Patented Oct. 31, 1950

2,527,987

UNITED STATES PATENT OFFICE

2,527,987

FUEL OIL COMPOSITION

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

No Drawing. Application March 29, 1948, Serial No. 17,804

20 Claims. (Cl. 44—76)

1

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, caused 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 700° 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 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 for 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 turn, deposit on and clog the screens or filters used

2

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 particular type of an alkali metal salt of a petroleum sulfonic acid, which metal salt may be considered as acting as surface-active agents. If desired, a minor amount of a detergent and/or a 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.

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.

The properties of a caustic-treated catalytically cracked light gas oil, and of a 50–50 blend of an untreated catalytically cracked light gas oil and of a straight-run acid-treated gas oil, both of which have marked tendencies toward clogging screens, etc., are given in the following table:

Properties	50–50 Blend of Catalytically Cracked Light Gas Oil and Straight-Run Light Gas Oil	Catalytically Cracked Gas Oil
Gravity, °API	32.6	31.0
ASTM Dist, °F.:		
IBP	414	434
EBP	664	620
Sulfur, Per Cent W	0.839	0.783
Conradson Carbon Residue (10% Btms) Per Cent W	0.01	0.01
Pour Point, °F.	5	−5

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 alkali metal salts of petroleum sulfonic acids, which acids are preferably of high molecular weight and are derived from petroleum hydrocarbon crudes and fractions thereof which normally possess lubricating properties, which hydrocarbons are of the so-called mixed type, i. e. containing naphthenic type hydrocarbons. Specifically, the preferred petroleum sulfonic acids used to form the alkali metal salts are derived from naphthenic, Gulf Coastal or Mid-Continent oils.

A naphthenic oil which is particularly preferred for the production of said acids may be a distilled naphthenic oil having the following properties:

Viscosity SSU at 100° F.	400 to 900, and preferably 550
Viscosity index	50 to 60
Pour point, ° F.	10 to 15
Iodine No. (Hanus)	10
Unsulfonatable residue	80° min.

A Mid-Continent oil which may be used may have the following properties:

Gravity, ° API	26.0 to 29.5
Pour point, ° F.	25 to 10
Flash (C. O. C.), ° F.	410–445
Fire, ° F.	500
Viscosity SSU at 100° F.	400–540

Cracked and recycle stock of the gasoline or kerosene boiling range, as well as Pennsylvania or paraffinic oils, are generally unsuitable as starting materials for the manufacture of sulfonates of this invention.

According to the present invention, a naphthenic or Mid-Continent oil having a viscosity SSU (at 100° F.) in the range of from 400 to 900, may be sulfonated with sulfuric acid, oleum, chlorosulfonic acid, sulfur trioxide or their mixtures. After the oil has been sulfonated, the sludge formed is removed and the acid-treated oil containing the dissolved oil-soluble sulfonic acids may be neutralized with a solution of sodium hydroxide, or any other base of a suitable alkali metal, such as potassium, lithium, rubidium, or cesium, or mixtures thereof. The aqueous alkali solution thus formed is removed from the mixture, and the alkali metal salt of petroleum sulfonic

acid extracted with alcohol. The alcohol layer containing the sulfonate may be subjected to distillation or any other suitable treatment to remove the alcohol, and thus leave the sulfonate.

The sulfonated oil thus formed should have a molecular weight of from about 475 to about 650, and preferably from about 480 to about 570, and contain a plurality of cycloalkyl groups in the molecule.

In cases where the sulfonate is obtained from a naphthenic oil, the produce need not be subjected to a high degree of purification. However, if Mid-Continent oils, or blends of Mid-Continent and naphthenic oils, are used, it is preferable that the resultant oil-soluble sulfonated product be subjected to purification. This purification (which removes inorganic salts and other undesirable contaminants) may be carried out as follows: The crude sulfonate may be admixed with approximately an equal volume of a light hydrocarbon, such as a highly paraffinic hydrocarbon having a boiling range of from about 100° F. to about 260° F., and hydrocarbon layer removed by settling, decantation or the like, to produce the purified sulfonates as a distillation residue. Alternately, the highly paraffinic hydrocarbon may be added prior to neutralization of the alcohol—sulfonic acid mixture, and the entire mixture neutralized. The paraffinic hydrocarbon is then removed in the manner described above or by any other suitable means.

