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2,927,013

FUEL COMPOSITION

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This invention relates to an improvement in hydrocarbon fuels, and particularly hydrocarbon distillate fuels, to the extent that they are stabilized against deposit formation under varying conditions of static and dynamic flow incident to ultimate introduction into a combustion zone.

The deposit-forming tendencies of hydrocarbon fuels, and particularly the petroleum distillate fuels, are largely dependent upon their composition and the conditions to which they are subjected prior to energy-release through combustion in a combustion zone. Compositionwise, the deposit-forming tendencies or instability of the fuel are usually associated with the presence of thermally and/or catalytically cracked components in the fuel and become increasingly pronounced in the higher boiling range fuels. However, in addition to the effect of the organic components of the fuel, certain conditions of storage, transportation and service prior to combustion also contribute materially to the deposit-forming tendencies of the fuel. These conditions are generally conditions of oxidation and result in the formation of soluble and insoluble oxidation products which form the bulk of the deposits laid down on the various metal and other surfaces within the fuel system. Additionally, the presence of nonhydrocarbon contaminants in the fuel, and particularly metals such as copper and iron, accelerates the oxidative reactions and coincident deposit formation.

The more general oxidative deterioration is obtained as a low temperature oxidation during storage in the presence of air, and the resulting deposit formation is substantially dependent upon the composition or stability of the fuel. Other types of oxidative conditions which, in addition promote deposit formation are encountered in the conditions and fuel systems specific to the various types of hydrocarbon fuels. Thus, in the operation of internal combustion engines, whether compression-ignition or spark-ignition, deposit formation is encountered within the induction system and particularly at the intake valves, injector nozzles, and injection plungers. At the areas of deposit formation, the hydrocarbon fuel is subjected to comparatively high temperatures and comes in contact with combustion and exhaust gases containing oxidation precursors, etc. Another illustration of specific deposit formation of hydrocarbon fuels is in the operation of aircraft gas turbine engines wherein the fuel may be employed as a coolant and in heat exchange with the circulating lubricating oil. In such situations, the fuel is subjected to skin temperatures of up to 500° F. and results in the deposition of coke-like deposits on the heat exchanger surfaces.

Although certain of these deposit-forming tendencies of the hydrocarbon distillate fuels may be eliminated or minimized by additional refinery processing designed to extract, alter, and/or remove the oxidation-sensitive and/or unstable components of the fuel, such practices greatly depreciate the yield of fuel and materially increase the unit fuel costs. However, contrasting the disadvantages of additional process refining of the distillate fuels, it has now been discovered that hydrocarbon fuels may be stabilized against objectionable deposit formation prior to combustion by the incorporation of a unique class of addition agents.

According to the present invention it has been found that the incorporation in a hydrocarbon fuel, and prefer-

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ably a petroleum hydrocarbon distillate fuel, of a minor amount of a specific class of relatively high molecular weight copolymer compositions will effect a material reduction in the formation of insoluble sludges, etc., which may be precipitated or carried with the fuel to form deposits within the fuel system and thereby reduce the operating efficiency of the combustion engine or burner.

The class of copolymer compositions which have been determined to be unique in the improving characteristics as described above may be defined as a relatively high molecular weight copolymer which may be obtained by the copolymerization of (A) at least one compound containing an ethylenic linkage and 8 to 30 aliphatic carbon atoms which is copolymerizable through the ethylenic linkage and (B) at least one α,β -unsaturated aliphatic monocarboxylic acid containing from 3 to 8 carbon atoms, which copolymer is so constituted that at least one of the carboxyl groups of component (B) is present in the form of an ester of a polyalkylene glycol or alkyl ether thereof having from 2 to 7 carbon atoms in each alkylene group and an average molecular weight in excess of 800, said (A) component constituting from about 35 to 99.9 mole percent of the polymer composition.

The polymeric additives of the present invention may also be more particularly defined as oil-soluble copolymers of monomers selected from at least each of the first two classes of the classes consisting of (A) oil-solubilizing compounds having a polymerizable ethylenic linkage and containing a hydrocarbon group of from 8 to 30 aliphatic carbon atoms, (B) esters of α,β -unsaturated monocarboxylic acids of from 3 to 8 carbon atoms each wherein the carboxyl groups of said acids are monoester-linked to a member of the group consisting of polyalkylene glycols and alkyl ethers thereof having from 2 to 7 carbon atoms in each alkylene group and average molecular weights of more than 800 and (C) α,β -unsaturated monocarboxylic acids of from 3 to 8 carbon atoms each, said (A) component constituting from about 35 to 99.9 mole percent and said (B) and (C) components constituting a total of from about 65 to 0.1 mole percent of the polymer composition, there being present at least one monomer of said (B) component.

Within the foregoing definition of the hydrocarbon fuel improving agent, the particular composition chosen for optimum effectiveness is dependent largely upon the particular type of hydrocarbon fuel, its composition and the environmental conditions to which the fuel is subjected prior to introduction into a combustion zone. Thus, the specific copolymer composition employed in a motor gasoline for maximum effectiveness in reducing the intake manifold deposits in a spark-ignition, internal combustion engine will usually differ chemically within the foregoing classification from the copolymer additives incorporated in a high boiling burner fuel containing high concentrations of cracked gas oil stocks to effect the maximum reduction in clogging and plugging of filters, screens, pumps, and the like. In general, the greatest improvement in reduction of deposit-forming characteristics of a hydrocarbon distillate fuel by the incorporation of the subject copolymer addition agent is obtained with distillate fuels composed predominantly of hydrocarbons boiling above about 300° F., and the effective concentration of the copolymer additive will usually vary between 0.0005 to 1.0% by weight.

