

UNITED STATES PATENT OFFICE

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FUEL OIL COMPOSITION

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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 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 700° F. and particularly those fuels having a distillation range of 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, cause 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 towards 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 causes formation and precipitation of sludge materials which, in, turn, deposit

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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 and particularly fuel oils obtained during cracking of hydrocarbons, which 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 a particular type of distillate fuel oil compositions, and blends thereof, which are non-corrosive and stable, and which are effective for cleaning and sludge removing.

The above and other objects of this invention may be attained by dispersing, admixing 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 polyhydric alcohol-polybasic acid resin and/or a modified resin of this type, and a detergent salt. If desired, a glycol-ether type drying agent may be admixed with the synthetic resin and detergent salt mixture or to the fuel composition containing these additives.

The hydrocarbon distillate fuel oils in which the active ingredients of this invention are dispersed or blended with may be treated or untreated catalytically cracked fuel oils, or mixtures of cracked fuels with straight run fuel oils having components normally distilling at about 500° F. and having an end distillation point not exceeding 700° F. Generally such fuels of the type under discussion have a boiling range of from about 340° F. to about 700° F. and preferably have 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 the cracked fuels as well as blends of cracked and straight run fuels may be acid or caustic treated to improve their stability. Specifically hydrocarbon distil-

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lates 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 straight run fuels.

The properties of typical undoped fuel oils which have a marked tendency towards clogging screens, etc., are given in the following table:

Properties	Fuel A— Catalytically cracked gas oil	Fuel B—44% acid treated clay filtered straight-run gas oil and 56% caustic washed, clay filtered cat- alytically cracked gas oil
Gravity, °API.....	31.0	32.4
Color, NPA.....	1½+	1½+
ASTM Dist., °F.: IBP.....	434	410
EBP.....	620	670
Sulfur, Per Cent Weight.....	0.783	0.79
Pour point, °F.....	-5	5

The primary additives of this invention which possess the unique property of inhibiting sludge formation or removing preformed deposits from surfaces, thereby preventing clogging of systems utilizing fuels normally susceptible to such deterioration are synthetic resins, particularly the polyhydric alcohol-polybasic acid resins, generally known as alkyl resins.

The acids or their anhydrides which may be used to form the resins are phthalic, succinic, maleic, malic, malo-malic, diphenic, citric, tartaric, camphoric, benzophenone dicarboxylic acids and mixtures thereof.

The polyhydric alcohols suitable for forming the resin with acids of the above type are glycol and homologues, glycerol and homologues, sorbitol, mannitol, erythritol, pentaerythritol, polyglycols, etc.

Various methods may be used for forming the resinous material. The simplest method being to heat the polyhydric alcohol and the polybasic acid, with or without modifying ingredients until resinification is substantially complete. The resinous material should possess some degree of solubility in a liquid hydrocarbon fuel or be readily dispersible therein. By modifying agents is meant to include such materials as drying oils, semi-drying oils and/or non-drying oils and derivatives or fractions thereof free fatty acids, naphthenic acids, etc., which can be admixed with and reacted with the polyhydric alcohol and polybasic acid to form the resinous product.

The mol ratio of the reacting ingredients may vary over wide limits and generally about 1 to 3 mols of the polybasic acid may be used for each mol of polyhydric alcohol used.

Typical compositions of the polyhydric alcohol-polybasic acid resins are as follows:

Resin A made from glycerol and phthalic anhydride

Resin B made from glycerol and maleic anhydride

Resin C made from ethylene glycol and phthalic anhydride

Resin D made from diethylene glycol and phthalic anhydride

Resin E made from mannitol and phthalic anhydride

Resin F made from erythritol and phthalic anhydride

Resin G made from glycerol and malic anhydride

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Resin H made from glycerol, phthalic anhydride and castor oil

Resin I made from glycerol, phthalic anhydride and linseed oil

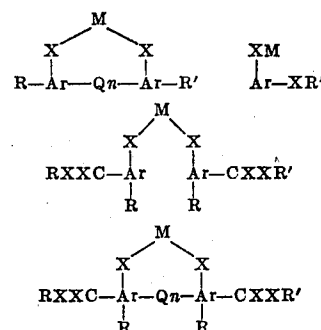
5 Resin J made from glycerol, phthalic anhydride and linseed oil acids

The amount of a polyhydric alcohol-polybasic acid resin which can be used to form a base composition of this invention, may vary from about 5% to about 35% and preferably from about 10 to about 30%.