Analysis of the impurities present in sulfonates before and after purification is given below:

Impurities	Crude (Unpurified) Sulfonates (Per cent wt.)	Purified sulfonates (Per cent wt.)
Sodium sulfate	3.0–6.5	less than 0.1
Sodium hydroxide	0.3–3.5	less than 0.1
Water	5.6–9.6	0.2–7.8

Thus, petroleum sulfonates produced from 400 SSU at 100° F. Mid-Continent oil may be purified in the following manner: The purification of the sulfonates can be carried out by extracting the sulfonates from the acid alcoholic sludge with a low boiling highly paraffinic hydrocarbon and neutralizing the mixture with 30° Bé. caustic. The neutralization separates the mixture into two layers. The bottom layer containing the caustic sludge layer is drawn off. The top layer is drawn off. The top layer is distilled to remove the light hydrocarbon and the purified sulfonates remain as heavy bottoms. Analysis of the purified product was as follows:

	Per cent
Sodium petroleum sulfonate obtained from a 400 SSU at 100° F. (Mid-Continent raffinate)	53.6
Oil	46.0
Free alkali	0.0
Sodium sulfate	0.0
Water and alcohol	0.4

Oil-soluble alkali metal petroleum sulfonates from naphthenic, Gulf Coast and/or Mid-Continent Stocks, may be also obtained by other processes, 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 2,406,753.

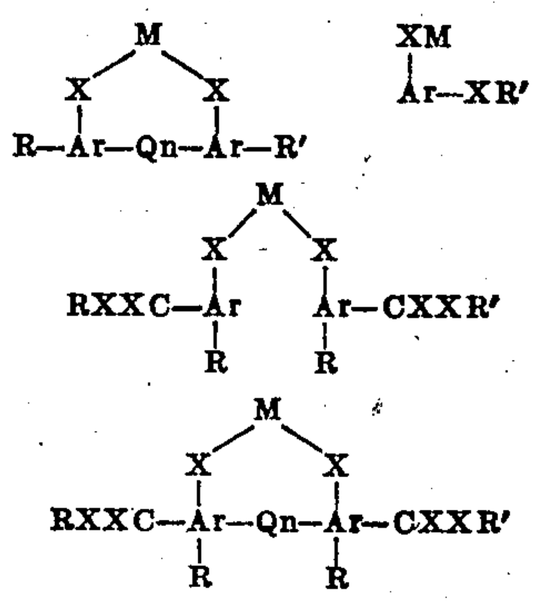
The amount of alkali metal salt of the petroleum sulfonic acid derived from a non-paraffinic petroleum stock defined above, which salt

is to be present 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 also be used.

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 invention 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, thio-carbamates, xanthates, etc., may be used.

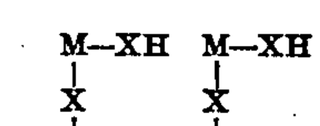
Particularly preferred detergents are the salts of alkyl substituted phenol sulfides, or their selenide and/or their telluride equivalents. These phenolic salts may be represented by the general formulas:



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, Cr, Sn, Mo, etc. Alkaline earth metals are particularly preferred because of their solubility in hydrocarbons and their excellent detergent properties.

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



wherein the symbols are the same as referred to in the previous formulas. These basic salts may be formed by reacting the aromatic acidic compound with more than the amount of metal oxide or hydroxide necessary to form the normal salt.

The following are illustrative examples of the above detergents: barium tertiary-octyl phenol sulfide, its disulfide, barium di-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 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 mono-decyl ether, etc.; also dipropylene glycol mono ethyl 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, e. g. hexylene glycol, decylene glycols, 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 n-butyl ether, ethylene glycol mono-isobutyl ether, ethylene glycol mono-tert-butyl ether, ethylene glycol mono-hexyl-butyl 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:

	General Range	Preferred
	Per cent	*Per cent*
Alkali metal salt of petroleum sulfonic acid of high molecular weight	10–20	15
Detergent e. g. salt of alkyl phenol sulfide	0–10	10
Drying agent	0–50	
Fuel oil	20–90	75

Specific base compositions may be illustrated by the following examples:

