

UNITED STATES PATENT OFFICE

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FUEL OIL COMPOSITION

Calmy Wies, New York, N. Y., and John B. R. Caron, North Plainfield, and Everett B. Glendenning, Cranford, N. J., 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 including diesel fuel oil compositions capable of removing preformed deleterious matter from filters, screens, and the like, caused by deterioration and/or 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 700° F. and particularly from about 340° F. to about 640° F., generally have a marked tendency to deteriorate under oxidizing conditions, and 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 and other properties. 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 exceed 700° F. and preferably are below 675° F. for use as diesel fuels are further examples of the type of oils which under conditions described have a tendency toward screen or filter clogging, particularly when they 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 cause formation and precipitation of sludge material which, in

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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 of this invention to inhibit sludging and precipitation of contaminants in hydrocarbon distillate fuel oils, and particularly in cracked hydrocarbon fuels. It is still another object of this invention 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 of this invention is to provide a distillate fuel oil composition which is effective in removing preformed sludge deposits formed in fuel oil systems. Still another object of this invention is to provide distillate fuel oil compositions, and blends thereof, which are non-corrosive and stable, and which are effective for cleaning and for sludge removing.

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 basic salt of a polyvalent metal represented by the partial general formula:



where n is an integer of from 1 to 5, M is a polyvalent metal, X is an element of the group consisting of O, S, Se and Te; Y is an acidic portion of the anionic part of the basic salt to which M is linked and is a $-SO_3H$ radical, wherein the X 's may be the same or different elements from the group consisting of O, S, Se and Te. If desired a minor amount of a detergent and/or solutizer 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 700° 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.

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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, e. g. fuel oils, etc.

Fuel oils which have marked tendencies towards sludging and clogging of screens, filters, etc., are primarily cracked or blends of cracked and straight-run fuel oils which have the following properties:

Gravity, °API-----	29-35
A. S. T. M. dist., °F.:	
IBP-----	400-500
EBP-----	600-700
Sulfur percent weight-----	0.5-1.05
Carbon residue (10% Btms.) percent weight-----	0.1-0.4
Pour point, °F-----	0-15

The surface active agents which possess the unique property of inhibiting sludge formation or of removing preformed deposits from surfaces (thereby preventing clogging of systems utilizing fuels normally susceptible of causing such deterioration) are the basic salts of polyvalent metals represented broadly by the partial general formula referred to above.

A. Sulfonic acids:

Benzene sulfonic acid
Toluene sulfonic acid
Triisopropyl naphthalene sulfonic acid
Diphenyl sulfonic acid
Diwax benzene sulfonic acid
Xylene sulfonic acid
Benzene disulfonic acid
Alkane sulfonic acids, e. g. amyl, octyl, nonyl, lauryl
Dodecyl sulfonic acid

Petroleum sulfonic acids derived from various petroleum fraction such as:

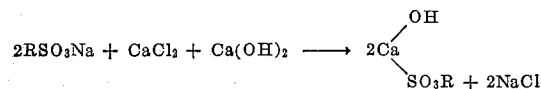
Gas oil
Kerosene
Light oil
Turbine oil
Mineral lubricating oil
Heavy oil
Petroleum waxes, e. g.:
 Petrolatum
 Paraffin wax and mixtures of various hydrocarbon fractions
Wax sulfo salicyclic acid
Diwax naphthalene sulfonic acids, etc.

Petroleum sulfonic acids are produced by treating suitable petroleum hydrocarbon fractions with sulfuric acid. For example, a turbine oil having a Saybolt Universal viscosity at 100° F. of from about 400 to 540 seconds is treated with fuming sulfuric acid, preferably in small increments. After a calculated amount of sulfuric acid has been added to the oil, the sludge which forms is removed and the acid-treated oil containing dissolved oil-soluble sulfonic acids is neutralized with a solution of sodium hydroxide. The aqueous alkali solution is removed from the mixture and the sodium salts of petroleum sul-

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fonic acid extracted with alcohol. The alcohol layer containing the sulfonates can be removed by distillation or by any other suitable means.

The sodium petroleum sulfonate can be converted to the basic metal salt of petroleum sulfonic acid by treating said sodium petroleum sulfonate with calculated amounts of, for example, a mixture of calcium chloride and calcium hydroxide. The reaction may be represented by the following equation:



wherein R is a long chain hydrocarbon.

Petroleum sulfonic acids which are particularly preferred are derived from naphthenic, Gulf-Coastal, or Mid-Continent oils.

