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FUEL OIL COMPOSITION

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5 Claims. (Cl. 44—78)

This invention has to do with improved fuel oil compositions. More specifically it has to do with fuel oils which have been stabilized and which are particularly suitable for use as industrial and domestic fuels.

The fuel oils improved in accordance with this invention are hydrocarbon fractions having initial boiling points of at least about 100° F. and end points not higher than about 750° F., and which boil substantially continuously throughout their distillation ranges. Such fuel oils are generally known as distillate fuel oils. It is to be understood, however, that this term is not restricted to straight-run distillate fractions. Thus, as is well known to those skilled in the art, the distillate fuel oils can be straight-run distillate fuel oils, catalytically or thermally cracked distillate fuel oils or mixtures of straight-run distillates, naphthas and the like, with cracked distillate stocks. Moreover, such fuel oils can be treated in accordance with well known commercial methods, such as, acid or caustic treatment, solvent refining, clay treatment, etc.

The distillate fuel oils are characterized by their relatively low viscosities, pour points and the like. The principal property which characterizes the contemplated hydrocarbon fractions, however, is the distillation range. As mentioned hereinbefore, this range will lie between about 100° F. and about 750° F. Obviously, the distillation range of each individual fuel oil will cover a narrower range falling, nevertheless, within the above-specified limits. Likewise, each fuel oil will boil substantially, continuously throughout its distillation range.

The fuel oils particularly contemplated herein are Nos. 1, 2 and 3 fuel oils used in domestic heating and as diesel fuel oils, particularly those made up chiefly or entirely of cracked distillate stocks. The domestic heating oils generally conform to the specification set forth in ASTM Specifications D396–48T. The specifications for diesel fuels are defined in ASTM Specifications D975–48T. Contemplated herein also are fuels for jet combustion engines. Typical jet fuels are defined in Military Specification MIL–F–5624B.

As is well known, fuel oils of the above-defined character have a tendency to deteriorate in storage and to form colored bodies and sludge therein. This deterioration of the oil is highly undesirable in that it causes serious effects on the characteristics of the oil, particularly on the ignition and burning qualities thereof. It is also a contributory factor, along with the presence of other impurities in the oil, such as rust, dirt and moisture, in causing clogging of the equipment parts, such as screens, filters, nozzles, etc., as is explained hereinbelow. An important economical factor is also involved in the problem of oil deterioration in storage, viz., customer resistance. Thus, customers judge the quality of an oil by its color and they oftentimes refuse to purchase highly colored oils. It will be appreciated, then, that since fuel oils of necessity are generally subject to considerable periods of storage prior to use, the provision of a practical means for preventing the deterioration of the fuel oil during

such storage would be a highly desirable and important contribution to the art.

Another and distinct problem that has plagued fuel oil manufacturers and users is that referred to as "screen-clogging." This involves the deposition of foreign substances, such as water droplets, rust and dirt particles, as well as any sludge material formed by the deterioration of the oil, on the metallic surfaces of screens and filters of burners and engines in which the oil is utilized. Additives have been developed to impart anti-clogging properties to fuel oils, functioning therein to inhibit the aforesaid deposition of foreign substances. The mechanism by which the clogging is prevented involves the adsorption of the anti-clogging agent or additive on the metal surfaces whereby the contacting of these surfaces by the foreign substances and/or preformed sludge is prevented. In this way, deposition and build-up of these materials on the metal surfaces is avoided. It will be appreciated, therefore, that the problem of preventing screen-clogging by fuel oils is entirely different from that of preventing the formation of sediment and color therein as occurs in the oil during prolonged periods of storage. Thus, it will be appreciated that any fuel distribution system will contain small amounts of foreign substances, such as condensed moisture and particles of rust and dirt, which become entrained in the oil, even though the oil has not been stored for any appreciable length of time. On the other hand, fuel oils which have been in storage for substantial periods of time will also contain another kind of sediment, or sludge, which is produced by the gradual deterioration of the oil per se. This sediment, or sludge, is formed in the oil as the result of chemical phenomena. Thus, during storage, oxidation of the various components of the oil, such as pyrrolic compounds, phenols and thiophenols present therein, takes place forming quinoid molecules which condense with one another and/or with other active hydrogen compounds also present in the oil to produce highly colored bodies of increasing molecular weight. When an oil has been in storage for any substantial period of time these compounds separate out as insoluble sludge. Additives have also been developed to inhibit the formation of sediment or sludge in the oil due to oxidative deterioration of the oil in storage, as above described. Such additives act by inhibiting the initial oxidation and the subsequent reactions which produce such sludge.