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 appear to act as peptizer and thereby prevent the settling and adhering of impurities and sludge and allowing them to pass through the screen or filter system.

15 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, halogen and sulfur groups and the like. Also phenates, alcohates, carbamates, thiocarbamates, xanthates, etc., may be used.

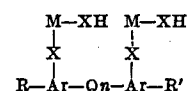
20 Particularly preferred class of detergents are the salts of alkyl substituted phenol sulfides or its selenide and/or its telluride equivalent. These phenolic salts may be represented by the general formulas



wherein M is a metal; R and R' represent at 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 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 or base may vary from between about 5 and 15% and preferably is kept below 10%.

Another preferred class of detergents are the alkali and alkaline earth metal 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.

Oil-soluble petroleum sulfonates from naphthenic, Gulf Coastal and/or Mid-Continent stocks, may be obtained by various processes, such as those disclosed in the U. S. Patents 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 2,236,933, 2,334,532, 2,357,866, 2,368,452, and 2,406,753.

Other than alkali metals may be used to form the sulfonates and may include the Ca, Ba, Sr, Mg sulfonates and their mixtures.

The amount of metal salt of the specific type of petroleum sulfonic acid under discussion may be added to the concentrate or base from about 5 to 15 and preferably 2 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 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 such as 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 tert-butyl ether, ethylene glycol mono hexyl ether, propylene glycol mono ethyl ether, propylene glycol mono isoamyl ether, etc. Also glycerine and the like may be used.

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

A general formula of a base (concentrate) composition of this invention which will hence-

forth be referred to as Composition A may consist of:

Composition A

	General Range	Limited Range
Polyhydroxy alcohol-polybasic acid resins.....	Per Cent 5-35	Per Cent 10-30
Detergents, e. g. barium salt of an alkyl phenol sulfide and/or calcium petroleum sulfonate or the like.....	5-15	10 or less
Drying agent, e. g. diethylene glycol monobutyl ether.....	0-25	0-20
Hydrocarbon distillate fuel oil.....	balance	balance

Specific base compositions may be illustrated by the following examples:

Composition B

	Per cent
Glycerol-phthalic anhydride resin.....	20
Barium salt of alkyl phenol disulfide.....	10
Hydrocarbon fuel oil (B).....	70

Composition C

	Per cent
Glycerol-phthalic anhydride resin.....	20
Barium salt of alkyl phenol disulfide.....	10
Hydrocarbon fuel oil (A).....	70

Composition D

	Per cent
Glycerol-phthalic anhydride resin.....	20
Ca salt of petroleum sulfonate.....	10
Hydrocarbon fuel oil.....	70

The following table further illustrates suitable anti-clogging base compositions

Components ¹	1	2	3	4	5	6	7	8
<i>Surface active agent</i>								
Glycerol-phthalic anhydride resin.....	x	x				x	x	x
Glycerol-maleic anhydride resin.....			x					
Ethylene glycol-phthalic anhydride resin.....				x				
Mannitol-phthalic anhydride resin.....					x			
<i>Detergent</i>								
Ba salt of alkyl phenol sulfide.....			x		x			
Ca salt of alkyl phenol sulfide.....		x						
Na naphthenate.....						x		
Na petroleum sulfonate.....							x	
Ca petroleum sulfonate.....				x			x	
<i>Drying agent</i>								
Diethylene glycol monobutyl ether.....							x	
Diethylene glycol monoethyl ether.....								
Cetylene 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 added generally mixed in amount of 1 pint or less with from about 250 gallons 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:

	Per cent
Polyhydric alcohol-polybasic acid resin.....	0.0025 to 0.005
Detergents, e. g. Ba salt of alkyl phenol disulfide.....	0.0025 to 0.0042
Drying agent (glycol-ether)....	0 to 0.002

Compositions B and D when added in amounts of approximately 1 pint per 250 gallons of fuel oil correspond to approximately the following

concentrations of the active ingredients present in the final composition.

Composition B'

	Per cent
Glycerol-phthalic anhydride resin.....	0.005
Barium salt of alkyl phenol disulfide.....	0.0025
Hydrocarbon fuel oil.....	Balance

Composition D'

	Per cent
Glycerol-phthalic anhydride resin.....	0.005
Calcium salt of petroleum sulfonic acid.....	0.0025
Hydrocarbon fuel oil.....	Balance

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

The following examples illustrate the effectiveness of compositions of this invention:

Example I

A fuel tank was cleaned with acetone and the entire system flushed with kerosene and the tank charged with 250 gallons of fuel oil (B) as noted in column 3. The oil was steamed with saturated steam for about 1 1/4 minutes. In other tank 1 pint of composition B was added to 250 gallons of the above fuel oil and steamed in the same manner.