The petroleum sulfonic acids may be obtained by the method described above or by any other means such as those disclosed in the U. S. Patents Nos. 2,388,677, 2,395,713, 2,413,199, 2,413,311, 2,414,773, 2,416,397, and if desired purified by such means as those disclosed in U. S. Patents, Nos. 2,236,933, 2,334,532, 2,357,866, 2,368,452, and 2,406,763, prior to or after the basic salts of said acids have been made.

The basic salts may be formed by saponifying any of the acids or acid-forming materials referred to above with an excess of a polyvalent metal compound such as the hydroxides or the like. A preferred method for forming the basic salts of this invention is to react the desired acidic compound with a polyvalent metal halide or a sulfate and thereafter treating the salt thus formed with metal hydroxide or alcoholate. Instead of forming the basic salt in stepwise fashion the basic salt may be made by adding a mixture of the polyvalent metal hydroxide and halide in such proportions and amounts as are sufficient to form the basic salt with a desired organic acidic compound.

The metal portion of basic salts of this invention may be any polyvalent metal such as Ca, Ba, Mg, Sr, Al, and mixtures thereof:

The following table gives typical examples of preferred basic metallic salts which are excellent anti-clogging agents in fuels.

The part of the basic salt containing the metal may be represented by HXM, wherein X is O, S, Se and Te and M may be any of the following:

Cation part:

Calcium
Barium
Magnesium
Strontium
Aluminum

Acid or anion part:

Petroleum sulfonic acid
Triisopropyl naphthalene sulfonic acid
Diaryl naphthalene sulfonic acid
Diwax benzene sulfonic acid
Diwax naphthalene sulfonic acid
Benzene disulfonic acid
Lauryl sulfonic acid

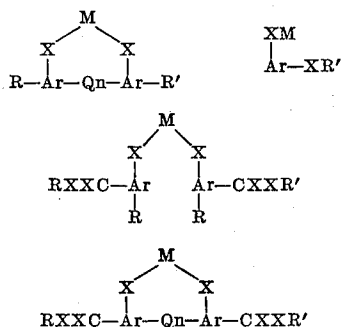
The amount of basic salt used in the base or concentrate fuel oil, may vary from about 2% and 25%, and preferably between about 5% and 20% by weight. However, greater or lesser concentrations may be used also.

If desired, and under certain conditions of use, it is preferred to add detergents to compositions of this invention. The function of the detergent agents in compositions of this inven-

tion is to act as peptizers, to aid in inhibiting or preventing the settling and adhering of impurities and of sludge to surfaces, and to allow 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 consist of naphthenic acids, aromatic and hydroxy aromatic carboxylic acids, and aliphatic acids, said acids containing if desired, substituent groups, e. g. amino, hydroxide, mercapto, halo and sulfur groups, and the like. Also phenates, alcoholates, carbamates, thiocarbamates, xanthates, etc., may be used.

Particularly preferred detergents are the salts of alkyl substituted phenol sulfides, or their selenide and/or their telluride equivalents. These phenolic salts may be represented by the general formulas:



wherein M is a metal; R and R' represent at 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, S, Se and/or Te; Q is S, Se or Te; and n is an integer of from 1 to 4.

These salts may be formed by treating the phenolic compounds with such metal compounds as Li, Na, K, Cu, Hg, Fe, Mn, Mg, Ca, Ba, Sr, Pb, Ni, Co, Sn, Mo, etc. Alkaline earth metals are particularly preferred because of their solubility in hydrocarbons and their excellent detergent properties.

The following are illustrative examples of the above detergents: barium tertiary-octyl phenol sulfide, its disulfide, barium ditertiary-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 in the concentrate may vary from between about 5 and 15%, and preferably is kept below 10%.

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 thereof 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-ethers, such as diethylene glycol monomethyl, ethyl, N- and isopropyl ether, diethylene glycol mono-butyl ether, diethylene glycol monodecyl ether, etc.; also dipropylene glycol monoethyl ether, dipropylene glycol mono-isopropyl ether, dipropylene glycol mono-isoamyl ether, diisobutylene glycol-mono isopropyl ether, ethyl-

ene-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, e. g. hexylene glycol, decylene glycols, cetylene glycols, etc.; diglycols such as dipropylene glycol, 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 monon-butyl ether, ethylene glycol mono-isobutyl ether, ethylene glycol mono-tert-butyl ether, ethylene glycol mono-hexyl ether, propylene glycol mono-isoamyl ether, etc. Also glycerine and the like may be used.