It is apparent, then, that the problem of preventing screen-clogging by fuel oils is entirely different from the problem of preventing the formation of sediment and color therein as occurs in the oil during prolonged periods of storage. As evidence of the difference between these problems, additives which prevent screen-clogging have generally little or no effectiveness in preventing the formation of sediment and color. Correspondingly, other additives which effectively inhibit sediment and color formation generally have little or no anti-screen clogging properties.

It is the object of this invention to stabilize fuel oils.

It is a further object of the invention to provide fuel oils stabilized against the formation of sediment therein.

Still another object of the invention is to provide a fuel oil free from screen-clogging tendencies.

An important object of the invention is to provide a fuel oil stabilized against the formation of sediment and color and also free from screen-clogging tendencies.

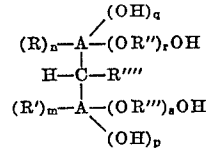
A still further object of the invention is to provide a fuel oil having excellent anti-rust properties.

Additional objects of the invention will be apparent from the following descriptions:

It has now been found that the aforesaid objects are realized by incorporating in a fuel oil of the foregoing

character, a small amount of a fuel-oil-soluble reaction product obtained by reacting an aldehyde and paraffin-wax-substituted hydroxyaromatic compound, and further reacting the resulting product with an alkylene oxide. The products so obtained, most probably, contain one or more of the compounds represented by the following general formula:

(I)



wherein R and R' are the same or different paraffin wax groups; *n* and *m* the same or different small whole numbers each being from 1 to 3; A is phenyl or naphthyl; *p* and *q* are the same or different small whole numbers each being from 1 to 3; R'' and R''' are the same or different alkylene or hydroxy alkylene groups, each containing at least 2 carbon atoms and preferably 2 to 4 carbon atoms; *r* and *s* are the same or different small whole numbers, each being at least 1 and preferably from 1 to 20; and R'''' is hydrogen, or an alkyl, cycloalkyl, aryl or hetero group.

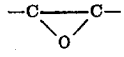
As indicated, one of the reactants is a paraffin-wax-substituted phenol or naphthol, the aromatic nucleus of which is preferably otherwise unsubstituted. The aromatic nucleus carries from 1 to 3 hydroxy groups directly attached thereto, and from 1 to 3 paraffin wax groups. Such compounds are represented by the general Formula II:

(II) $(R)_{n \text{ or } m}—A—(OH)_{p \text{ or } q}$

wherein R, A, *n*, *m*, *p* and *q* are as defined above. Representative of these compounds are paraffin-wax-substituted phenols, resorcinols, hydroquinones, pyrogallols, and the corresponding paraffin-wax-substituted hydroxy naphthalenes. Particularly preferred herein are the paraffin-wax-substituted phenols.

The aldehydes used in the reaction with the aforementioned phenols and naphthols, can be aliphatic, cycloaliphatic, aromatic or heterocyclic. Representative of such aldehydes are formaldehyde (e.g., paraformaldehyde), acetaldehyde, propionaldehyde, stearylaldehyde, benzaldehyde, tolualdehyde, salicylaldehyde, furfural, and thiophene aldehyde. Preferred herein is formaldehyde, in view of the particularly advantageous products obtained therewith.

Alkylene oxides, as indicated above, are used herein. These can be either monooxides or polyoxides. Thus, they can contain one or more of the characterizing group



Typical of such compounds are ethylene oxide, propylene oxide, butylene oxide, butane dioxide, bis-(2,3-epoxy propyl) ether otherwise referred to as diglycide ether, isoprene dioxide, hexadiene dioxides, limonene dioxide, etc. Particularly preferred herein is ethylene oxide.