For specific illustration of the effectiveness of these addition agents in reducing the deposit-forming tendencies of a hydrocarbon fuel, reference is made to the higher boiling range fuels, such as the aircraft gas turbine engine fuels, commonly referred to as "jet fuels"; kerosene; gas oils, and particularly the thermal and catalytically cracked gas oils; compression-ignition, internal combustion fuels, such as diesel fuels; and the conventional

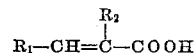
burner or furnace oils. Particularly for these types of fuel applications, it is desirable to employ an addition agent within the class of relatively high molecular weight copolymers, which may be produced through copolymerization of (A) at least one compound comprising an aliphatic (including cycloaliphatic) ester containing 8 to 30 carbon atoms and a copolymerizable ethylenic linkage alpha or beta to the carboxyl group, and (B) at least one copolymerizable compound comprising an α,β -unsaturated aliphatic monocarboxylic acid containing from 3 to 8 carbon atoms, to produce a copolymer composition in which the component (A) is present in the ratio of from about 50 to 99.9 mole percent of the polymer composition and in which 50 to 100% of the carboxyl groups of the component (B) are present in the form of an ester of a poly-1,2-alkylene glycol or alkyl ether thereof having from 1 to 7 carbon atoms in each alkylene group and an average molecular weight between 800 and 12,000.

The above class of addition agents may be described more particularly in terms of (A), (B) and (C) as oil-soluble copolymers of monomers selected from at least each of the first two classes of the classes consisting of (A) oil-solubilizing compounds comprising an aliphatic (including cycloaliphatic) ester having a polymerizable ethylenic linkage alpha or beta to the carboxyl group and containing a hydrocarbon group of from 8 to 30 aliphatic carbon atoms, (B) ester of α,β -unsaturated monocarboxylic acids of from 3 to 8 carbon atoms each wherein the carboxyl groups of said acids are monoester-linked to a member of the group consisting of poly-1,2-alkylene glycols and alkyl ethers thereof having from 2 to 7 carbon atoms in each alkylene group and average molecular weights between 800 and 12,000 and (C) α,β -unsaturated monocarboxylic acids of from 3 to 8 carbon atoms each, said (A) component constituting from about 50 to 99.9 mole percent of the polymer composition and said (B) component constituting from about 50 to 100 mole percent of the balance or remainder of the polymer composition.

The copolymerizable component (A) is primarily employed to impart the required degree of oil solubility to the copolymer composition, and, according to the aforementioned definitions, includes the following: olefin hydrocarbons and particularly alkenes such as polyisobutylene and dodecene-1, cycloalkenes such as cyclohexene and vinylcyclohexane, and styrenes such as p-octylstyrene and p-t-butylstyrene; olefinic ethers, representative of which are the vinyl ethers such as vinyl n-butyl ether, vinyl 2-ethylhexyl ether, and vinyl p-octylphenyl ether, allyl ethers such as allyl cyclohexyl ether and allyl isobutyl ether, and methallyl ethers, such as methallyl n-hexyl ether and methallyl octadecyl ether; organic esters in which the copolymerizable ethylenic linkage is contained in the ester radical, such as the vinyl, allyl, methallyl and crotyl esters of long-chain aliphatic and cycloaliphatic monobasic acids, illustrative of which are vinyl oleate, vinyl palmitate, allyl laurate, allyl stearate, allyl ricinoleate, allyl naphthenate, methallyl caproate, methallyl palmitate, crotyl oleate, crotyl naphthenate, α -methylcrotyl palmitate; organic esters in which the copolymerizable ethylenic linkage is contained in the acid portion of the molecule, such as the esters of acrylic, methacrylic, crotonic, maleic, citraconic acids, etc., representative of which are dodecyl acrylate, dodecyl methacrylate, cyclohexyl methacrylate, decyl vinylacetate, octadecyl isocrotonate, didodecyl maleate, di-2-ethylhexyl fumarate, didodecyl citraconate, etc. For present purposes, the preferred copolymerizable component (A) is an alkyl ester of an α,β -unsaturated monocarboxylic acid of from 3 to 8 carbon atoms having an alkyl group of from 8 to 30 carbon atoms with the esters of acrylic and methacrylic acids being even more desirable from the standpoint of availability and the effectiveness of copolymers prepared from them.

The term "oil-soluble" is employed in this description in its commonly accepted sense and is used particularly to denote a solubility for the copolymers of at least 0.0005% by weight of the polymer in the fuel oil.

The other copolymerizable components identified for convenience either as component (B) or as components (B) and (C) in the two types of description given above are employed for the purpose of supplying the requisite active polar constituents in the copolymer composition. As previously indicated, the fundamental structure of these components consists of a monocarboxylic acid and glycol esters thereof, preferably an aliphatic monocarboxylic acid with a copolymerizable olefinic linkage in the α,β position to the carboxyl group. More specifically, the acid of component (B) and components (B) and (C) is preferably selected from the α,β -unsaturated aliphatic monocarboxylic acids which contain from 3 to 8 carbon atoms in the molecule. Particularly preferred acids are the acrylic and methacrylic acids with their alkyl-substituted derivatives falling within the scope of the general formula



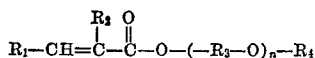
in which R_1 and R_2 are members of the group consisting of hydrogen and alkyl radicals containing from 1 to 3 carbon atoms each.