The amount of these materials, when used, constitutes a substantial portion of the base or concentrate, and generally is about 50% or more. However, under certain conditions these materials may be omitted from the base.

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

	Amount, percent wt.	
	Broad	Preferred
Basic metal salt of an organic acid compound, e. g.:		
Basic aluminum sulfonate.....	10-20	15
Basic calcium sulfonate.....		
Detergent, e. g.:		
Normal alkali.....	0-10	10
petroleum sulfonate.....		
metal salt of alkyl phenol sulfide, etc.....		
Drying agent, e. g.: Polyhydric alcohol glycol ethers, etc.....	0-50	
Fuel oil.....	Balance	Balance

Specific base compositions may be illustrated by the following examples:

	Per cent
Composition A:	
Basic aluminum sulfonate	20
Fuel oil	80
Composition B:	
Basic magnesium sulfonate	20
Fuel oil	80

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

	1	2	3	4	5
Components: ¹					
Surface Active Agents—					
Basic calcium petroleum sulfonate.....	x	x	x	x	x
Basic zinc stearate.....					x
Detergents—					
Normal Ba salt of alkyl phenol sulfide....		x			
Normal Ca salt of alkyl phenol sulfide....					x
Normal Ca alkyl salicylate.....				x	
Na naphthenate.....			x		
Drying Agents—Diethylene glycol mono-butyl ether.....			x		

¹ All of the above compositions are diluted with a hydrocarbon fuel oil in amounts indicated above.

Compositions of this invention are generally mixed in amounts of one pint or less with from about 250 to about 1000 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:

Basic metal salt of an organic acidic compound, from about 0.0025% to about 0.005%; detergent (salt of an alkyl phenol sulfide), from zero to

about 0.0025% or 0.0042%; 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 compound, 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 examples illustrate the effectiveness of compositions of this invention:

Example I

Doped and undoped fuel oils were filtered and then clouded with steam. The fuel compositions or undoped fuel oil were circulated through a screen under a constant head. The oil was pumped from a reservoir into a vertical conduit and allowed to flow by gravity through the screen and decrease in flow rate of the various undoped and doped fuel oils noted after being circulated for 24 hours. The results are tabulated below:

Base	Primary additive	Concentration, percent weight	Maximum decrease in flow rate, percent
Fuel oil containing moisture.			84.1 in 25 min.
Do	Basic aluminum sulfonate.	0.005	6.2 in 24 hrs.
Do	Basic magnesium sulfonate.	.005	6.7 in 24 hrs.
Do	Basic aluminum sulfonate.	.025	3.5 in 24 hrs.
Do	Normal aluminum naphthenate.	.01	86.9 in 35 min.
Do	Aluminum tristearate.	.025	78.5 in 24 hrs.
Do	Normal copper-sulfonate.	.005	29.6 in 24 hrs.
Fuel oil containing no moisture.			60.0 in 24 hrs.

To compositions of this invention may be added minor amounts of foam inhibitors, such as silicone liquids, e. g. dimethyl silicon, fluoro organic compounds, e. g. fluoro paraffins, organic esters of mono- and poly-carboxylic acids and mono and polyhydric alcohols, e. g. methyl stearate, dioctyl sebacate, dioctyl phthalate, glyceryl mono and diolate 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. A fuel oil normally susceptible to cause clogging due to the presence of cracked components and entrained moisture having incorporated therewith a small amount, sufficient to inhibit said clogging tendencies, of a basic polyvalent metal hydrocarbon sulfonate selected from the group of alkaline earth metal hydrocarbon sulfonate and basic aluminum hydrocarbon sulfonate.

2. A fuel oil normally susceptible to cause clogging due to the presence of cracked components and entrained moisture having incorporated therewith a small amount, sufficient to inhibit said clogging tendencies, of a basic magnesium hydrocarbon sulfonate.

3. A fuel oil normally susceptible to cause clogging due to the presence of cracked components and entrained moisture having incorporated therewith a small amount, sufficient to inhibit said clogging tendencies, of a basic calcium hydrocarbon sulfonate.

4. A fuel oil normally susceptible to cause clogging due to the presence of cracked com-

ponents and entrained moisture having incorporated therewith a small amount, sufficient to inhibit said clogging tendencies, of a basic aluminum hydrocarbon sulfonate.

5. A non-clogging fuel oil normally susceptible to cause clogging due to the presence of cracked components and entrained moisture having incorporated therewith from about 0.0025% to about 0.005% of a basic aluminum petroleum sulfonate.

