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FUEL OIL COMPOSITION

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4 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 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 distillate napthas 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 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 adverse 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.

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 differenet 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.

This invention is primarily concerned with preventing or retarding screen clogging of fuel oils and the like, by incorporating with said fuel oils a small amount of an additive.

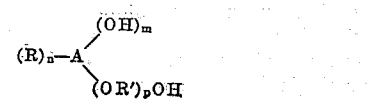
It is an object of this invention, therefore, to stabilize fuel oils.

It is a further object of this invention to provide a fuel oil free from screen-clogging tendencies.

Additional objects of the invention will be apparent from the following description.

The foregoing objects have been achieved by incorporating in a fuel oil of the aforementioned character, a small amount of a fuel-oil-soluble reaction product of a paraffin-wax-substituted hydroxyaromatic compound and an alkylene oxide. The products so obtained, most probably, contain one or more of the compounds represented by the following general Formula I:

(I)



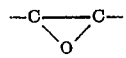
wherein R is a paraffin wax group; *n* is a small whole number from 1 to 3; A is phenyl or naphthyl; *m* is a small whole number from 1 to 3; R′ is an alkylene or hydroxy alkylene group, and contains at least 2 carbon atoms and preferably 2 to 4 carbon atoms; and *p* is a whole number of at least 1 and preferably from 1 to 20.

As indicated, one of the reactants is an alkyl-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) $(R)_n—A—(OH)_m$

wherein R, A, *n* and *m* are as defined above. Representatives 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. As shown in the illustrative examples hereinbelow, the aromatic nucleous (A) should not contain a hydrocarbon chain having a relatively small number of carbon atoms; for example, a cresol (R=1) and octyl phenol (R=8) react with ethylene oxide to form products ineffective as anti-screen clogging agents.

Alkylene oxides, as indicated above, ar 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 diglycid ether, isoprene dioxide, hexadiene dioxides, limonene dioxide, etc. Particularly preferred herein is ethylene oxide.

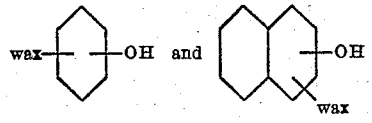
The products contemplated herein for use in fuel oils are prepared by reacting one molar proportion of a paraffin-wax-substituted phenol with from about one to twenty or more molar proportions of an alkylene oxide. Temperatures at which the compounds are reacted are from about 20° C. to about 250° C., most advantageously within the range of 100° C. to 200° C.

Generally, atmospheric pressure suffices in completing the reaction of the compounds; however, super-atmospheric pressures can also be employed.

Basic catalysts are used in facilitating reaction. Typical of such catalysts are sodium, potassium, lithium, calcium and barium hydroxides, and preferably sodium hydroxide; amines such as pyridine; quaternary ammonium hydroxides.

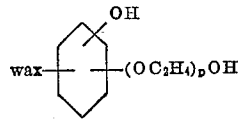
It is to be understood that the products of this invention can also be prepared by an alternative but less advantageous procedure, which involves reaction of the paraffin-wax-substituted hydroxyaromatic compound with a halohydrin or an epichlorhydrin and an alkali such as sodium hydroxide.

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

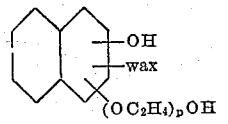


Therefore, when the paraffin-wax-substituted phenols and naphthols are reacted with an alkylene oxide, such as ethylene oxide, the resulting product can not be defined as a single specific compound. It follows, however, that

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 additives 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 addiiton 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% by weight of chlorine, to provide 3 atomic pro-

portions 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) (150 parts by weight), diluent oil (300 parts by weight), and sodium hydroxide (3 parts by weight), was heated to 200° C. Ethylene oxide gas was bubbled through the mixture at 200° C. until the reaction mixture increased nine (9) parts by weight (about 0.07 mol). The resulting mixture 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 wax phenoxy mono-ethanol in oil, 2 parts of oil for one of product.

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

Example II

A mixture of wax-phenol (3–14) (150 parts by weight), diluent oil (300 parts by weight), and sodium hydroxide (3 parts by weight), was heated to 200° C. Ethylene oxide gas was bubbled through the mixture at 200° C. until the reaction mixture increased twenty-seven (27) parts by weight (about 0.6 mol). The resulting mixture was then neutralized with concentrated hydrochloric acid and the sodium chloride formed thereby was removed by filtration. The product—referred to herein as Product II—is predominantly a wax phenoxy diethoxy ethanol in oil, 2 parts of oil for one of product.

The diluent oil is the same as used in Example I.

Example III

The product of this example was prepared following the procedure of Example I, above, except that 63 parts by weight (about 1.4 mols) of ethylene oxide was used. The product—Product III—is predominantly a wax phenoxy hexaethoxy ethanol, one part thereof in two parts of oil.

Example IV

A mixture of tetradecylphenol (approximately 1 mol; 282 parts by weight) and 6 parts of sodium hydroxide, was heated to 200° C. Ethylene oxide gas was bubbled through the mixture at 200° C. until the reaction mixture increased 171 parts by weight (approximately 4 mols). The resulting mixture was then neutralized with concentrated hydrochloric acid and the sodium chloride formed thereby was removed by filtration. The product—Product VI—is predominantly a tetradecylphenol triethoxy monoethanol.

