

UNITED STATES PATENT OFFICE

2,553,183

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 July 3, 1948,
Serial No. 37,085

17 Claims. (Cl. 44-71)

1

This invention pertains to improvement of 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, tanks, Diesel and combustion engines, and 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 700° F., and particularly those 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, are further examples of the type of oils which under conditions described herein have a tendency to clog screens or filters, 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 fuel oil storage tanks, which latter may be connected to burner systems or engines, etc. The stored fuel generally comes in contact with air, moisture, etc., which cause formation and precipita-

2

tion of sludge materials, the latter depositing on and clogging the screens or filters used for protecting the burners or engines using such fuel oils.

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, particularly in cracked hydrocarbon fuels. It is still another object to provide distillate fuel oils, particularly fuel oils obtained during cracking of hydrocarbons, which fuel oils 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 formed in fuel oil systems. Still another object is to provide a particular type of distillate fuel oil composition or a blend thereof, which is non-corrosive, stable, and effective for removing sludge and for cleaning metal surfaces.

The above and other objects of this invention may be attained by dispersing, admixing with or dissolving in hydrocarbon fuel oils (which normally have a tendency to cause clogging or plugging of screens or the like), a minor amount, which amount, however, is sufficient to inhibit said tendencies of one or more surface-active glyoxalidines, and derivatives thereof. If desired, a minor amount of a detergent and/or solutizer may also be added to the composition.

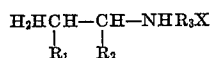
The hydrocarbon distillate fuel oils in which the active ingredient and/or ingredients of this invention are dispersed or dissolved may be treated or untreated cracked fuel oils, or mixtures of cracked fuels with straight run fuel oils, said fuel oils having components normally distilling from about 300° F. to about 700° F. Preferred fuels have a boiling range of from about 340° F. to about 700° F., and particularly from about 400° F. to about 675° F. 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., or mixtures of said cracked fuels with the corresponding or like straight run hydrocarbon fractions.

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
ASTM dist., °F.: -----	
IBP -----	400-500
EBP -----	600-700
Sulfur, per cent w -----	0.5-1.05
Carbon residue (10 Btms.) per cent w -----	0.1-1.4
Pour point, °F -----	0-15

Glyoxalidines and derivatives thereof which may be prepared for instance by reacting a polyamine or a hydroxyl alkyl alkylene polyamine with a higher carboxylic acid at an elevated temperature of about 120° C. and preferably at between about 225° C. and about 300° C.

The polyamines which are used to prepare the glyoxalidines may be represented by the general formula:



wherein one R represents hydrogen or R₁ and R₂ can represent hydrogen or a lower alkyl group and R₃ represents an alkylene group, a lower alkyl substituted alkylene group, or a radical of the structure —CHR₁CHR₂(NHCHR₁CHR₂)_y— where R₁ also represents hydrogen or a lower alkyl group and y is an integer; and X represents a OH, SH, SeH, TeH, NH₂ group or an amino alkylene substituent imino group. Specifically, the polyamines which can be used are: ethylene diamine, diethylene triamine, triethylene tetraamine, tetraethylene pentamine, tetramethyl methylene diamine, propylene diamine, dipropylene triamine, tripropylene tetraamine, N-n-dodecyl diethylene triamine, N-octyle ethylene diamine, hydroxy ethyl-ethylene diamine, hydroxy isopropyl propylene diamine, hydroxy ethyl diethylene triamine, hydroxy ethyl triethylene tetraamine, N-beta-hydroxy-propyl propylene diamine and the like.

Acids which are reacted with the above polyamines to form the glyoxalidines may include: capric, nonanoic, hendecanoic, lauric, n-tridecanoic, myristic, pentadecanoic, palmitic, margaric, stearic, arachidic, behenic, heneicosoic, chuytinic, lignoceric, pentacosic, cerotic, montanic, palmitoleic, oleic, gadoleic, erucic, cetoleic, myristoleic, lanopalmic, hydroxy stearic, dihydroxy stearic, ricinoleic acids, linoleic, elaidic, linolenic, clupanodonic acids and the like. In addition fatty acids obtained from animal, vegetable and fish oils can be used and the fatty acids derived from the following fixed fatty oils are particularly preferred: coconut oil, palm kernel oil, rape oil, linseed oil, soya bean oil, sunflower oil, perilla oil, tung oil, whale oil, cod and cod liver oil, marine animal oil, various fish oils such as herring oil, sardine oil and the like. Instead of using the free fatty acids, their salts, esters or amides can be used.

