Patented July 20, 1954

2,684,292

UNITED STATES PATENT OFFICE

2,684,292

FUEL OIL COMPOSITION

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No Drawing. Application March 13, 1951, Serial No. 215,384

8 Claims. (Cl. 44—68)

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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 of 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 precipitation of sludge materials, the latter depositing on and

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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 inihibit said tendencies of one or more surface-active, non-ash forming oil-soluble amines, amides thereof, and the like, said nitrogen-containing compounds having one or more than one hydrocarbyl radical having at least 14 carbon atoms; said hydrocarbyl radical can contain polar substituents such as halo, cyano, sulfo, keto, carboxyl, hydroxyl, thiol, etc.

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 percent W	0.5–1.05
Carbon residue (10 Btms) percent W	0.1–0.4
Pour point, °F	0–15

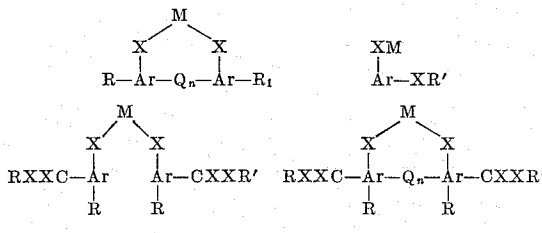
The oil soluble amines or derivatives thereof which possess the above-outlined properties include: mono, di and tri tetradecyl, hexadecyl, octadecyl, octadecadienyl, oleyl, ricinoleyl, abietyl amines; wax amines prepared by chlorination of paraffin wax and ammonolysis of the product: cyclo-aliphatic amines, e. g. tetradecyl cyclohexylamine, octadecyl cyclohexylamine, octadecyl dicyclohexylamine; heterocyclic amines, e. g., octadecenyl morpholine, octadecenyl piperidine, octadecenyl pyridine, etc.; polyamines, e. g., N-n-hexadecyl diethylene triamine, N-octadecenyl ethylene diamine and the like.

Preferred nitrogen compounds are: octadecylamine, dioctadecylamine, trioctadecylamine, oleylamine, dioleylamine, trioleylamine, dihexadecylamine, dihexadecyloctadecylamine, hexadecyloctadecylamine, tetradecylcyclohexylamine, octadecylmorpholine; octadecylamine oil-soluble petroleum sulfonate, trioctadecylamine oil-soluble petroleum sulfonate, octadecyl morpholine oil-soluble petroleum sulfonate.

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 naphthenic 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.

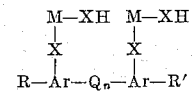
Particularly preferred class of detergents are the salts of alkyl substituted phenol sulfides or its selenide and/or telluride equivalent. These phenolic salts may be represented by the general formulas:



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 or a methylene group, 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 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, Ca salt of octylphenol-formaldehyde condensation product, etc. The amount of detergent salt used may vary from between about 5 and 15% and preferable 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, 2,357,366, 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-ether, 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, dibu-

tylene 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:

Surface active agent e. g. high molecular weight amines as defined above	4–20%
Detergent e. g. phenate, metal 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
Octadecylamine	4
Ethylene glycol monobutyl ether	10
Hydrocarbon fuel oil	86

Composition C

	Per cent
Dodecyl diethylene triamine	10
Hydrocarbon fuel oil	90

Composition E

	Per cent
Dodecyl diethylene triamine	15
Barium salt of alkyl phenol disulfide	10
Hydrocarbon fuel oil	75

Composition G

	Per cent
Octadecylamine	15
Barium salt of alkyl phenol disulfide	5
Sodium petroleum sulfonate	5
Hydrocarbon fuel oil	75

Composition H

	Per cent
Dodecyl diethylene triamine	15
Barium salt of alkyl phenol disulfide	5
Sodium petroleum sulfonate	5
Hydrocarbon fuel oil	75

Compositions of this invention are generally mixed in amounts of one pint or less of the concentrate with from 200 or 250 to about 1000 gallons of fuel oil. Preferred formulation is to add one pint of the concentrate per 250 gallons of fuel oil.

Thus, for example, on a percentage basis of fuel oil used, one pint of any one of the above compositions, per 250 gallons of fuel oil, would correspond to approximately the following concentration of the active ingredients: nitrogen-containing compounds as described 0.002%; detergent 0 to about 0.002%, drying agent 0 to about 0.26%.

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.	Excellent.	Excellent.	Excellent.	Excellent.	Excellent.
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 wtih 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 of this invention, however, is not to be limited thereto or otherwise restricted, except by the prior art and the scope of the appended claims.

This application is a continuation-in-part of application Serial No. 37,085, filed July 3, 1948, which has matured into U. S. Patent 2,553,183.

We claim as our invention:

1. A finished non-ash distillate fuel oil containing a substantial amount of cracked com-

ponents and entrained moisture to which non-clogging properties have been imparted by the incorporation therein from about 0.002% to about 0.05% by weight of octadecylamine.

2. A finished non-ash distillate fuel oil containing a substantial amount of cracked components and entrained moisture to which non-clogging properties have been imparted by the incorporation of about 1 pint of a concentrate consisting of a hydrocarbon oil containing from about 4% to about 20% by weight of an oil-soluble aliphatic amine having at least one alkyl chain of at least 14 carbon atoms and up to 18 carbon atoms, to 200 to 1000 gallons of fuel oil.

3. A non-ash containing anti-clogging concentrate adapted to be added to a hydrocarbon fuel oil, said concentrate consisting essentially of a major amount of a liquid hydrocarbon distillate fraction containing a substantial amount of cracked components and from about 4% to about 20% by weight of an oil-soluble aliphatic amine having at least one alkyl radical of at least 14 carbon atoms and up to 18 carbon atoms.

4. A non-ash containing anti-clogging concentrate adapted to be added to a hydrocarbon fuel oil, said concentrate consisting essentially of a major amount of a liquid hydrocarbon distillate fraction containing a substantial amount of cracked components and from about 4% to about 20% by weight of octadecylamine.

5. A concentrate according to claim 4 containing in addition thereto up to 10% of a metal salt of alkyl phenol disulfide.

6. A concentrate according to claim 4 containing in addition thereto up to 10% of a metal oil-soluble petroleum sulfonate.

7. A concentrate according to claim 4 containing in addition thereto up to 10% of a sodium oil-soluble petroleum sulfonate.

8. A concentrate according to claim 4 containing in addition thereto up to 50% of a glycol ether as a drying agent.

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