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FUEL OIL COMPOSITIONS

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This invention relates to fuel oils and, more particularly, to stabilized fuel oils adapted to withstand the prolonged oxidizing conditions of storage without deterioration and at the same time to have a much reduced tendency to form emulsions with water.

Fuel oils, that is, hydrocarbon oils boiling above the gasoline range and used as burner and furnace oils and diesel fuels and the like, are produced not only from straight run petroleum hydrocarbon distillates but, also, by thermocracking and catalytic cracking. Until recently, most fuel oils have been straight run but catalytic cracking is fast becoming the most popular method for supplying the increased demand for fuel oils.

Fuel oil blends containing substantial proportions of catalytic cracked stocks, e. g., from approximately 20% to 60% by weight of the blend, with straight run fuel oils are now being marketed. It would be preferable to increase the proportion of catalytic cracked oil or sell catalytic cracked oil exclusively for fuel purposes but this has not always been practical because of a serious storage stability problem.

Fuel oils are frequently prone to deterioration on storage and catalytic cracked fuel oil in particular is frequently very unstable and deteriorates badly in storage. The deterioration resulting from the mild but prolonged oxidizing conditions of storage results not only generally in discoloration but in the formation of sludge or sediment which, if not removed, plugs filter screens, orifices, and other parts of the equipment used in burning such fuel. The high susceptibility to deterioration of many catalytic cracked fuel oils has made it necessary to blend them off with larger proportions of the less plentiful but more stable straight run stocks to meet even the minimum stability requirements. Nevertheless, difficulty has been experienced with such fuels.

The problem of stabilizing catalytic cracked fuel oils is relatively new and various approaches to the problem have been developed. One of these has been the development of refining techniques or treating processes to remove the unstable components of catalytic cracked fuel oil to improve its storage stability. Some refiners have been able to achieve quality improvements by certain treating methods, such as acid washing of the oil, but these methods are too costly for commercial application and do not seem to present a solution to the problem. Also, while catalytic cracked fuel oils are among the worst performers in the matter of deterioration during storage, the problem does exist to greater or lesser extent with fuel oils generally.

This problem of stabilizing catalytic cracked fuel oils has been solved by the invention disclosed in copending application S. N. 281,047, filed April 7, 1952, by W. E. Catlin and G. B. Robbins, and assigned to the assignee of this case, now U. S. P. 2,737,452, of incorporating in a fuel oil a small proportion, at least 0.001% by weight of the fuel oil, of an oil-soluble, basic amino nitrogen-containing addition polymer of a plurality of polymerizable ethylenically unsaturated compounds, at least one

of which is amine-free and at least one of which contains at least 8 carbon atoms, preferably predominantly straight chain in nature, said polymer containing 0.1% to 3.5%, by weight thereof, of basic amino nitrogen.

The polymers used in the above application for stabilizing the fuel oils accordingly are made from (1) polymerizable compounds containing basic amino nitrogen groups or groups capable of giving them by after-treatment of the polymer, (2) polymerizable compounds containing at least 8 carbon atoms preferably in a straight chain (the oleophilic components), and in some cases, (3) polymerizable compounds containing neither of the above structures but present in the final polymer in proportions fulfilling the above requirements as to oil solubility and content of basic amino nitrogen. The ability of the components to polymerize is due to their ethylenic unsaturation.

Incorporation of these polymers into fuel oils in the proportions defined not only stabilizes fresh fuel oils against the formation of sludge and sediment but also suspends and disperses the sludge and sediment present in aged oils in such a way as to be relatively harmless and also retards discoloration of the oils and reduces their corrosiveness toward metals.

It has been found, however, that even the small amounts of these polymers which are added to fuel oils as stabilizers and sludge dispersants, have the undesirable effect of causing the emulsification in the oil of small amounts of water which may be in contact with the oil. This presence of water may come about, for example, by the seepage of water into underground tanks, by rain falling into improperly protected tanks, by condensation from moist air, by the incomplete removal of water used as ballast in empty tankers, and by incomplete removal of water after earlier steps in the refining of the oil. The emulsification of even small quantities of water in the fuel oils, when it occurs, may make the oil unsuitable for many uses.