Both oils were circulated through a pump and strainer system for 28 days and the appearance of the system and oil noted.

	Undoped Fuel Oil B	Undoped Fuel B and Composition B (1 pt/250 gallons)
Strainer basket.....	100% covered with 1/8 inch thick layer of black emulsion.	Several small spots of fiber and lint; no stain.
Screen disks.....	Completely covered with black emulsion about 1/16" thick.	Narrow ring of sludge at outer edge adjacent to cork gasket.
Tank.....	Medium to heavy coating of light grey sludge on bottom and sides.	Very slight amount of sludge.

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, fluoro 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 fluid 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 normally susceptible to cause clogging containing in combination therewith about 0.005% glycerol-phthalic anhydride resin and about 0.0025% barium salt of alkyl phenol disulfide.

2. A non-clogging fuel oil normally susceptible to cause clogging containing in combination therewith about 0.005% glycerol-phthalic anhydride resin, about 0.0025% barium salt of alkyl

phenol disulfide and a minute amount of diethylene glycol monobutyl ether.

3. A non-clogging fuel oil normally susceptible to cause clogging containing in combination therewith about 0.005% glycerol-maleic anhydride resin, about 0.0025% barium salt of alkyl phenol disulfide.

4. A non-clogging fuel oil normally susceptible to cause clogging containing in combination therewith about 0.005% glycerol-phthalic anhydride resin and about 0.0025% calcium petroleum sulfonate.

5. A non-clogging fuel oil containing a substantial amount of cracked hydrocarbon fractions normally susceptible to cause clogging containing in combination therewith about 0.005% glycerol-phthalic anhydride resin and about 0.0025% barium salt of alkyl phenol disulfide.

6. A non-clogging fuel oil containing a substantial amount of cracked hydrocarbon fractions normally susceptible to cause clogging containing in combination therewith about 0.005% glycerol-phthalic anhydride resin and about 0.0025% calcium petroleum sulfonate.

7. A non-clogging fuel oil containing a hydrocarbon fuel oil from the group consisting of cracked and mixtures of cracked and straight run fuel oil normally susceptible to cause clogging containing in combination therewith about 0.005% glycerol-phthalic anhydride resin and about 0.0025% barium salt of alkyl phenol disulfide.

8. A non-clogging fuel oil containing a hydrocarbon fuel oil from the group consisting of cracked and mixtures of cracked and straight run fuel oil normally susceptible to cause clogging containing in combination therewith about 0.005% glycerol-phthalic anhydride resin and about 0.0025% calcium petroleum sulfonate.

9. A non-clogging fuel oil normally susceptible to cause clogging containing in combination therewith from about 0.0025% to about 0.005% of a polyhydric alcohol-polybasic acid resin, from about 0.0025% to 0.0042% of a salt of an organic acidic compound and from about 0 to about 0.002% of a glycol-ether.

10. A non-clogging fuel oil normally susceptible to cause clogging containing in combination therewith from about 0.0025% to about 0.005% of a polyhydric alcohol-polybasic acid resin, from about 0.0025% to 0.0042% of a salt of an organic acidic compound.

11. In a system having small orifices which are normally subject to clogging by liquid hydrocarbon fuel oils, the method of inhibiting such clogging by employing in said systems a liquid hydrocarbon fuel oil containing about 0.005% glycerol-phthalic anhydride resin and about 0.0025% barium salt of alkyl phenol disulfide.

12. In a system having small orifices which are normally subject to clogging by liquid hydrocarbon fuel oils, the method of inhibiting such clogging by employing in said systems a liquid hydrocarbon fuel oil containing about 0.005% glycerol-phthalic anhydride resin and about 0.0025% calcium petroleum sulfonate.

13. In a system having small orifices which are normally subject to clogging by liquid hydrocarbon fuel oils, the method of inhibiting such clogging by employing in said systems a liquid hydrocarbon fuel oil containing about 0.005% glycerol-maleic anhydride and about 0.0025% barium salt of alkyl phenol disulfide.

14. In a system having small orifices which are normally subject to clogging by liquid hydrocar-

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bon fuel oils, the method of inhibiting such clogging by employing in said systems a liquid hydrocarbon fuel oil containing a minute amount of a polyhydric alcohol-polybasic acid resin and a salt of an organic acidic compound.

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