6. A non-clogging fuel oil normally susceptible to cause clogging due to the presence of cracked components and entrained moisture having incorporated therewith from about 0.0025% to about 0.005% of a basic magnesium petroleum sulfonate.

7. A non-clogging fuel oil normally susceptible to cause clogging due to the presence of cracked components and entrained moisture having incorporated therewith from about 0.0025% to about 0.005% of a basic calcium petroleum sulfonate.

8. A fuel oil normally susceptible to cause clogging due to the presence of cracked components and entrained moisture, said fuel oil rendered non-clogging by having incorporated therein one pint of a concentrate consisting essentially of from 10 to 20% of a basic polyvalent metal hydrocarbon sulfonate selected from the group of basic alkaline earth metal hydrocarbon sulfonate and basic aluminum hydrocarbon sulfonate, said concentrate being diluted with from 250 to 1,000 gallons of fuel oil.

9. A fuel oil normally susceptible to cause clogging due to the presence of cracked components and entrained moisture, having incorporated therewith a small amount, sufficient to inhibit said clogging tendencies, of a basic calcium hydrocarbon sulfonate and a minor amount sufficient to impart detergency to said composition of normal barium salt of alkyl phenol sulfide.

10. A fuel oil normally susceptible to cause clogging due to the presence of cracked components and entrained moisture, having incorporated therewith a small amount, sufficient to inhibit said clogging tendencies, of a basic calcium hydrocarbon sulfonate and a minor amount sufficient to impart detergency to said composition of normal calcium alkyl salicylate.

11. A fuel oil normally susceptible to cause clogging due to the presence of cracked components and entrained moisture, having incorporated therewith a small amount, sufficient to inhibit said clogging tendencies, of a basic calcium hydrocarbon sulfonate and a minor amount sufficient to impart detergency to said composition of sodium naphthenate.

12. A fuel oil normally susceptible to cause clogging due to the presence of cracked components and entrained moisture, having incorporated therewith a small amount, sufficient to inhibit said clogging tendencies, of a basic calcium hydrocarbon sulfonate and minor amounts of basic zinc stearate and normal calcium salt of alkyl phenol sulfide.

13. A fuel oil normally susceptible to cause clogging due to the presence of cracked components and entrained moisture, having incorporated therewith a small amount, sufficient to inhibit said clogging tendencies, of a basic calcium petroleum sulfonate and a minor amount sufficient to impart detergency to said composition of normal barium salt of alkyl phenol sulfide.

14. A fuel oil normally susceptible to cause

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clogging due to the presence of cracked components and entrained moisture, having incorporated therewith a small amount, sufficient to inhibit said clogging tendencies, of a basic calcium petroleum sulfonate and a minor amount sufficient to impart detergency to said composition of normal calcium alkyl salicylate.

15. A fuel oil normally susceptible to cause clogging due to the presence of cracked components and entrained moisture, having incorporated therewith a small amount, sufficient to inhibit said clogging tendencies, of a basic calcium petroleum sulfonate and a minor amount sufficient to impart detergency to said composition of sodium naphthenate.

16. A fuel oil normally susceptible to cause clogging due to the presence of cracked components and entrained moisture, having incorporated therewith a small amount, sufficient to inhibit said clogging tendencies, of a basic calcium petroleum sulfonate and minor amounts of basic zinc stearate and normal calcium salt of alkyl phenol sulfide.

17. A fuel oil normally susceptible to cause clogging due to the presence of cracked com-

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ponents and entrained moisture, having incorporated therewith a small amount, sufficient to inhibit said clogging tendencies, of a basic calcium petroleum sulfonate and a minor amount sufficient to impart detergency to said composition of sodium petroleum sulfonate.

CALMY WIES.

JOHN B. R. CARON.

EVERETT B. GLENNING.

REFERENCES CITED

The following references are of record in the file of this patent:

UNITED STATES PATENTS

Number	Name	Date
2,141,848	Adams et al.	Dec. 27, 1938
2,230,642	Fischer et al.	Feb. 4, 1941
2,301,795	Proell	Nov. 10, 1942
2,338,578	Downing et al.	Jan. 4, 1944
2,406,564	Rogers et al.	Aug. 27, 1946
2,409,687	Rogers et al.	Oct. 22, 1946
2,433,716	Smith	Dec. 30, 1947
2,483,505	Rogers et al.	Oct. 4, 1949