The final copolymer composition may present up to 100% of the carboxyl groups of the acids of component (B) or components (B) and (C) in the copolymers according to the two descriptions given above in the form of their polyglycol ester derivatives. These derivatives may be introduced initially into the copolymerization reaction by employing as the (B) monomer or (B) and (C) monomers appropriate mixtures of the monocarboxylic acid derivatives and the free monocarboxylic acid, or the copolymerization may be effected with the monocarboxylic acid monomer and the resulting copolymer reacted with the desired polyglycol in appropriate ratio to effect the desired degree of derivative formation.

The desirability of modifying the basic copolymer structure through the use or by the formation of the carboxylic acid derivatives is primarily dependent upon the environmental conditions to which the compounded hydrocarbon fuel is subjected. In addition to the previous variables in composition of the base fuel and projected service conditions, a further selection of optimum copolymer compositions is predicated upon the fuel system, e.g., wet or dry fuel system. It has been found that, in general, the modified copolymers in which up to 100%, and preferably from about 50 to 100% of the carboxyl groups of component (B) or components (B) and (C) are presented in the form of their polyglycol esters possess certain performance advantages when employed as an improving agent for hydrocarbon fuels in a wet fuel system. Aside from the improved deposit reduction noted in performance tests in a wet burner fuel system, other collateral improvements, such as corrosion inhibition and improved demulsibility, are attained with proper selection of the copolymer derivatives.

The polyalkylene glycols and alkyl ethers thereof used in the esterification of the copolymeric (B) component of the copolymer additives of the invention contain from 2 to 7 carbon atoms in each alkylene group and have an average molecular weight in excess of 800, as already mentioned. Poly-1,2-alkylene glycols and their alkyl ethers having molecular weights between 800 and about 12,000 are preferred. Such glycols may be obtained by polymerizing 1,2-alkylene oxides or mixtures thereof in the presence of a catalyst and a suitable initiator for the reaction such as water, monohydric alcohol in the case of the allyl ethers, mercaptan and the like. The preparation of polyglycol compounds of this type has been fully described heretofore in U.S. Patents 2,448,664 and 2,457,139, for example, and, therefore, requires no detailed discussion here.

The polyglycol ester of the (B) component of the polymer can also be described as having the general structural formula



where R_1 and R_2 , as indicated above in connection with the definition of the monocarboxylic acid component, are hydrogen atoms or C_1 - C_3 alkyl radicals, the R_3 's are 1,2-alkylene radicals of 2 to 7 carbon atoms, n is an integer greater than 30 and R_4 is a hydrogen atom or a substituted or unsubstituted hydrocarbon group, the substituent groups here contemplated being the polar groups $-\text{COOH}$,



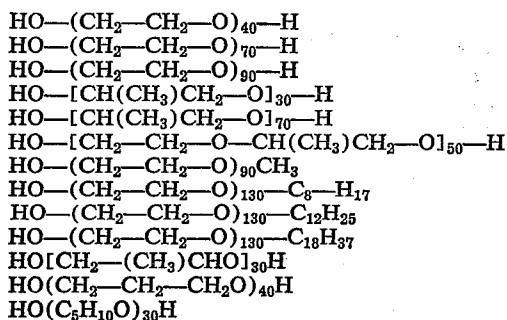
$-\text{OH}$, $-\text{NO}_2$, $-\text{SH}$, $-\text{NR}_5-\text{R}_6$, or



where the R_5 's and the R_6 's are hydrogen atoms or hydrocarbon groups. For present purposes, however, a more preferred group of (B) monomer components is made up of those compounds wherein, in the above structural formula, R_1 represents a hydrogen atom, R_2 represents hydrogen or a methyl group, the R_3 's are ethylene or propylene groups, and R_4 is hydrogen or an alkyl group of from 1 to 18 carbon atoms.

For present purposes, the most suitable poly-1,2-alkylene glycols are those derived from ethylene oxide or from 1,2-propylene oxide or mixtures thereof and their alkyl ethers of 1 to 18 carbon atoms per alkyl group which have molecular weights or average molecular weights between about 800 and 8,000. Esterification with these polyalkylene glycols is found to provide the most effective compositions.

The following polyalkylene glycols containing from 2 to 7 carbon atoms in each alkylene group are illustrative of the types described above.



Polyethylene glycol mixtures having average molecular weights of 880, 1000, 1540, 2000 or 8,000.

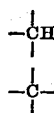
Poly-1,2-propylene glycol mixtures having average molecular weights of 836, 1025 or 10,000.

In preparing the copolymers of this invention it is important to obtain a final product which is oil-soluble, i.e., which is soluble in the fuel oil employed, to the extent of at least 0.0005%, and preferably 0.001 or more by weight. Since the various oil-solubilizing monomer characteristics, preliminary tests are made with the polymeric additive to determine whether the relative proportion of oil-solubilizing monomer compound in the copolymer is high enough to impart the desired degree of oil-solubility. If the solubility in oil is unduly low, and if there remain uncombined carboxyl groups in the copolymer, the oil-solubility thereof can normally be remedied by esterifying a portion of said carboxyl groups with a higher alcohol, e.g., a C_8 or higher aliphatic alcohol such as *n*-octanol, 2-ethylhexanol, decanol, dodecanol (lauryl alcohol) or the like.