This invention has as an object to provide a new and improved stabilized fuel oil. A further object is to provide a stabilized fuel oil having a much reduced tendency to form emulsions with water. A still further object is to provide a composition which, when added to a fuel oil, stabilizes and reduces the emulsification tendencies of the fuel oil. Other objects will appear hereinafter.

These and other objects are accomplished by the following invention of incorporating into a fuel oil stabilized against sludge deposition by means of at least 0.001% by weight of an oil-soluble, basic amino nitrogen-containing addition polymer of a plurality of polymerizable ethylenically unsaturated compounds, at least one of which contains at least 8 carbon atoms, preferably predominantly straight chain in nature, said polymer containing 0.1% to 3.5% by weight thereof, of basic amino nitrogen, from 0.00025 to 0.1% of a fatty acid amide of an ethylene polyamine or propylene polyamine having the general formula

$$Ac—NH—(C_nH_{2n}—NH)_m—C_nH_{2n}—NR_1R_2$$

where Ac is an aliphatic acyl group of from 8 to 18 carbon atoms, where m is zero or an integer from 1 to 3, where n equals 2 or 3, where R_1 and R_2 may be hydrogen or a normal alkyl group of 1 to 4 carbon atoms, and where each pair of nitrogen atoms is separated by at least 2 carbon atoms.

These monoamides are conveniently prepared by heating one mole of an amine which contains two amino groups with one mole of a fatty acid at temperatures between about 150° to 200° C. until one mole of water has been evolved. The polyamine reactants contain 1,2-ethylene, 1,2-propylene and 1,3-propylene units in

the molecule; they may contain two terminal NH_2 groups, or one terminal NH_2 group and one terminal mono or dialkylated amino group as defined. Typical ethylene amines are: ethylene diamine, diethylene triamine, tetraethylene pentamine, and the corresponding N-alkyl- and N, N-dialkyl-substituted ethylene diamines and polyethylene polyamines such as N,N-dimethylethylene diamine and N-(beta-diethylaminoethyl) ethylene diamine ($m=1$, $n=2$, $R_1=R_2=$methyl in the structural formula). Typical propylene amines are: 1,2-propylene diamine, 1,3-propylene diamine, N,N-dimethyl-1,3-propylene diamine, N,N-diethyl-1,3 - propylene diamine, and the dipropylene triamines, tripropylene tetramines and tetrapropylene pentamines containing either the 1,2- and/or 1,3-propylene unit. The preferred amine reactants are diethylene triamine, N,N-dimethyl-1,3-propylene diamine and N,N-diethyl - 1,3 - propylene diamine, particularly N,N-dimethyl-1,3-propylene diamine.

The fatty acids forming the amides, the acyl portion of which is represented by Ac in the general formula, are monobasic aliphatic acids containing 8 to 18 carbon atoms, such as caprylic, pelargonic, capric, lauric, myristic, palmitic, margaric, stearic, oleic, and linoleic. The readily available technical grades of these acids, containing small amounts of homologs, may be used to advantage instead of the rigorously purified chemical individuals. The preferred acid is oleic acid.

The "basic amino nitrogen-containing polymers" which are present in the fuel oils and which stabilize it against sludge deposition, are prepared by polymerizing polymerizable "oleophilic components" which make the polymer oil-soluble, polymerizable "basic amino nitrogen-containing components," which introduce the required basic groups, and, in many cases, polymerizable "filler components," which extend the active components. The copolymers must contain at least 0.1% but not more than 3.5% by weight thereof, of basic amino nitrogen, preferably between 0.2 and 3.0%, and must have at least a limited solubility in the fuel oil, i. e., at least 0.001% by weight. The term "oil soluble" is used herein to denote a solubility of at least 0.001% by weight, of the polymer in the fuel oil.