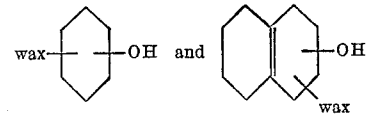
The products contemplated herein for use in fuel oils are prepared by reacting one molar proportion of a paraffin wax-substituted phenol or naphthol with at least 1 molar proportion and preferably 1 to 2 molar proportions of an aldehyde, and thereafter reacting 1 molar proportion of the intermediate phenol-aldehyde product with at least one molar proportion and preferably 1 to 20 molar proportions of an alkylene oxide. Temperatures at which the phenol and aldehyde are reacted are from about 50° C. to about 250° C., most advantageously within the range of 100° C. to 200° C. Similarly, temperatures used during reaction of the intermediate phenol-aldehyde product and the alkylene oxide can be varied from about 20° C. to about 250° C., preferably from 100° C. to 200° C. Generally, atmospheric pressure

suffices in completing the reactions; however, superatmospheric pressures can also be employed.

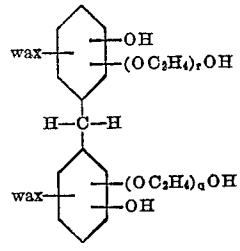
Acid or basic catalysts are used in facilitating reaction of the aldehyde and the phenol or naphthol. Such catalysts are well know for this reaction. Basic catalysts are used in reacting the alkylene oxide with the aldehyde-phenol or aldehyde-napthhol product. Typical of such catalysts are sodium, potassium, lithium, calcium and barium hydroxides, and preferably sodium hydroxide; amines such as pyridine; quaternary ammonium hydroxide.

It is to be understood that the products of this invention can also be prepared by an alternative but less advantageous procedure, which involves reaction of the intermediate reaction products with a halohydrin or an epichlorhydrin and an alkali, such as sodium hydroxide.

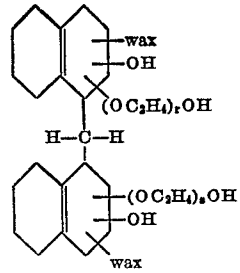
The products of this invention have been described as reaction products rather than as specific chemical compounds since the structure of some, at least, is yet unknown. In particular, paraffin-wax-substitued phenols and naphthols have not been fully identified, but it would appear that they contain predominant amounts of the following respective compounds:



Therefore, when the paraffin-wax-substituted phenols and naphthols are reacted with an aldehyde, such as formaldehyde, the resulting product cannot be defined as a single specific compound. Obviously, then, when the aldehyde product is reacted with an alkylene oxide, such as ethylene oxide, the resulting product cannot be defined as a definite structure. It follows, however, that the resulting product most probably contains a predominant amount of the following respective compounds:



and



The following specific examples are for the purpose of illustration. It is to be understood, however, that this invention is not to be limited by the particular additive and fuel oils, or to the operations and manipulations described herein. Other reaction products and fuel oils of the above-described character are utilizable, as those skilled in the art will readily appreciate.

PREPARATION OF WAX-PHENOL (3–14)

A paraffin wax melting at approximately 120° F. and predominantly comprised of hydrocarbons, having at least 20 and an average of about 24 carbon atoms in their molecules, is melted and heated to about 200° F., after which chlorine is bubbled therethrough until the wax

has absorbed about 14%, by weight, of chlorine. A sufficient quantity of this chlorinated wax to provide 3 atomic proportions of chlorine is then heated to a temperature varying from just above its melting point to not over 150° F. One mol of phenol (C_6H_5OH) is then mixed with the chlorowax. The mixture is then heated to about 150° F. and a quantity of anhydrous aluminum chloride, corresponding to about 3% of the weight of the chlorowax in the mixture, is slowly added with active stirring. The rate of addition of the aluminum chloride should be sufficiently slow to avoid violent foaming and during the addition the temperature should be held at about 150° F. After the aluminum chloride has been added the temperature of the mixture may be increased slowly over a period of from 15 to 25 minutes to a temperature of about 250° F. and then should be more slowly increased to about 350° F. To control the evolution of HCl gas, the temperature of the mixture is preferably raised from 250° F. to 350° F. at a rate of approximately one degree per minute, the whole heating operation occupying approximately two hours from the time of adding the aluminum chloride. If the emission of HCl gas has not ceased when the final temperature is reached, the mixture may be held at 350° F. for a short time to allow completion of the reaction. However, to avoid possible cracking of the wax, the mixture should not be heated appreciably above 350° F. nor should it be held at that temperature for any extended length of time.