In general, however, satisfactory oil-solubility, anti-

wear and detergency properties are obtained with polymers wherein the (A), or oil-solubilizing component constitutes from about 35 to 99.9 mole percent, of the overall polymer composition, with the (B) and (C), or polar polyglycol ester and acid monomer components representing a total of from 65 to 0.1 mole percent of the polymer composition, there being in all cases at least one and usually several monomer units of said (B) polyglycol ester monomer components in the copolymer. Expressed percentagewise, of the total polar monomer content of the copolymer, the (B), or polyglycol ester component constitutes from 100 to 3 mole percent, while the (C), or acid component constitutes from 0 to 97 mole percent. By a careful program of exploratory research, supported by testing data, preferred ranges can be established within the aforesaid ranges for particular polymers and classes of polymers coming within the scope of this invention. Thus, with copolymers of (A) a higher alkyl methacrylate (e.g., lauryl methacrylate), (B) an acrylate or methacrylate of a polyethylene glycol or a polypropylene glycol, or a monoalkyl ether of said glycols, or mixture of said glycols or glycol ethers, or a polyglycol monoether, where the glycols are of the molecular weights previously specified for these compounds, and (C) acrylic or methacrylic acids, there preferably is employed from 50 to 99.9 mole percent of the oil-solubilizing, (A) component. The balance or polar portion of the polymer, taken on the basis of 100 mole per cent polar portion, is made up from 50 to 100 mole percent of the (B) component and 50 to 0 mole percent of the (C) component.

It has been particularly noted in the preferred application of the subject copolymer improving agents in the higher boiling range fuels, such as those boiling predominantly within the range of from 300° to 700° F., and preferably such fuels as contain appreciable concentrations of catalytically cracked gas oil stocks, that a certain optimum relationship between the total number of aliphatic carbon atoms to polar groups within the molecule appears to exist. Evidence has been obtained that for a given concentration the copolymer compositions containing a ratio of aliphatic carbon atoms to polar groups within the range of from 7 to 70 appear to embrace the optimum composition for deposit reduction effectiveness. In determining this apparent balance between the polar and nonpolar constituents, the aliphatic carbon atoms to be considered are the following: CH_3 —, $-\text{CH}_2$ —,



and excluding aromatic ring carbon atoms or the carbon atom of the carbonyl groups. As polar groups, the following representative radicals are included: $-\text{O}$ —, $-\text{OH}$ (either acid, alcohol or phenol), and excluding the carboxyl group of the substituted derivatives.

In order to attain the optimum ratios of (A) to (B) in the final copolymer composition, it may be necessary or desirable to employ a mixture of monomers for either or both components (A) and (B). For example, it is recognized that certain monomers falling within the scope of the definition of component (A), such as the allyl esters, allyl ethers, vinyl esters, vinyl ethers, and alkenes, are difficult to copolymerize with a component (B) and (C) monomer to a greater than 1/1 ratio. However, in the event a ratio, (A) to (B) and (C), greater than 1 is desired, this may be accomplished by employing a mixture of monomers using as the additional monomer, for example, the acrylate esters, methacrylate esters, and/or diesters of maleic, fumaric, citraconic, etc., acids, to result in a copolymer composition having the desired ratio of oil-solubilizing (A) component to (B) and (C) polar components.

The copolymerization of the monomers of component

(A) and component (B) and (C) may be conducted in accordance with the conventional bulk, solution or emulsion methods of polymerization, with or without the presence of a polymerization catalyst or initiator, and the choice of the particular method of preparation will depend largely upon practical considerations and the particular types of monomers to be copolymerized. However, the reaction is preferably effected in the presence of an inert organic solvent, such as benzene, toluene, xylene, or petroleum naphtha, to facilitate control of the reaction and handling of the resulting copolymer. Various conventional types of free radical-liberating initiators or polymerization catalysts may be employed; as, for example, the organic peroxides such as benzoyl peroxide, acetyl peroxide, *t*-butyl hydroperoxide, or dibenzoyl peroxide; or an azonitrile such as 1,1'-azodicyclohexanecarbonitrile or α,α' -azodiisobutyronitrile. In addition, other means for initiating the copolymerization reaction may be employed, such as the use of ultraviolet or gamma radiation, as may be obtained from irradiation with a cobalt 60 source. The organic catalyst or initiator may be employed in amounts of 0.1 to 10% by weight, and preferably in the range of 0.25 to 2%, which amounts may be incorporated in increments as the reaction proceeds. The temperature of copolymerization will vary, depending upon the selected monomeric reactants and solvent employed, and may vary from about 75° to 150° C. The copolymers formed may have a wide range of apparent molecular weight, and usually of the order of at least several thousands.

The majority of the desired copolymer compositions to be employed as improving agents are substantially miscible in hydrocarbon oils, and may be compounded into additive concentrates of at least 10% by weight, and preferably up to 70% by weight. In the preparation of additive concentrates, the concentration of copolymer in the hydrocarbon vehicle, such as toluene, mixed xylenes, kerosene, or other petroleum fractions, may be limited by the tendency toward gel formation, and in such instances it has been found desirable to incorporate a modifying agent or polar solvent, such as dimethyl formamide, tetrahydrofuran, 2-methyltetrahydrofuran, dioxane, cresylic acids, propylene carbonate, etc., which function as solubilizing agents and cosolvents in the copolymer concentrate. These modifying agents or cosolvents are generally employed in concentrations ranging from 1 to 25% of the concentrate. In addition to the copolymer improving agent of this invention, other conventional fuel additives which are compatible with the copolymer improving agent may be incorporated into the concentrate for the purpose of facilitating the handling and blending problems involved in the production of the finished hydrocarbon fuel.