The optimum proportion of polymer in the fuel oil will be determined by its inherent viscosity, which can be within the range of 0.1 to 3.0 as determined at 0.1% weight/volume concentration in benzene at 25° C. From a practical point of view, 0.001% to 0.1% of the polymer additive having an inherent viscosity between about 0.2 and 1.0, normally will be found to give optimum results.

As the oleophilic components of copolymers useful in the preparation of the improved fuel oil compositions there can be employed polymerizable esters, amides, ethers, and hydrocarbons characterized by the presence of at least 8 carbon atoms, preferably with 6 or more in a straight chain, and at least one carbon-to-carbon double bond capable of participation in free radical initiated addition copolymerization reactions. Examples of oleophilic components are: saturated and unsaturated long-chain esters of unsaturated carboxylic acids such as decyl acrylate, 3,5,5 - trimethylhexyl methacrylate, 9-octadecenyl methacrylate; unsaturated esters of long-chain carboxylic acids such as vinyl stearate; long-chain esters of vinylene dicarboxylic acids such as methyl lauryl fumarate; N-long-chain hydrocarbon substituted amides of unsaturated acids such as N-octadecyl acrylamide; long-chain monoolefins such as the alkyl or acyl substituted styrenes, e. g., dodecylstyrene, and the like. Obviously, these components can be employed alone or in various combinations and, in general, make up the majority of the polymeric additive in order to insure proper oleophilic character. The technical lauryl methacrylate obtained from the commercial mixture of long-chain alcohols in the C_{10} to C_{18} range derived from coconut oil is an especially useful oleophilic component of the copolymer but the group of acrylic and alkacrylic esters of aliphatic alcohols of at least 8 carbons is, in general, well suited as the oleophilic component of the copolymer.

The basic amino nitrogen-containing component that imparts sludge-inhibiting and dispersant properties to the polymers can be introduced through the use of appropriate copolymerizable monomers containing primary, secondary, or tertiary amino nitrogen that is attached ultimately to the chain of the polymer as part of an extralinear substituent group in which the nitrogen is joined extranuclearly only to non-benzenoid carbon atoms. There can be employed in the copolymerization monomers such as glycidyl acrylate or vinyl chloroacetate which introduce groups reactive toward ammonia or amines and thus provide a means of attaching the necessary basic amino groups to the polymer chain. Attachment of the amino groups to the polymer carbon chain can be through strictly hydrocarbon structures or through ether, ester, or amide linkages.

Particular examples of the basic amino-containing monomers include the basic amino substituted olefins such as p-(beta-diethylaminoethyl)styrene; basic nitrogen-containing heterocycles carrying a polymerizable ethylenically unsaturated substitutent, e. g., the vinyl pyridines and the vinyl alkyl pyridines such as 2-vinyl-5-ethyl pyridine; esters of basic amino alcohols with unsaturated carboxylic acids such as the alkyl and cycloalkyl substituted aminoalkyl and cycloalkyl esters of the acrylic and alkacrylic acids, e. g., beta-methylaminoethyl acrylate, 4-diethylaminocyclohexyl methacrylate, beta-beta-didodecylaminoethyl acrylate, and the like, unsaturated ethers of basic amino alcohols such as the vinyl ethers of such alcohols, e. g., beta-aminoethyl vinyl ether, beta-diethylaminoethyl vinyl ether, and the like; amides of unsaturated carboxylic acids wherein a basic amino substituent is carried on the amide nitrogen such as N-(beta-dimethylaminoethyl)acrylamide; polymerizable unsaturated basic amines, e. g., diallylamine, and the like.

Because of their relatively greater basicity and more effective sludge suspending and inhibiting properties, the polymerizable ethylenically unsaturated compounds containing a basic tertiary amino group are preferred and those having only primary basic amino groups are least desirable. Particularly outstanding and readily available basic amino nitrogen-containing components are the alkyl and cycloalkyl substituted tertiary aminoalkyl and cycloalkyl esters of acrylic and alkacrylic acids.