Specific glyoxalidines which may be used in compositions of this invention include:

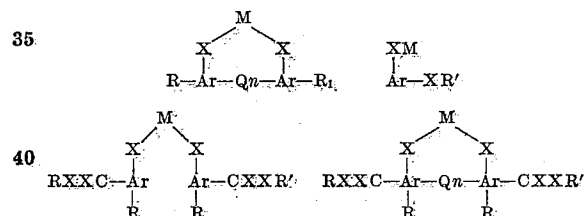
- 1-amino ethyl 2-heptadecenyl glyoxalidine
- 1-amino ethyl 2-heptadecyl glyoxalidine
- 1-amino ethyl 2-undecyl glyoxalidine
- 1-amino isopropyl 2-heptadecenyl-5-methyl glyoxalidine
- 1-amino isopropyl 2-heptadecyl-5-methyl glyoxalidine
- 1-hydroxy ethyl-2-heptadecyl glyoxalidine
- 1-hydroxy ethyl-2-heptadecyl glyoxalidine
- 1-hydroxy ethyl-2-undecyl glyoxalidine
- 1-hydroxy isopropyl-2-heptadecenyl-4-methyl glyoxalidine

The glyoxalidine having free amino group may be reacted with acid to form salts, while those glyoxalidines having free hydroxy or other groups can be esterified, with either inorganic or organic mono or polycarboxylic acids or reacted to form salts of soaps of alkali, alkaline earth metals, ammonium, amine or quaternary ammonium compounds.

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 and aid in inhibiting or preventing the settling and adhering of impurities and sludge to surfaces and 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 metals and organic nitrogen base salts of various organic acids. The acidic portion of such detergents may be naphtheneic acid, sulfonic acids, aromatic and hydroxy aromatic carboxylic acids, aliphatic acids, said acids containing, if desired substituent groups, e. g. an amino, hydroxide, mercapto, halo and sulfur groups and the like. Also phenates, alcoholates, carbamates, thiocarbamates, xanthates, etc. may be used.

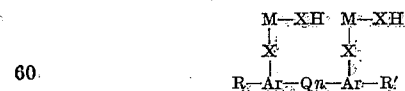
Particularly preferred class of detergents are the salts of alkyl substituted phenol sulfides or its selenide and/or telluride equivalent. These phenolic salts may be represented by the general formulas:



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 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 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 be formed by reacting the aromatic acidic compounds 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 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 may vary from between about 5 and 15% and preferably is kept below 10%.

Another preferred class of detergents comprises 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 various 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 2,406,753.

The metal salts of the specific type of petroleum sulfonic acid under discussion, or the other types of detergents, may be added to the concentrate or base in amounts of from about 5% to about 15%, and preferably in amounts 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 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 mono-methyl, 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 such as hexylene glycol, decylene glycol, 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 mono-tert-butyl ether, ethylene glycol mono-butyl ether, propylene glycol mono-ethyl ether, propylene glycol mono-isoamyl ether, etc. Also 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 following is a general formula of a base composition of this invention:

	Per cent
Surface active agent e. g. glyoxalidines and derivatives thereof	4-20
Detergent e. g. phenate, sulfonate, etc.	0-10

Drying agent e. g. glycol-ether	0-50
Hydrocarbon fuel oil	Balance

Specific base (concentrate) compositions may be illustrated by the following examples:

Composition A

	Per cent
1-hydroxy ethyl-2-heptadecenyl glyoxalidine	10
Hydrocarbon fuel oil	90

Composition B

	Per cent
1-hydroxy ethyl-2-heptadecyl glyoxalidine	15
Sodium petroleum sulfonate	10
Hydrocarbon fuel oil	75

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 above compositions, for example per 250 gallons of fuel would correspond to approximately the following concentration of the active ingredients: Organic nitrogenous compounds as described, 0.0025%; detergent 0 to about 0.0025%; drying agent, 0 to about 0.265%.

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

The following illustrates the effectiveness of compositions of this invention as sludge inhibitors and anti-clogging agents.

Example I

To a number of sample bottles each containing approximately 50 cc. of fuel oil normally susceptible to cause clogging a minute amount of about 0.15 cc. of water was added and also to each sample bottle about 0.05% of a specific base composition as noted in the table below was also added. The bottles were shaken thoroughly and then permitted to stand for about one hour. Suspension properties of water and inert particles were observed and noted after one hour. After one hour of standing the bottles were shaken again and the contents poured into a very fine strainer container. Wetting and drainage properties on the bottle were observed just before and after removal of contents. The time of efflux of the composition was noted for each composition and the condition of the strainer observed.

Example II

Another test, the results of which are also tabulated below, in order to determine the effectiveness of compositions of this invention for anti-sludging and clogging properties was conducted in the following manner: About 0.05% of base compositions of this invention was added to fuel oils containing entrained moisture. The samples were allowed to age for two days. These samples were then shaken and evaluated for their anti-clogging properties, as related in the preceding paragraph.