As an illustration of the preparation of representative copolymers of the invention, together with their derivatives, the following examples are presented. It is to be understood, however, that these examples are presented solely for illustration and are not to be construed as limitations of the invention compositions. The proportions, unless otherwise specified, are on a weight basis.

EXAMPLE I

100 g. (0.328 mole) of mixed alkyl methacrylates having an equivalent weight of 305, and consisting of 60 mole percent tridecyl methacrylate and 40 mole percent octadecyl methacrylate, 8.5 g. (0.0007 mole) of dodecyl-capped polyethylene glycol methacrylate in which the polyethylene glycol has an average molecular weight of about 12,000 and 0.06 g. (0.0007 mole) of glacial methacrylic acid were charged to a reaction flask. 100 g. of benzene and 150 cc. of methylethyl ketone were added. 3.2 cc. of a catalyst solution of 15 g. benzoyl peroxide in 100 cc. of methylethyl ketone was added. The mixture was blanketed with nitrogen and heated to reflux temperature of 175 to 180° F. and maintained at this temperature for about 24 hours with stirring. At 4 hours 1.8 cc. of

catalyst solution was added and at 8 hours another 0.9 cc. of catalyst solution was added. At the end of 24 hours there was added 164 g. of 150 neutral mineral oil. The mixture was stripped to 280° F. at 3 mm. mercury pressure to remove the solvents. The product thus obtained was a mineral oil concentrate containing 35% by weight of the copolymer of tridecyl methacrylate, octadecyl methacrylate, dodecyl ether of triheptacontadodecyl ethylene glycol (av. mol. wt. 12,000) methacrylate and methacrylic acid in a molar ratio of 281/187/1/1.

EXAMPLE II

115.9 g. (0.381 mole) of mixed alkyl methacrylate having an equivalent weight of 305 and containing 60 mole percent tridecyl methacrylate and 40 mole percent octadecyl methacrylate, 21.3 g. (0.005 mole) dodecyl-capped polyethylene glycol methacrylate in which the polyethylene glycol has an average molecular weight of approximately 3900 and 0.43 g. (0.005 mole) of glacial methacrylic acid were charged to a reaction flask. 100 g. of benzene and 150 cc. of methylethyl ketone were added. 3.2 cc. of catalyst solution consisting of 15 g. benzoyl peroxide in 100 cc. of methylethyl ketone was then added. The mixture was heated under a blanket of nitrogen to reflux temperature of about 175 to 180° F. and maintained at this temperature for about 24 hours. At 18 hours 1.8 cc. of catalyst solution was added, and at 22 hours 0.9 cc. of catalyst solution was added. 207 g. of 150 neutral mineral oil was added at the end of the 24 hours, and the mixture was stripped to 280° F. at 3 mm. mercury pressure to remove the solvents. The product was a mineral oil concentrate containing 35% of the copolymer of tridecyl methacrylate, octadecyl methacrylate, dodecyl ether of octaoctacontaeethylene glycol methacrylate and methacrylic acid in a molar ratio of 46/30/1/1.

EXAMPLE III

207 g. (0.7 mole) of mixed tridecyl methacrylate and octadecyl methacrylate in 60/40 mole ratio, 32 g. (0.017 mole) dodecyl-capped polyethylene glycol (1600 average molecular weight) methacrylate, 1.3 g. (0.015 mole) glacial methacrylic acid, 320 g. benzene, 178 cc. methylethyl ketone and 3.1 cc. of 15% catalyst solution of benzoyl peroxide in benzene were charged to a reaction flask fitted with stirrer, thermometer, reflux condenser, nitrogen inlet and dropping funnel. The flask was placed in a bath at 166° F. blanketed with nitrogen and stirred for 18 hours. 360 g. of 150 neutral mineral oil was added. The mixture was stripped to 300° F. pot temperature at 50 mm. mercury pressure to remove solvents. 600 g. of product were thus obtained consisting of a mineral oil concentrate containing 36% by weight of the copolymer of tridecyl methacrylate, octadecyl methacrylate, dodecyl ether of hexatricoethaethylene glycol methacrylate and methacrylic acid in a molar ratio of 30/20/1/1.

EXAMPLE IV

Into a reaction flask of the type described above were charged 60 g. (0.224 mole) tridecyl methacrylate, 49 g. (0.145 mole) octadecyl methacrylate, 22 g. (0.052 mole) dodecyl-capped polyethylene glycol (3900 average molecular weight) methacrylate, 126 g. mixed hexanes and 189 g. methylethyl ketone. 3.2 cc. of 15% catalyst solution of benzoyl peroxide in methylethyl ketone was added. The mixture was refluxed at 158° F. for 24 hours with catalyst solution additions of 1.8 cc. at 13 hours and 3.2 cc. at 22 hours. 195 g. of 150 neutral mineral oil was then added. The mixture was stripped to 270° F. at 10 mm. mercury pressure to remove solvents. The yield was 326 g. of mineral oil concentrate containing 40% by weight of the copolymer of tridecyl methacrylate, octadecyl methacrylate and dodecyl ether of octaoctacontaeethylene glycol methacrylate in approximately 46/30/1 molar ratio.