The basic amino nitrogen-containing component of the copolymer must be present in a minor proportion by weight corresponding to no more than 3.5% and no less than 0.1% of basic amino nitrogen by weight of the polymer. Above the higher level, which, for example, corresponds to about 50% by weight of amino monomer in a lauryl methacrylate/beta-diethylaminoethyl methacrylate copolymer, and at less than the lower level, the performance of the polymer as a sludge inhibitor falls off rapidly. It is preferred that the basic amino nitrogen content be within the range of 0.2% to 3.0% by weight of the polymer.

The sludge-inhibiting and dispersing polymers can contain limited amounts of copolymerizable components that do not necessarily contribute either to improve solubility or inhibiting and dispersing action but merely serve as fillers or extenders for the active components. Typical examples of the filler components include the well-known shorter chain ethylenically unsaturated addition polymerizable monomers such as the vinyl and allyl formates, acetates, propionates, butyrates, and the like; polymerizable unsaturated short-chain hydrocarbons, e. g., the monoolefins such as ethylene, propylene, isobutylene, styrene, vinyltoluene, and the like, and the short-chain dienes such as 1,3-butadiene, isoprene, and the like; unsaturated short-chain carboxylic acids and their derivatives such as the alpha-methylene carboxylic acids and

their derivatives, e. g., acrylic acid, methyl methacrylate, acrylonitrile, methacrylamide, and the like; the short-chain unsaturated ethers, particularly the vinyl and allyl ethers, e. g., ethyl vinyl ether, butyl vinyl ether, allyl glycidyl ether, and the like. These and other familiar monomers that are available at moderate cost, can be employed for this purpose in proportions ranging up to as much as 79%, by weight, in representative polymers although it is preferred they should not exceed 65% by weight of the polymer.

In addition, inclusion of minor proportions of N-hydrocarbon-substituted amides of unsaturated carboxylic acids will be found beneficial. Especially suitable as polymerizable components of the polymer are the N-hydrocarbon-substituted acrylamides including N-tertiary-butylacrylamide, N-tertiary-octylacrylamide, and particularly, the N-arylacrylamides such as methacrylanilide and acrylanilide.

The preferred basic amino nitrogen-containing polymers are those made from long-chain aliphatic acrylates and methacrylates as the oleophilic components, dialkyl aminoalkyl acrylates or methacrylates to furnish the basic nitrogen, and, in some cases, styrene as filler.

The copolymers can be prepared by conventional bulk, solution, or dispersion polymerization methods involving known initiators, including oxygen-yielding compounds, such as benzoyl peroxide, and azo compounds, such as alpha,alpha'-azodiisobutyronitrile. Convenient solvents are high-boiling hydrocarbons, particularly those similar to the hydrocarbons in which the copolymers are to be used, such as kerosine. The polymerization processes usually are carried out in an inert atmosphere, e. g., nitrogen or helium, at temperatures ranging from 30° C. to 150° C., depending on the catalyst used, and generally at temperatures between 50° C. and 90° C. when alpha, alpha'-azodiisobutyronitrile is used as the catalyst. It is important to carry the copolymerization substantially to completeness so that no unpolymerized monomers remain and the proportions of each component in the final product are essentially those of the original monomer mixture.

The concentration of the stabilizing polymer in the oil will vary to some extent depending on the effectiveness of the particular polymer, the initial stability of the oil and the degree of stability required. Generally, concentrations between 0.001 and 0.1% and particularly between 0.002 and 0.01%, will be used. Similiarly the concentration of the fatty acid monoamide in the oil should be between about 0.00025 and 0.1% and preferably between about 0.0004 and 0.005% of the weight of the oil.

The following examples will better illustrate the nature of the present invention; however, it is to be understood that the invention is not intended to be limited to these examples. Parts are by weight unless otherwise indicated.