Composition A

	Per cent
Sodium petroleum sulfonate derived from a naphthenic oil	15
Ba salt of alkyl phenol disulfide	10
50–50 blend of catalytically cracked light gas oil and straight run acid-treated gas oil	75

Composition B

	Per cent
Sodium petroleum sulfonate derived from a 400 SUS at 100° F. Mid-Continent crude	15
Barium salt of alkyl phenol disulfide	10
Caustic treated catalytically cracked light gas oil	75

Composition C

	Per cent
Sodium petroleum sulfonate derived from a 400 SUS at 100° F. Mid-Continent crude	20
No. 2 fuel oil comprising a mixture of straight run and cracked gas oil having an end distillation point of from about 580° F. to 610° F.	80

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

Components:[1]								
Surface Active Agent								
Na petroleum sulfonate from non-paraffinic petroleum stock	x	x		x		x		x
K petroleum sulfonate from non-paraffinic petroleum stock			x				x	
Li petroleum sulfonate from non-paraffinic petroleum stock					x			
Detergent:								
Ba salt of alkyl phenol sulfide			x		x			
Ca salt of alkyl phenol sulfide	x							
Ca alkyl salicylate		x						
Na alkyl salicylate								
Ba alkyl salicylate						x		
Na petroleum naphthenate				x				
Ca petroleum naphthenate								
Ethanolamine oleate							x	
Ethanolamine stearate								x
Drying agent:								
Diethylene glycol monobutyl ether	x		x	x	x			
Diethylene glycol monoethyl ether						x		
Ethylene glycol monobutyl ether								
Cetylene glycol								x
Dipropylene glycol							x	

[1] 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 to about 100 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

Alkali metal salt of petroleum sulfonic acid derived from a non-paraffinic oil, from about 0.0025% to about 0.01% (and 0.025% when calculated that 1 pint of the concentrate containing 20% sulfonate is used for 100 gallons of fuel oil); 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

Approximately 5 gallons of an undoped fuel oil as defined in Composition A 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. A decrease in flow rate of approximately 69.5% for this undoped fuel oil was observed, and the screen, on examination, was found to be stained and coated with sludge.

Example II

The undoped fuel oil used in Example I (i. e. a 50–50 blend of a catalytically cracked light gas oil and of a straight-run acid-treated gas oil) was doped with Composition A in an amount equal to approximately 1 pint of Composition A per 250 gallons of the fuel oil. The thus doped fuel was then tested as described in Example I. At the end of the test period, no decrease in flow rate was observed, and the screen was perfectly clean.

Example III

Approximately 5 gallons of an undoped caustic-treated catalytically cracked light gas oil was treated and tested in the same manner as described in Example I. At the end of the test period a decrease in flow rate of approximately 85% was observed, and the screen was found to be stained and coated with sludge.

Example IV

The undoped fuel oil of Example III was doped with Composition B in the same amount as noted in Example II, and the above described test repeated. At the end of the test period no decrease in flow rate was observed, the screen being found to be perfectly clean.

Example V

Approximately 5 gallons of an undoped fuel identified as No. 2 fuel oil in Composition C, was treated and tested in the same manner as described in Example I. At the end of 15 minutes the decrease in flow rate was about 83.5%, and the test was therefore stopped On examination, the screen was found to be badly stained and heavily coated with sludge.

Example VI

The undoped fuel oil of Example V was doped with Composition C in the same amount as noted in Example II, and the test repeated. At the end of the fuel test period no decrease in flow rate was observed, and the screen was clean.

Example VII

Two fuel tanks were cleaned with acetone and the entire burner system flushed with kerosene. One tank was charged with about 125 gallons of an undoped fuel oil, while the other tank was charged with 125 gallons of fuel oil doped with a half pint of Composition A. Both the doped and undoped fuels were clouded by passage of steam prior to testing. The tests were conducted for 28 days by circulating the oil through burner systems. The condition of each oil, as well as the condition of the equipment at the end of the tests, were as follows:

	Area plugged in sq. in.	Per cent of this area plugged
Blend of catalytically cracked and straight-run acid-treated gas oil	7	9
Same oil (125 gallons) and 1½ pts. of Composition A	0	0