To ascertain the merits of the copolymer composi-

tions of this invention and particularly their merits with regard to deposit reduction in unstable, high boiling fuels such as those as contain appreciable concentrations of cracked oils, a test procedure was established which has been determined to correlate with actual service conditions. This test, briefly described, involves the determination of the filter residue or the amount of insoluble solids of filter plugging dimensions which form in distillate fuels during aging.

The filter residue of a fuel on aging is determined by filtering tests in which a 500 ml. sample of the fuel to be tested is first passed through filter paper into an unstoppered, 1 quart bottle where the filtered sample is stored and aged at 140° F. for four weeks. In an alternative, accelerated aging procedure, the filtered fuel is heated at a temperature of 212° F. while oxygen is bubbled through it for a period of 6 hours. At the termination of the aging process, the filter residue of the sample is determined by filtering it through a weighed

Gooch crucible with an asbestos mat. The material adhering to the container is dissolved in 25 ml. of 80/20 benzene-alcohol solution. The gums in this solution are precipitated by the addition of 500 ml. of petroleum ether and the mixture is also filtered through the Gooch crucible. The crucible is then washed with 500 ml. of petroleum ether, dried in an oven at 190° F., cooled in a constant humidity vessel and weighed. The filter residue is calculated as parts per million.

The following filter residue test results in Table I were obtained with a number of copolymer improving agents of the invention prepared as described above. In these tests the base fuels employed were all 50/50 blends of a raw Thermofor catalytically cracked gas oil and a straight run gas oil blended to meet the U.S. commercial standards specification of a No. 2 fuel oil. The copolymer-improving agents were incorporated in base fuels (A) and (B) in concentrations of 50 p.p.m., while in base fuel (C) the concentration was 100 p.p.m.

Table I

Polymer Additive in Fuel Oil	Ratio of (1) Monomer to (2) Monomer to (3) Monomer, Etc.	Filter Residue Formed During 6-Hour O ₂ Blow Test at 212° F., p.p.m.	Filter Residue Formed During 4-Week Aging at 140° F., p.p.m.
None—Base Fuel (A) alone.....		82	203
Copolymer of (1) tridecyl methacrylate, (2) octadecyl methacrylate and (3) dodecyl ether of decaethylene glycol (av. mol. wt. 440) methacrylate in base fuel (A).....	5.7/3.8/1	60	192
Do.....	6.6/4.4/1		201
Do.....	7.5/5/1		183
Do.....	12/8/1	50	179
Copolymer of (1) tridecyl methacrylate, (2) octadecyl methacrylate and (3) dodecyl ether of octadecaethylene glycol (av. mol. wt. 780) methacrylate in base fuel (A).....	9/6/1	33	86
Do.....	10.5/6.5/1		124
Copolymer of (1) tridecyl methacrylate, (2) octadecyl methacrylate and (3) octadecyl ether of eicosaeethylene glycol (av. mol. wt. 880) methacrylate in base fuel (A).....	13.2/8.8/1		108
Copolymer of (1) tridecyl methacrylate, (2) octadecyl methacrylate and (3) dodecyl ether of hexatriacontaeethylene glycol (av. mol. wt. 1,600) methacrylate in base fuel (A).....	15.6/10.3/1	21	56
Do.....	19.1/12.7/1		5
Do.....	24/16/1		31
Do.....	30/20/1		38
Copolymer of (1) tridecyl methacrylate, (2) octadecyl methacrylate and (3) dodecyl ether of octaoctacontaeethylene glycol (av. mol. wt. 3,900) methacrylate in base fuel (A).....	24/16/1	0	7
Do.....	39.1/26.3/1		0
Do.....	45.6/30.4/1	1	0
Do.....	52.8/35.2/1	0	
Copolymer of (1) tridecyl methacrylate, (2) octadecyl methacrylate and (3) dodecyl ether of dooctacontaehekataethylene glycol (av. mol. wt. 8,000) methacrylate in base fuel (A).....	132/88/1	0	0
Copolymer of (1) tridecyl methacrylate, (2) octadecyl methacrylate and (3) dodecyl ether of triheptacontadohekataethylene glycol (av. mol. wt. 12,000) methacrylate in base fuel (A).....	281/187/1	0	0
None—Base Fuel (B) alone.....		101	
Copolymer of (1) tridecyl methacrylate, (2) octadecyl methacrylate, (3) dodecyl ether of triheptacontadohekataethylene glycol (av. mol. wt. 12,000) methacrylate and (4) methacrylic acid in base fuel (B).....	281/187/1/1	30	
Copolymer of (1) tridecyl methacrylate, (2) octadecyl methacrylate, (3) dodecyl ether of octaoctacontaeethylene glycol (av. mol. wt. 3,900) methacrylate and (4) methacrylic acid in base fuel (B).....	45.6/30.4/1/1	0	
Copolymer of (1) tridecyl methacrylate, (2) octadecyl methacrylate, (3) dodecyl ether of octadecaethylene glycol (av. mol. wt. 780) methacrylate and (4) methacrylic acid in base fuel (B).....	90/60/10/1	102	
Copolymer of (1) tridecyl methacrylate, (2) octadecyl methacrylate and (3) dodecyl ether of octaoctacontaeethylene glycol (av. mol. wt. 3,900) methacrylate in base fuel (B).....	46/30/1	0	
Copolymer of (1) tridecyl methacrylate, (2) octadecyl methacrylate, (3) dodecyl ether of hexatriacontaeethylene glycol (av. mol. wt. 1,600) methacrylate and (4) methacrylic acid in base fuel (B).....	30/20/1/1	0	
None—Base Fuel (C) alone.....			158
Copolymer of (1) tridecyl methacrylate, (2) octadecyl methacrylate and (3) dodecyl ether of octaoctacontaeethylene glycol (av. mol. wt. 3,900) methacrylate in base fuel (C).....	24/16/1		4
Do.....	45.6/30.4/1		3
Do.....	39.2/26.2/1		3
Copolymer of (1) tridecyl methacrylate, (2) octadecyl methacrylate and (3) dodecyl ether of hexatriacontaeethylene glycol (av. mol. wt. 1,600) methacrylate in base fuel (C).....	24/16/1		45
Do.....	19.1/12.7/1		38
Do.....	15.6/10.3/1		54
Do.....	30/20/1		15
Copolymer of (1) tridecyl methacrylate, (2) octadecyl methacrylate and (3) dodecyl ether of decaethylene glycol (av. mol. wt. 440) methacrylate in base fuel (C).....	5.7/3.8/1		145
Do.....	7.5/5/1		133
Do.....	12/8/1		163