Example I

A catalytically cracked fuel oil No. 2 distillate was inhibited against insoluble residue formation by the addition of 0.005 weight percent of a polymer, referred to as polymer (A), made by copolymerizing a mixture of 50 parts by weight of octadecenyl methacrylate (technical), 40 parts by weight of styrene, and 10 parts by weight of beta-diethylaminoethyl methacrylate. Samples of the inhibited fuel were treated with small proportionate amounts of technical grades of aliphatic acid amides of alkylene polyamines. These fuel samples were subjected to an emulsification test designed to simulate actual conditions present when the oil is run into and withdrawn from a tank containing water at the bottom and at the same time to provide much more severe emulsifying conditions. The test consisted of agitating 190 ml. of the fuel and 10 ml. of distilled water together for 5 minutes in a 600 ml. glass beaker which was 2¾ inches in diameter and 5¾ inches deep. The mixing was done with an ordinary commercial motor-driven milk shake machine. After mixing, the samples were covered with a watch glass and permitted to set for 24 hours or until clear oil separated. The clear oil was then drawn off from the water and another 190 ml. of the oil containing the two additives was added and the mixing was repeated. A total of 5 oil changes and mixings were carried out to determine the emulsification tendencies of the oils.

The results of the emulsification tests are summarized in Table I.

TABLE I

[Effect of various amides on the emulsification of fuel oil containing an octadecenyl methacrylate/styrene/diethylaminoethyl methacrylate copolymer]

Test No.	Fuel	Results of Emulsification
1	Control, fuel oil containing polymer (A).	Stable, milky, water-in-oil emulsion formed during first mixing.
2	Fuel oil containing polymer (A)+0.001 wt. percent oleic acid amide of ethylenediamine.	Water separated completely after each mixing.
3	Fuel oil containing polymer (A)+0.0008 wt. percent oleic acid amide of diethylenetriamine.	Do.
4	Fuel oil containing polymer (A)+0.001 wt. percent oleic acid amide of triethylenetetramine.	Do.
5	Fuel oil containing polymer (A)+0.001 wt. percent oleic acid amide of tetraethylene-pentamine.	Do.
6	Fuel oil containing polymer (A)+0.001 wt. percent lauric acid amide of diethylene triamine.	Water separated completely after first four mixes; some emulsion on fifth mixing.
7	Fuel oil containing polymer (A)+0.001 wt. percent palmitic acid amide of diethylenetriamine.	Water separated completely after each mixing.
8	Fuel oil containing polymer (A)+0.001 wt. percent dodecylamine (technical).	Water partially emulsified after first mixing; completely emulsified after second mixing.
9	Fuel oil containing polymer (A)+0.0008 wt. percent tetradecylamine (technical).	Do.

Example II

A catalytically cracked fuel oil No. 2 distillate containing 0.05 wt. percent of a copolymer made by copolymerizing a mixture of 80 parts by weight of lauryl methacrylate (technical) and 20 parts by weight of diethylaminoethyl methacrylate gave a stable, milky emulsion when agitated with water as described in the emulsion test of Example I. Addition (to the emulsion) of 0.1 wt. percent, based on the oil, of oleic acid amide of diethylene triamine and remixing caused the emulsion to break immediately.

Example III

An 80/20 copolymer of lauryl methacrylate (technical) and diethylaminoethyl methacrylate was dissolved in a diesel fuel to give 0.005 wt. percent of the additive in the fuel. The inhibited oil gave stable milky emulsions with synthetic sea water (prepared in accordance with specification VV-L-791, method 4011) when subjected to the emulsion test described in Example I. Addition of 0.005 wt. percent oleic acid amide of diethylene triamine to the inhibited oil overcame its emulsion tendencies.

Example IV

A catalytically cracked fuel oil No. 2 distillate containing 0.005 wt. percent of a copolymer made by copolymerizing a mixture of 77 parts by weight of lauryl methacrylate (technical) and 23 parts by weight of dibutylaminoethyl methacrylate gave a milky emulsion when agitated with water as described in the emulsion test of Example I. Adding 0.0025 wt. percent of N(3-dimethylaminopropyl) oleamide to a sample of the in-

hibited oil and repeating the test resulted in no emulsification.

