
EBP, ° F.	676

To compositions of this invention may be added minor amounts of foam inhibitors, such as silicon liquids, e. g. dimethyl silicone; fluoro organic compounds, e. g. fluoro paraffins; organic esters of mono and polycarboxylic acids and mono and polyhydric alcohols, e. g. methyl stearate, dioctyl sebacate, dioctyl phthalate, glycercyl mono and dioleate or stearate, etc. Compositions of this invention are non-corrosive and do not interfere with the function of the fuel in which they are dispersed.

We claim as our invention:

1. An anti-clogging concentrate adapted to be added to a hydrocarbon distillate fuel normally susceptible toward clogging said concentrate comprising from about 10% to about 20% aluminum petroleum naphthenate; from about 5% to about 15% of a metal salt of an organic sulfonic acid and the balance of the composition being a fuel oil.

2. An anti-clogging concentrate adapted to be added to a hydrocarbon distillate fuel normally susceptible toward clogging said concentrate comprising from about 10% to about 20% Fe petroleum naphthenate; from about 5% to about 15% of a metal salt of an organic sulfonic acid and the balance of the composition being a fuel oil.

3. A non-clogging fuel oil containing entrained moisture and normally susceptible to cause clogging containing in combination therewith from about 0.0025% to about 0.005% of aluminum petroleum naphthenate, and from about 0.0015% to about 0.004% of a metal salt of an organic sulfonic acid.

4. A non-clogging fuel oil containing entrained moisture and normally susceptible to cause clogging containing in combination therewith from about 0.0025% to about 0.005% of Fe petroleum naphthenate, and from about 0.0015% to about 0.004% of a metal salt of an organic sulfonic acid.

5. An anti-clogging concentrate adapted to be added to a hydrocarbon distillate fuel normally susceptible toward clogging said concentrate comprising from about 10% to about 20% of a polyvalent metal naphthenate selected from the group consisting of iron naphthenate and aluminum naphthenate; from about 5% to about 15% of a metal salt of an organic sulfonic acid and the balance of the composition being a fuel oil.

6. An anti-clogging concentrate adapted to be added to a hydrocarbon distillate fuel normally susceptible toward clogging said concentrate comprising from about 10% to about 20% of a polyvalent metal petroleum naphthenate selected from the group consisting of iron naphthenate and aluminum naphthenate; from about 5% to about 15% of a metal salt of a petroleum sulfonic

acid and the balance of the composition being a fuel oil.

7. A non-clogging fuel oil containing entrained moisture and normally susceptible to cause clogging containing in combination therewith from about 0.0025% to about 0.005% of a polyvalent metal naphthenate selected from the group consisting of iron naphthenate and aluminum naphthenate, and from about 0.0015% to about 0.004% of a metal salt of an organic sulfonic acid.

8. A non-clogging fuel oil containing entrained moisture and normally susceptible to cause clogging containing in combination therewith from about 0.0025% to about 0.005% of a polyvalent metal petroleum naphthenate selected from the group consisting of iron naphthenate and aluminum naphthenate, and from about 0.0015% to about 0.004% of a metal salt of a petroleum sulfonic acid.

9. An anti-clogging concentrate adapted to be added to a hydrocarbon distillate fuel normally susceptible toward clogging said concentrate comprising from 10% to 20% aluminum petroleum naphthenate, from about 5% to about 15% of sodium petroleum sulfonate and the balance of the composition being a fuel oil.

10. An anti-clogging concentrate adapted to be added to a hydrocarbon distillate fuel normally susceptible toward clogging said concentrate comprising from 10% to 20% iron petroleum naphthenate, from about 5% to about 15% of sodium petroleum sulfonate and the balance of the composition being a fuel oil.

11. A non-clogging fuel oil containing entrained moisture and normally susceptible to cause clogging containing in combination therewith from about 0.0025% to about 0.005% of aluminum petroleum naphthenate, and from about 0.0015% to about 0.004% of sodium petroleum sulfonate.

12. A non-clogging fuel oil containing entrained moisture and normally susceptible to cause clogging containing in combination therewith from about 0.0025% to about 0.005% of iron petroleum naphthenate, and from about 0.0015% to about 0.004% of sodium petroleum sulfonate.

JOHN B. R. CARON.

EVERETT B. GLENDENNING.

CALMY WIES.

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