Example V

The product—Product V—is an octylphenoxy tetraethoxy ethanol, supplied by Rohm and Haas Chemical Company.

Example VI

A mixture of wax-o-cresol (3–14) (409 parts by weight) and sodium hydroxide (8 parts by weight), was heated to 200° C. Ethylene oxide gas was bubbled through the mixture at 200° C. until the reaction mixture increased 23 parts by weight (approximately 0.5 mol). The resulting reaction mixture was then neutralized with concentrated hydrochloric acid and the sodium chloride formed thereby was removed by filtration. The product—Product VI—is predominantly a wax orthocresyloxy monoethanol.

The effectiveness of the additives of this invention in reducing screen-clogging 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 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 this test is a blend comprising sixty percent (by weight) of catalytically cracked component and forty percent 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

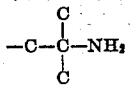
Inhibitor	Conc., lbs./1,000 bbls.	Screen Clogging, Percent
Uninhibited Fuel Blend	0	100
Fuel+Product I	50	18
Fuel+Product II	50	15
Fuel+Product III	50	14
Fuel+Product IV	50	96
Fuel+Product V	50	100
Fuel+Product VI	50	100
Fuel+Wax-Phenol (3-14)	50	100

The results set forth in Table I reveal that Products I through III, contemplated herein, are effective as anti-screen clogging agents. The results also show that related products, Products IV and V, which do not have a paraffin wax substituent, are ineffective. Correspondingly, a product derived from a wax-substituted o-cresol rather than phenol is ineffective; this is Product VI. In addition, wax-phenol (3–14) above is ineffective.

The reaction products of this invention are used in fuel oils in concentrations varying between about 10 pounds per thousand barrels of oil, and about 200 pounds per thousand barrels of oil. Preferably, the concentration will vary between about 25 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 0.01 percent and about 0.05 percent.

The fuel oils of this invention can also contain, in addition to the reaction products described herein, an additive serving as a sediment- and color-forming inhibitor. Outstanding inhibitors which cooperate with the esters are tertiary alkyl primary amines described in application Serial No. 299,249, filed July 16, 1952, and Serial No. 578,881, filed April 18, 1956. Briefly, such amines are tertiary alkyl, primary, monoamines having from about four to about twenty-four carbon atoms per molecule and having the primary amino nitrogen atom at-

tached directly to a tertiary carbon atom. These amines all contain the terminal unit:



Mixtures of the foregoing alkyl primary amines having from about 4 to about 24 carbon atoms are also highly suitable for use in the invention. A typical mixture of amines, for example, is one comprised of tertiary alkyl primary amines of from about 12 to about 15 carbon atoms, said mixture averaging about 12 carbon atoms per amine molecule. This mixture, designated hereinafter as "Mixture A," contains, by weight, about 85% of tertiary dodecyl amine, about 10% tertiary pentadecyl amine and relatively small amount, i.e., less than about 5% of amines having less than 12 or more than 15 carbon atoms.

Another mixture of tertiary alkyl primary amines which is highly suitable for use in the invention is composed of tertiary alkyl primary amines of from about 18 to 24 carbon atoms and averaging about 20 carbon atoms per molecule. This mixture designated herein as "Mixture B," contains the C_{18}–C_{24} tertiary alkyl primary amines in about the following proportions:

	Percent
Tertiary octadecyl amine	40
Tertiary eicosyl amine	30
Tertiary docosyl amine	15
Tertiary tetracosyl amine	10
Other amines and non-amine	5

The amount of tertiary alkyl, primary monoamine additives used, together with the reaction products described above, can vary from about 25 to about 100 pounds per thousand barrels of oil (i.e., about 0.01 percent to about 0.05 percent by weight) depending upon the particular oil to be stabilized, and the conditions of storage.

If it is desired, the fuel oil compositions 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, dini-tropropane, 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 reduce the screen-clogging tendencies thereof, of a fuel-oil-soluble reaction product of at least one molar proportion of an alkylene oxide and one molar proportion of a paraffin-wax-substituted hydroxyaromatic compound represented by the general formula

$$(R)_n—A—(OH)_m$$

wherein R is a paraffin wax group, n and m are each small whole numbers from 1 to 3, and A is an aromatic group selected from the group consisting of phenyl and naphthyl; said oxide and hydroxyaromatic compound being reacted at a temperature between about 20° C. and about 250° C. in the presence of a basic catalyst.

2. A distillate fuel oil containing a small amount, from about 0.01 to about 0.05 percent by weight of the fuel oil, of a fuel-oil-soluble reaction product of at least one molar proportion of an alkylene oxide and one molar proportion of a paraffin-wax-substituted hydroxyaromatic compound represented by the general formula

$$(R)_n—A—(OH)_m$$

wherein R is a paraffn wax group; n and m are each small whole numbers from 1 to 3, and A is an aromatic group selected from the group consisting of phenyl and naphthyl; said oxide and hydroxyaromatic compound being reacted at a temperature between about 20° C. and about 250° C. in the presence of a basic catalyst.

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 paraffin-wax-substituted hydroxyaromatic compound is a wax phenol.

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