Example VIII

An undoped caustic-treated catalytically cracked light gas oil was used in this test. The first test was effected using about 125 gallons of this material, while for the second test a like quantity of this fuel was first doped with Composition B employed in an amount equal to 1

pint of said Composition B per 1000 gallons of the fuel oil. Both oils were clouded by steaming and aged by maintaining them at 150° F. for a period of 24 hours. Each oil was circulated through screens for 24 hours at a rate of about 25 gallons per hour. The conditions of the screens at the end of these tests were as follows:

	Area plugged in sq. in.	Per cent of this area plugged
Caustic treated catalytically cracked light gas oil	13	85
Same oil (1000 gallons)+1 pint of Composition B	0	0

To compositions of this invention may be added minor amounts of foam inhibitors, such as a silicone liquid, e. g., dimethyl silicone, fluoro organic compounds, fluoro paraffins, salts of alkyl alkylene phosphates, and the like. Compositions of this invention are non-corrosive and do not interfere with the function of the fluid in which they are dispersed.

We claim as our invention:

1. An anti-clogging concentrate adapted to be added to a hydrocarbon distillate fuel from the group consisting of cracked and mixtures of cracked and straight run fuel oils and normally susceptible toward clogging, said concentrate comprising 15% by weight of oil-soluble sodium salt of oil-soluble petroleum sulfonic acid having a molecular weight of from about 475 to about 650 and derived from a naphthenic petroleum stock, 10% by weight of a barium salt of alkyl phenol disulfide, and 75% by weight of a 50–50 blend of catalytically cracked light gas oil and of a straight run acid treated gas oil.

2. An anti-clogging concentrate adapted to be added to a hydrocarbon fuel from the group consisting of cracked and mixtures of cracked and straight run fuel oils and normally susceptible towards clogging, said concentrate comprising 15% of oil-soluble sodium salt of oil-soluble petroleum sulfonic acid having a molecular weight of from about 475 to about 650 and derived from a naphthenic petroleum stock, 10% of a barium salt of alkyl phenol disulfide, and 75% of a caustically treated catalytically cracked light fuel oil.

3. An anti-clogging concentrate adapted to be added to a hydrocarbon fuel from the group consisting of cracked and mixtures of cracked and straight run fuel oils and normally susceptible towards clogging, said concentrate comprising 15% of oil-soluble sodium salt of oil-soluble petroleum sulfonic acid having a molecular weight of from about 475 to about 650 and derived from Mid-Continent crude distillate fraction having a Saybolt viscosity at 100° F. of from 400–600, 10% of a barium salt of alkyl phenol disulfide and 75% of a caustic treated catalytically cracked light gas oil.

4. An anti-clogging concentrate adapted to be added to a hydrocarbon fuel from the group consisting of cracked and mixtures of cracked and straight run fuel oils and normally susceptible towards clogging, said concentrate consisting essentially of a major amount of hydrocarbon fuel oil, between about 10 and 20% of an oil-soluble alkali metal salt of oil-soluble petroleum sulfonic acid derived from a naphthenic petroleum stock and less than 10% of a polyvalent metal salt of an acidic hydroxy aromatic compound.

5. An anti-clogging concentrate adapted to be added to a hydrocarbon distillate fuel from the group consisting of cracked and mixtures of cracked and straight run fuel oils and normally susceptible towards clogging, said concentrate comprising a major amount of a hydrocarbon fuel from the group consisting of cracked and mixtures of cracked and straight run fuel oils and a minor amount of from about 10 to 20% of an oil-soluble alkali metal salt of oil-soluble petroleum sulfonic acid having a molecular weight of from about 475 to about 650 and derived from petroleum stocks consisting of the group of Naphthenic, Gulf Coastal, Mid-Continent crude distillate fractions and their mixtures and having a Saybolt Universal viscosity at 100° F. of above 400, and a minor amount of a polyvalent salt of an acidic hydroxy aromatic compound.

6. An anti-clogging concentrate adapted to be added to a liquid hydrocarbon fuel from the group consisting of cracked and mixtures of cracked and straight run fuel oils and containing entrained moisture and which is normally susceptible towards clogging, comprising a major amount of a hydrocarbon fuel from the group consisting of cracked and mixture of cracked and straight run fuel oils containing entrained moisture and a minor amount of from about 10 to 20% of an oil-soluble alkali metal salt of oil-soluble petroleum sulfonic acid having a molecular weight of from about 475 to about 650 and derived from petroleum stocks consisting of the group of Naphthenic, Gulf Coastal, Mid-Continent crude distillate fractions and their mixtures and having a Saybolt Universal viscosity at 100° F. of above 400, and a minor amount of a polyvalent salt of an acidic hydroxy aromatic compound.