Example V

An 80/20 copolymer of lauryl methacrylate (technical) and 4-vinyl pyridine was dissolved in a diesel fuel to give 0.005 wt. percent of the additive in the fuel. The inhibited oil gave stable milky emulsions when mixed with water as described in Example I. Addition of 0.0025 wt. percent of N(3-diethylaminopropyl) stearamide to the inhibited oil overcame its emulsification tendencies.

Example VI

A catalytically cracked fuel oil No. 2 distillate containing 0.01 wt. percent of a 92.5/7.5 copolymer of lauryl methacrylate (technical) and diethylaminoethyl methacrylate gave stable, milky emulsions when mixed with water as described in Example I. Addition of 0.005 wt. percent of N(3-dimethylaminopropyl) oleamide to the inhibited oil overcame its emulsification tendencies.

Example VII

Samples of JP–4 and JP–5 jet fuels inhibited with 0.01 wt. percent of a 50/40/10 tripolymer of octadecenyl methacrylate, styrene and diethylaminoethyl methacrylate gave milky emulsions when agitated with 10 vol. percent of synthetic sea water (prepared in accordance with specification VV–L–791, method 4011). Addition of 0.005 wt. percent of N(3-dimethylaminopropyl) oleamide to the inhibited fuels overcame their emulsification tendencies.

Example VIII

A diesel fuel containing 0.01 wt. percent of a 90/10 copolymer of lauryl methacrylate (technical) and N(3-dimethylaminopropyl) methacrylamide gave a stable, milky emulsion when agitated with water as described in the emulsion test of Example I. Addition to the emulsified sample of 0.01 wt. percent based on the oil, of N(3-dimethylaminopropyl) oleamide and remixing caused the emulsion to break immediately.

Example IX

A catalytically cracked fuel oil No. 2 distillate containing 0.01 wt. percent of an 80/20 copolymer of vinyl lauryl ether and vinyl diethylaminoethyl ether gave stable, milky emulsions when mixed with water as described in Example I. Addition of 0.01 wt. percent of N(3-dimethylaminopropyl) oleamide to the inhibited oil overcame its emulsification tendencies.

Example X

A catalytically cracked fuel oil No. 2 distillate containing 0.005 wt. percent of a copolymer made by copolymerizing a mixture of 92.5 parts of vinyl laurate and 7.5 parts diethylaminoethyl methacrylate gave stable, milky emulsions when mixed with water as described in Example I. Addition of 0.01 wt. percent of the oleic acid amide of dipropylenetriamine to the inhibited oil overcame its emulsification tendencies.

Example XI

In order to show the compatibility of the basic tertiary amino-containing polymers with the aliphatic acid amides of alkylene polyamines in fuel oil and the absence of interference by the latter with the inhibiting effects of the polymer, samples of a catalytic cracked fuel oil No. 2 distillate were inhibited with small amounts of polymer (see Table II below) and a small amount of oleic acid amide of diethylene triamine sufficient to prevent emulsification when the inhibited oil was contacted with water. This treated oil did not emulsify when subjected to the test described in Example I. The samples were subjected to an accelerated aging test in vented glass bottles at 110° F. for 12 weeks. At the end of the 12-week period, the samples were analyzed for insoluble residue using the following method. The sample (300 ml.) is

filtered at room temperature by suction through a sintered glass filter having a 1.25-inch diameter disc with an average pore size of 5 microns. The container and filter are washed with naphtha. The insoluble residue is dissolved from the container and filter with a 50–50 mixture of acetone and methanol and determined by air jet evaporation according to ASTM Method D–525–46. The insoluble residue is expressed in mg./100 ml. of fuel. The results of the tests are shown in Table II.