0.05% or less base composition as noted in fuel oil containing entrained moisture	Properties evaluated immediately after adding concentrate to fuel oil Example I			Same properties after aging of doped fuel oil Example II		
	Strainer	Drainage	Suspension	Strainer	Drainage	Suspension
Composition A	Excellent	Good	Good	Fair	Fair	Fair
Undoped Fuel Oil	Poor	Poor	Poor	Poor	Poor	Poor

To compositions of this invention may be added minor amounts of a foaming inhibitor such as silicon liquids, e. g. dimethyl silicone, fluoro organic compounds, chloro paraffins, salts of alkyl alkylene phosphates and the like. Compositions of this invention may be used to remove deposits, formed on metal surfaces such as in tubes, evaporators, heat exchangers, distillation and cracking equipment and the like. They are non-corrosive and do not interfere with the functioning of the liquid in which dispersed.

It is to be understood that while the features of the invention have been described and illustrated in connection with certain specific examples, this invention, however, is not to be limited thereto or otherwise restricted, except by the prior art and the scope of the appended claims.

We claim as our invention:

1. 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 1-aminoethyl-2-heptadecenyl glyoxalidine.

2. 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 1-aminoethyl-2-heptadecenyl glyoxalidine and about 0.0025% of alkali metal petroleum sulfonate.

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 1-aminoethyl-2-heptadecenyl glyoxalidine, and about 0.0025% of metal salt of alkyl phenol disulfide.

4. An anti-clogging concentrate adapted to be added to a hydrocarbon fuel oil containing cracked components, said concentrate consisting essentially of a major amount of a liquid hydrocarbon distillate fraction and 10% to 20% of 1-amino-ethyl-2-heptadecenyl glyoxalidine.

5. An anti-clogging concentrate adapted to be added to a hydrocarbon fuel oil containing cracked components, said concentrate consisting essentially of a major amount of a liquid hydrocarbon distillate fraction and 10% to 20% of 1-amino-ethyl-2-heptadecenyl glyoxalidine and a metal salt of alkyl phenol disulfide.

6. An anti-clogging concentrate adapted to be added to a hydrocarbon fuel oil containing cracked components, said concentrate comprising as an essential ingredient a major amount of a liquid hydrocarbon distillate fraction and 10-20% by weight of a glyoxalidine bearing at least one higher aliphatic hydrocarbon radical and in addition thereto a radical of the group consisting of lower amino alkyl and lower hydroxy alkyl substituents and salts thereof.

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 glyoxalidine bearing at least one higher aliphatic hydrocarbon radical and in addition thereto a radical of the group consisting of lower amino alkyl and lower hydroxy alkyl substituents and salts thereof.

8. A concentrate according to claim 6 containing in addition up to 10% by weight of a metal salt of an alkyl phenol disulfide.

9. A concentrate according to claim 6 containing in addition thereto up to 50% by weight of a glycol ether as a drying agent.

10. A non-clogging fuel oil containing entrained moisture and normally susceptible to cause clogging containing in combination therewith about 0.002% to 0.005% of 1-aminoethyl-2-heptadecenyl glyoxalidine and about 0.0025% of sodium petroleum sulfonate.

11. A non-clogging fuel oil containing entrained moisture and normally susceptible to cause clogging containing in combination therewith about 0.002% to 0.005% of 1-aminoethyl-2-heptadecenyl glyoxalidine and about 0.0025% of barium alkyl phenol disulfide.

12. An anti-clogging concentrate adapted to be added to a hydrocarbon fuel oil containing cracked components, said concentrate consisting essentially of a major amount of a liquid hydrocarbon distillate fraction and 10% to 20% of 1-aminoethyl-2-heptadecenyl glyoxalidine and an alkali metal petroleum sulfonate.

13. An anti-clogging concentrate adapted to be added to a hydrocarbon fuel oil containing cracked components, said concentrate consisting essentially of a major amount of a liquid hydrocarbon distillate fraction and 10% to 20% of 1-aminoethyl-2-heptadecenyl glyoxalidine and barium salt of alkyl phenol disulfide.

14. An anti-clogging concentrate adapted to be added to a hydrocarbon fuel oil containing cracked components, said concentrate consisting essentially of a major amount of a liquid hydrocarbon distillate fraction and 10% to 20% of 1-aminoethyl-2-heptadecenyl glyoxalidine and sodium petroleum sulfonate.

15. A concentrate according to claim 6 containing in addition up to 10% by weight of an alkali metal petroleum sulfonate.

16. 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 1-hydroxyethyl-2-heptadecenyl glyoxalidine.

17. A non-clogging fuel oil containing entrained moisture and normally susceptible to cause clogging containing in combination therewith about 0.002% to 0.005% of 1-hydroxyethyl-2-heptadecenyl glyoxalidine and about 0.0025% of sodium petroleum sulfonate.

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
2,249,626	Cook et al.	July 15, 1941
2,369,490	Proell	Feb. 13, 1945