7. An anti-clogging concentrate adapted to be added to a hydrocarbon fuel from the group consisting of cracked and mixtures of cracked and straight run fuel oils and normally susceptible towards clogging, said concentrate comprising a major amount of a hydrocarbon fuel oil containing a substantial amount of cracked hydrocarbon fractions and a minor amount of from about 10 to 20% of an oil-soluble alkali metal salt of oil-soluble petroleum sulfonic acid having a molecular weight of from about 475 to about 650 and derived from petroleum stock consisting of the group of Naphthenic, Gulf Coastal, Mid-Continent crude distillate fractions and their mixtures and having a Saybolt Universal viscosity at 100° F. of above 400, and a minor amount less than 10% of a barium salt of alkyl phenol disulfide.

8. An anti-clogging concentrate adapted to be added to a hydrocarbon fuel oil from the group consisting of cracked and mixtures of cracked and straight run fuel oils normally susceptible towards clogging, said concentrate comprising a major amount of a hydrocarbon fuel oil and a minor amount sufficient to inhibit clogging of an oil-soluble alkali metal salt of oil-soluble petroleum sulfonic acid having a molecular weight of from about 475 to about 650 and derived from a naphthenic petroleum stock and a polyvalent metal salt of an acidic hydroxy aromatic compound.

9. An anti-clogging concentrate adapted to be added to a hydrocarbon fuel oil from the group consisting of cracked and mixtures of cracked and straight run fuel oils normally susceptible towards clogging, said concentrate consisting essentially of a major amount of a hydrocarbon distillate fuel oil and a minor amount sufficient to inhibit clogging of an oil-soluble sodium salt of oil-soluble petroleum sulfonic acid having a

molecular weight of from about 475 to about 650 and derived from a naphthenic petroleum stock.

10. An anti-clogging concentrate adapted to be added to a hydrocarbon fuel oil from the group consisting of cracked and mixtures of cracked and straight run fuel oils normally susceptible towards clogging, said concentrate consisting essentially of a major amount of a hydrocarbon distillate fuel oil and a minor amount sufficient to inhibit clogging of an oil-soluble alkali metal salt of oil-soluble petroleum sulfonic acid having a molecular weight of from about 475 to about 650 and derived from a naphthenic petroleum stock.

11. A non-clogging fuel oil from the group consisting of cracked and mixtures of cracked and straight run fuel oils and normally susceptible to cause clogging containing in combination therewith from about 0.0025% to about 0.01% of oil-soluble sodium salt of oil-soluble petroleum sulfonic acid having a molecular weight of from about 475 to about 650 and derived from a naphthenic petroleum stock and from about 0.0025% to about 0.0042% of a barium salt of alkyl phenol disulfide.

12. A non-clogging fuel oil from the group consisting of cracked and mixtures of cracked and straight run fuel oils and normally susceptible to cause clogging containing in combination therewith from about 0.0025% to about 0.01% of oil-soluble alkali metal salt of oil-soluble petroleum sulfonic acid having a molecular weight of from about 475 to about 650 and derived from a naphthenic petroleum stock and from about 0.0025% to about 0.0042% of a salt of alkyl phenol disulfide.

13. A non-clogging fuel oil from the group consisting of cracked and mixtures of cracked and straight run fuel oils and normally susceptible to cause clogging consisting essentially of said fuel oil and in combination therewith from about 0.0025% to about 0.01% of oil-soluble sodium salt of oil-soluble petroleum sulfonic acid having a molecular weight of from about 475 to about 650 and derived from a naphthenic petroleum stock.

14. A non-clogging fuel oil from the group consisting of cracked and mixtures of cracked and straight run fuel oils and normally susceptible to cause clogging consisting essentially of said fuel oil and in combination therewith from about 0.0025% to about 0.01% of oil-soluble alkali metal salt of oil-soluble petroleum sulfonic acid derived from a naphthenic petroleum stock.