It is important that all unreacted, or non-alkylated, phenol remaining in the reaction mixture, as well as aluminum chloride, be removed. This can be conveniently effected by washing the product several times with a mixture of water and an alcohol, such as butanol, preferably at elevated temperature, say 175° F. The product may then be treated with steam. This latter step will insure complete removal of the unreacted material and also dry the product.

It will be understood that a wax-substituted phenol prepared according to the above procedure in which a quantity of chlorowax containing three atomic proportions of chlorine and having a chlorine content of 14% is reacted with one mol of phenol, is designated as "wax-phenol (3–14)." Similarly, "wax-phenol (3–10)" and "wax-phenol (1–10)" may also be prepared by the reaction of sufficient amounts of chlorinated wax, containing 10 percent by weight of chlorine, to provide 3 atomic proportions and 1 atomic proportion of chlorine per mol of phenol, respectively, in the reaction and are useful in the invention. In general, the amount of chlorowax, containing from about 10 to 18 percent by weight of chlorine, used in the reaction is sufficient to supply between 1 and 4 atomic proportions of chlorine per mol of phenol used.

Further details relative to the procedure for the preparation of wax phenols suitable for use herein may be had by reference to Patent No. 2,191,499, issued February 27, 1940, to Orland M. Reiff.

Example I

A mixture of wax-phenol (3–14) (400 parts by weight), diluent oil (400 parts by weight), sodium hydroxide (4 parts by weight) and paraformaldehyde (1 mol) (15 parts by weight), was slowly heated to 200° C. Ethylene oxide gas was bubbled through the mixture so formed at 200° C. until the resulting reaction mixture increased 92 parts by weight. The reaction product was then neutralized with concentrated hydrochloric acid and the sodium chloride formed thereby was removed by filtration. The product—referred to herein as Product I—is predominantly a methylene bis wax phenoxy triethoxy ethanol, one part of oil for one part of product.

The diluent oil is a paraffinic oil having a Saybolt viscosity of 100 seconds at 100° F.

The effectiveness of the additives of this invention in stabilizing a typical fuel oil against sediment formation therein, is shown by screen-clogging test data. The amount of screen-clogging is determined with a Sunstrand V3 or S1 home fuel oil burner pump having a self-contained, 100-mesh Monel metal screen. About 0.05 percent, by weight, of a naturally-formed fuel oil sludge, composed of fuel oil, water, dirt, rust, and organic sediment, is added to ten liters of the fuel oil under test. This mixture is circulated by the pump through the screen for six hours. Then the sludge deposited on the screen is washed off with normal pentane, and filtered through a tared asbestos (Gooch Crucible) filter. After it is dried, the material on the filter is washed with a 50–50 (volume) acetone-methanol mixture. The total amount of organic sediment is determined by evaporating the n-pentane and the acetone-methanol filtrates, and weighing the residue. The weight of the material on the filter is the amount of inorganic sediment deposited. The sum of the weights of the organic and the inorganic deposits, in milligrams, gives the weight of sludge deposited, which weight is compared with the weight of sludge deposited from the uninhibited ("blank") fuel oil to determine the percent of screen-clogging. The uninhibited fuel oil, after six hours on test, effects 100 percent screen-clogging. Thus, the comparison percentagewise between the weight of sludge deposited by the uninhibited fuel oil and the inhibited fuel oil affords a measure of the percent of screen-clogging. The fuel oil used in the test is a blend comprising sixty percent (by weight) of catalytically cracked component and 40% of straight-run component, the blend having a boiling range from about 320° F. to about 640° F. The data obtained from said tests are provided in Table I.

TABLE I

Inhibitor	Conc., lbs./1,000 bbls.	Screen Clogging, Percent
Uninhibited fuel oil blend	0	100
Fuel Oil+Product I	50	17
Fuel Oil+Wax-Phenol (3–14)	50	100

The results set out in Table I demonstrate that Product I, contemplated herein, is an effective anti-screen-clogging agent. The results demonstrate also that wax-phenol (3–14) is ineffective.