The effectiveness of the fuel oil compositions of the invention employing the combination of a conventional metal deactivator was also illustrated by the filter residue test results given in Table II which follows. In these tests the base fuel (A) was the same as described in connection with the test results of Table I above but included a metal deactivator, disalicylal-1,2-propylenediamine, which was employed in a concentration of 4 p.p.m. The copolymer improving agents were incorporated in the base fuels in concentrations of 23 p.p.m. 10

Table II

Polymer Additive in Fuel Oil	Ratio of (1) Monomer to (2) Monomer to (3) Monomer, Etc.	Filter Residue Formed During 6-Hour O ₂ Blow Test at 212° F., p.p.m.	Filter Residue Formed During 4-Week Aging at 140° F., p.p.m.
None—Base Fuel (A) alone.....		40	123
Copolymer of (1) tridecyl methacrylate, (2) octadecyl methacrylate and (3) dodecyl ether of decaethylene glycol (av. mol. wt. 440) methacrylate in base fuel (A).....	5. 7/3. 8/1	35	126
Do.....	7. 5/5/1		129
Do.....	12/8/1	35	129
Copolymer of (1) tridecyl methacrylate, (2) octadecyl methacrylate and (3) dodecyl ether of octadeca ethylene glycol (av. mol. wt. 780) methacrylate in base fuel (A).....	9/6/1	30	86
Do.....	10. 5/6. 5/1		115
Copolymer of (1) tridecyl methacrylate, (2) octadecyl methacrylate and (3) octadecyl ether of eicosaethylene glycol (av. mol. wt. 880) methacrylate in base fuel (A).....	13. 2/8. 8/1		87
Copolymer of (1) tridecyl methacrylate, (2) octadecyl methacrylate and (3) dodecyl ether of hexatriacontethylene glycol (av. mol. wt. 1,600) methacrylate in base fuel (A).....	15. 6/10. 3/1	15	43
Do.....	19. 1/12. 7/1		47
Do.....	24/16/1	15	48
Copolymer of (1) tridecyl methacrylate, (2) octadecyl methacrylate and (3) dodecyl ether of octacontaehtethylene glycol (av. mol. wt. 3,900) methacrylate in base fuel (A).....	24/16/1	3	
Do.....	39. 1/26. 3/1	2	4
Do.....	45. 6/40. 4/1	3	7
Do.....	52. 8/35. 2/1	2	
Copolymer of (1) tridecyl methacrylate, (2) octadecyl methacrylate and (3) dodecyl ether of dooctacontahakataethylene glycol (av. mol. wt. 8000) methacrylate in base fuel (A).....	132/88/1	0	9

From the test results of the foregoing tables it will be seen that each of the illustrative fuel oil compositions containing the copolymeric additives according to the invention possesses greatly improved properties compared to the base fuels alone.

This application is a continuation-in-part of Lowe and Stayner patent application Serial No. 496,077, filed March 22, 1955.

We claim:

1. An improved fuel composition comprising a major portion of a liquid hydrocarbon distillate fuel boiling predominantly above about 300° F. and a minor portion, sufficient to reduce the deposit-forming characteristics of said fuel of an oil-soluble copolymer of monomers selected from at least each of the first two classes of the classes consisting of (A) oil-solubilizing compounds having a single polymerizable ethylenic linkage and containing a monovalent hydrocarbon group of from 8 to 30 aliphatic carbon atoms, (B) esters of α,β -unsaturated aliphatic monocarboxylic acids of from 3 to 8 carbon atoms each wherein the carboxyl groups of said acids are monoester-linked to a member of the group consisting of poly-1,2-alkylene glycols and alkyl ethers thereof having from 2 to 7 carbon atoms in each alkylene group and average molecular weights of more than 800 and (C) α,β -unsaturated monocarboxylic acids of from 3 to 8 carbon atoms each, said (A) component constituting from about 35 to 99.9 mole percent and said (B) and (C) components constituting a total of from about 65 to 0.1 mole percent of the polymer composition, there being present in said (B) and (C) components, on the basis of 100 mole percent total (B) and (C) polar monomers from 3 to 100 mole percent of said (B) component, and from 0-97 mole percent of said (C) component.