15. A non-clogging fuel oil composition comprising a normally liquid hydrocarbon fuel oil containing substantial cracked components and minute amounts of entrained moisture, said fuel being normally susceptible to cause clogging, and in combination therewith from about 0.0025% to about 0.01% of oil-soluble sodium salt of oil-soluble petroleum sulfonic acid having a molecular weight of from about 475 to about 650 and derived from petroleum stocks consisting of the group of Naphthenic, Gulf Coastal, Mid-Continent distillate fractions and their mixtures and having a Saybolt Universal viscosity at 100° F. of above 400 and from about 0.0025% to about 0.0042% of a barium salt of alkyl phenol disulfide.

16. A non-clogging fuel oil composition comprising a normally liquid hydrocarbon fuel oil containing substantial cracked components and

minute amounts of entrained moisture, said fuel being normally susceptible to cause clogging, and in combination therewith from about 0.0025% to about 0.01% of oil-soluble sodium salt of oil-soluble petroleum sulfonic acid having a molecular weight of from about 475 to about 650 and derived from petroleum stocks consisting of the group of Naphthenic, Gulf Coastal, Mid-Continent distillate fractions and their mixtures and having a Saybolt Universal viscosity at 100° F. of above 400.

17. A non-clogging fuel oil comprising a normally liquid hydrocarbon fuel oil containing substantial cracked components and being normally susceptible to cause clogging in the presence of minute amounts of entrained moisture and in combination therewith from about 0.0025% to about 0.025% of oil-soluble alkali metal salt of oil-soluble petroleum sulfonic acid derived from a naphthenic petroleum stock.

18. A non-clogging fuel oil comprising a normally liquid hydrocarbon fuel oil containing substantial cracked components and being normally susceptible to cause clogging in the presence of minute amounts of entrained moisture and in combination therewith from about 0.0025% to about 0.0042% of a polyvalent metal salt of an acidic hydroxy aromatic compound.

19. An anti-clogging concentrate adapted to be added to a normally liquid hydrocarbon fuel oil containing substantial cracked components and being normally susceptible to cause clogging in the presence of minute amounts of entrained moisture, said concentrate consisting essentially of a major amount of a liquid hydrocarbon distillate having a boiling range within the range of from 300° to 700° F. and a minor amount sufficient to inhibit clogging of an oil-soluble alkali metal salt of oil-soluble petroleum sulfonic acid derived from a naphthenic stock.

20. An anti-clogging concentrate adapted to be added to a normally liquid hydrocarbon fuel oil containing substantial cracked components and being normally susceptible to cause clogging in the presence of minute amounts of entrained moisture, said concentrate consisting essentially of a major amount of a liquid hydrocarbon distillate having a boiling range within the range of from 300° to 700° F. and a minor amount sufficient to inhibit clogging of an oil-soluble alkali metal salt of oil-soluble petroleum sulfonic acid derived from a naphthenic stock and a polyvalent metal salt of an acidic hydroxy aromatic compound.

JOHN B. R. CARON.
CALMY WIES.
EVERETT B. GLENDENNING.

REFERENCES CITED

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

UNITED STATES PATENTS

Number	Name	Date
2,125,305	Murphy	Aug. 2, 1938
2,294,145	Winning	Aug. 25, 1942
2,336,074	Cook	Dec. 7, 1943
2,361,804	Wilson	Oct. 31, 1944
2,362,292	McNab	Nov. 7, 1944
2,454,825	Faust	Nov. 30, 1948
2,454,828	Faust	Nov. 30, 1948

Certificate of Correction

atent No. 2,527,987 October 31, 1950

JOHN B. R. CARON ET AL.

It is hereby certified that error appears in the printed specification of the above numbered patent requiring correction as follows:

Column 12, line 26, after the word "therewith" insert *from about 0.0025% to about 0.01% of oil-soluble alkali metal salt of oil-soluble petroleum sulfonic acid derived from a naphthenic petroleum stock and*;

and that the said Letters Patent should be read as corrected above, so that the same may conform to the record of the case in the Patent Office.

Signed and sealed this 20th day of February, A. D. 1951.

[SEAL]

THOMAS F. MURPHY,
Assistant Commissioner of Patents.