A demonstration of the sediment inhibiting character of the additives contemplated herein is shown by results of 110° F. storage tests. In this test, a 500-milliliter sample of the fuel oil under test is placed in a convected oven maintained at 110° F. for a period of twelve weeks. Then, the sample is removed from the oven and is cooled. The cool sample is filtered through a tared asbestos filter (Gooch Crucible) to remove the insoluble matter. The weight of such matter, in milligrams, is reported as the amount of sediment. In this test, a sample of the blank, uninhibited oil is run along with the fuel oil blend under test. The oil used is the same as that described above in connection with Table I. The effectiveness of a fuel oil composition containing an inhibitor is determined by comparing the test data therefor with the test data for the uninhibited blank oil. Results of the storage tests are given in Table II.

TABLE II

Inhibitor	Conc., lbs./1,000 bbls.	Sediment, Mgs./Liter
Uninhibited fuel oil blend	0	151
Fuel Oil+Product I	100	69

The results given in Table II reveal that Product I is effective in materially reducing sediment formation.

The reaction products of this invention are used in

fuel oils in concentrations varying between about 1 pound per thousand barrels of oil, and about 200 pounds per thousand barrels of oil. Preferably, the concentration will vary between about 10 and 100 pounds per thousand barrels. In terms of weight percent, based upon the weight of the fuel oil, the concentrations vary preferably between about 0.005% and about 0.05%.

If it is desired, the fuel oil compositions of this invention can contain other additives for the purpose of achieving other results. Thus, for example, there can be present foam inhibitors, anti-rust agents, and ignition and burning quality improving agents. Examples of such additives are silicones, dinitro-propane, amyl nitrate, metal sulfonates and the like.

Although the present invention has been described in conjunction with preferred embodiments, it is to be understood that modifications and variations may be resorted to, without departing from the spirit and scope of this invention. Such variations and modifications are considered to be within the scope and purview of the appended claims.

I claim:

1. A distillate fuel oil containing a small amount, sufficient to improve the stability thereof, of a fuel-oil-soluble reaction product obtained by: reacting, at a temperature between about 50° C. and about 250° C. in the presence of a catalyst selected from the group of acid and basic catalysts, at least one molar proportion of formaldehyde with one molar proportion of a paraffin wax-substituted hydroxyaromatic compound represented by the general formula

$$(R)_n—A—(OH)_p$$

wherein R is a paraffin wax group, *n* and *p* are each small whole numbers from 1 to 3, and A is an aromatic group selected from the group consisting of phenyl and naphthyl, whereby an intermediate reaction product is obtained; and reacting at a temperature between about 20° C. and about 250° C. in the presence of a basic catalyst, one molar proportion of said intermediate reaction product with between one and about 20 molar proportions of an alkylene oxide.

2. A distillate fuel oil defined by claim 1 wherein the said fuel-oil-soluble reaction product is present in an amount from about 0.01 to about 0.05 percent by weight of the fuel oil.

3. A distillate fuel oil defined by claim 1 wherein the alkylene oxide is ethylene oxide.

4. A distillate fuel oil defined by claim 1 wherein the alkyl-substituted hydroxyaromatic compound is a wax phenol.

5. A distillate fuel oil containing a small amount, sufficient to improve the stability thereof, of a fuel-oil-soluble reaction product obtained by: reacting, at about 200° C. in the presence of sodium hydroxide, one molar proportion of a paraffin-wax-substituted phenol with one molar proportion of formaldehyde, whereby an intermediate product is obtained; and reacting, at about 200° C. in the presence of sodium hydroxide, said intermediate product with about four molar proportions of ethylene oxide, whereby said fuel-oil-soluble reaction product is obtained.

References Cited in the file of this patent

UNITED STATES PATENTS

2,197,835	Reiff	Apr. 23, 1940
2,454,541	Bock et al.	Nov. 23, 1948
2,591,651	Young	Apr. 1, 1952
2,692,859	Talley et al.	Oct. 26, 1954
2,734,032	Coppock	Feb. 7, 1956
2,772,238	Lowe	Nov. 27, 1956
2,786,745	Stayner et al.	Mar. 26, 1957

OTHER REFERENCES

Soap and Sanitary Chemicals, August 1949, page 39.

"Antarox," Aromatic Polyglycol Ether, Antara Products, General Aniline & Film Corp., March 3, 1950, pp. 1–6.