2. An improved hydrocarbon fuel composition com-

prising a major portion of a liquid hydrocarbon distillate fuel boiling predominantly above about 300° F. having incorporated therein 0.0005 to 1.0% by weight of an oil-soluble copolymer of monomers selected from at least each of the first two classes of the classes consisting of (A) alkyl esters of α,β -unsaturated monocarboxylic acids of from 3 to 8 carbon atoms each in which the alkyl groups contain from 8 to 30 carbon atoms each, (B) esters of α,β -unsaturated aliphatic monocarboxylic acids of from 3 to 8 carbon atoms each wherein the

carboxyl groups of said acids are monoester-linked to a member of the group consisting of polyalkylene glycols and alkyl ethers thereof having from 2 to 7 carbon atoms in each alkylene group and average molecular weights of between 800 and 12,000 and (C) α,β -unsaturated monocarboxylic acids of from 3 to 8 carbon atoms each, said (A) component constituting from about 50 to 99.9 mole percent and said (B) and (C) components constituting a total of from about 50 to 0.1 mole percent of the polymer composition, there being present in said (B) and (C) components, on the basis of 100 mole percent total (B) and (C) polar monomers, from 50 to 100 mole percent of said (B) component, and from 0-50 mole percent of said (C) component.

3. An improved hydrocarbon fuel composition comprising a predominant portion of a hydrocarbon fuel composed predominantly of hydrocarbons boiling above 300° F. having incorporated therein 0.0005 to 1.0% by weight of an oil-soluble copolymer of monomers selected from at least each of the first two classes of the classes consisting of (A) alkyl esters of α,β -unsaturated monocarboxylic acids of from 3 to 8 carbon atoms each in which the alkyl groups contain from 8 to 30 carbon atoms each, (B) esters of α,β -unsaturated aliphatic monocarboxylic acids of from 3 to 8 carbon atoms each wherein the carboxyl groups of said acids are monoester-linked to a polyethylene glycol having an average molecular weight of between 800 and 12,000 and (C) α,β -unsaturated monocarboxylic acids of from 3 to 8 carbon atoms each, said (A) component constituting from about 50 to 99.9 mole percent and said (B) and (C) components constituting a total of from about 50 to 0.1 mole percent of the polymer composition, there being present in said (B) and (C) components, on the basis of 100 mole percent total (B) and (C) polar monomers, from

50 to 100 mole percent of said (B) component, and from 0-50 mole percent of said (C) component.

4. An improved hydrocarbon fuel composition comprising a major portion of a liquid hydrocarbon distillate fuel boiling predominantly above about 300° F. having incorporated therein 0.0005 to 1.0% by weight of an oil-soluble copolymer of monomers selected from at least each of the first two classes of the classes consisting of (A) alkyl methacrylates in which the alkyl groups contain from 8 to 30 carbon atoms each, (B) esters of methacrylic acid wherein the carboxyl group of said acid is monoester-linked to a polyethylene glycol having an average molecular weight of between 800 and 12,000 and (C) methacrylic acid, said (A) component constituting from about 50 to 99.9 mole percent and said (B) and (C) components constituting a total of from about 50 to 0.1 mole percent of the polymer composition, there being present in said (B) and (C) components, on the basis of 100 mole percent total (B) and (C) polar monomers, from 50 to 100 mole percent of said (B) component, and from 0-50 mole percent of said (C) component.

5. An improved hydrocarbon fuel composition comprising a major portion of a liquid hydrocarbon distillate fuel boiling predominantly above about 300° F. having incorporated therein 0.0005 to 1.0% by weight of an oil-soluble copolymer of (A) alkyl methacrylates in which the alkyl groups contain from 8 to 30 carbon atoms each and (B) esters of methacrylic acid wherein the carboxyl group of said acid is monoester-linked to a polyethylene glycol having an average molecular weight of between 800 and 12,000, said (A) component constituting from about 50 to 99.9 mole percent and said (B) component constituting a total of from about 50 to 0.1 mole percent of the polymer composition.

6. A concentrated adapted to be incorporated in liquid hydrocarbon distillate fuels boiling predominantly

above about 300° F. in concentrations effective to reduce the deposit-forming characteristics of said fuels consisting essentially of a hydrocarbon fuel containing from 10 to 70 percent by weight of an oil-soluble copolymer of (A) alkyl esters of α,β -unsaturated monocarboxylic acids of from 3 to 8 carbon atoms each in which the alkyl groups contain from 8 to 30 carbon atoms each, (B) esters of α,β -unsaturated aliphatic monocarboxylic acids of from 3 to 8 carbon atoms each wherein the carboxyl groups of said acids are monoester-linked to a member of the group consisting of poly-1,2-alkylene glycols and alkyl ethers thereof having from 2 to 7 carbon atoms in each alkylene group and average molecular weights of between 800 and 12,000 and (C) α,β -unsaturated monocarboxylic acids of from 3 to 8 carbon atoms each, said (A) component constituting from about 50 to 99.9 mole percent and said (B) and (C) components constituting a total of from about 50 to 0.1 mole percent of the polymer composition, there being present in said (B) and (C) components, on the basis of 100 mole percent total (B) and (C) polar monomers, from 50 to 100 mole percent of said (B) component, and from 0-50 mole percent of said (C) component.

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