TABLE II

[Effect of using oleic acid amide of diethylenetriamine with octadecenyl methacrylate (technical)/styrene/diethylaminoethyl methacrylate, 50/40/10, tripolymer, (OM/S/DEAEM), on fuel oil stored 12 weeks in vented glass bottles in the dark]

	Insoluble residue, mg./100 ml.
1. Catalytically cracked fuel oil alone	7.2
2. Fuel oil + 0.0033 wt. percent OM/S/DEAEM	2.1
3. Fuel oil + 0.0033 wt. percent OM/S/DEAEM + 0.0011 wt. percent oelic acid amide of diethylene triamine [1]	2.3

[1] These additives were added as a mixture comprised of 37.5% OM/S/DEAEM, 37.5% kerosine, 12.5% oleic acid amide of diethylene triamine and 12.5% cresylic acid.

It is apparent from the preceding examples that the fatty acid monoamides of the present invention are very effective in suppressing the emulsification tendencies of fuel oils containing oil-soluble, basic amino nitrogen-containing addition polymers and at the same time exhibit no significant adverse effect on the stabilizing properties of the polymeric additive. The resulting non-emulsifying compositions, i. e., the fuel oil containing the stabilizing polymer plus the fatty acid monoamide, avoid the undesirable emulsification effects brought about by the presence of water caused by the seepage of water into underground tanks, by rain falling into improperly protected tanks, by condensation from moist air, by the incomplete removal of water used as ballast in empty tankers or by incomplete removal of water after earlier steps in the refining of the oil.

While the invention has been illustrated by means of adding the fatty acid monoamide of an ethylene polyamine or a propylene polyamine as defined to the emulsion formed by the fuel oil containing the polymer only or by adding the monoamide before the emulsifying test, it is to be understood that a concentrated solution containing both the sludge-stabilizing nitrogen-containing polymer and the emulsion-preventing monoamide may be added to the fuel oil so that the oil may be completely treated by a suitable small quantity of a single liquid. Such a concentrated solution may contain from 25 to 75% by weight of the agents, in suitable ratio to each other, dissolved in kerosine, fuel oil, or a mixture of these in cresylic acid. The ratio of stabilizing polymer to de-emulsifying agent in these concentrated solutions should be between about 1:100 and 400:1 and preferably between about 1:2.5 and 25:1.

The following examples are illustrative of the preparation and use of a concentrated solution containing both the sludge-stabilizing nitrogen-containing polymer and the emulsion-preventing fatty acid monoamide of an ethylene polyamine and fatty acid monoamide of a propylene polyamine.

Example XII

A concentrate, adaptable for use as a non-emulsifying additive for liquid hydrocarbons, was made by mixing together 75 parts by wt. of a 50% solution in kerosine of a 50/40/10 tripolymer of octadecenyl methacrylate (technical), styrene, and diethylaminoethyl methacrylate, 12.5 parts by wt. of oleic acid amide of diethylenetriamine and 12.5 parts by weight of mixed cresols (cresylic acid). This product was found to be a very effective gum inhibitor for catalytically cracked fuel oil and was emulsifi-

cation-inhibiting as indicated by the emulsification test described in Example I, using the same amount of active ingredients.

The present invention is applicable in reducing the emulsification tendencies of any fuel oil which has been stabilized with an oil-soluble, basic amino nitrogen-containing addition polymer either prior to the addition of the emulsion-preventing monoamide or concurrently with the addition of the monoamide. It is particularly useful wherein the fuel oils are entirely composed of catalytic cracked oil or containing a substantial proptrion thereof, e. g., at least 20%.

Example XIII

A concentrate, adaptable for use as a non-emulsifying additive for liquid hydrocarbons such as burner oils, diesel fuels, and jet fuels, was made by mixing together 25 parts by weight of a 50/40/10 tripolymer of octadecenyl methacrylate (technical), styrene and diethylaminoethyl methacrylate, 25 parts by weight of N(3-dimethylaminopropyl) oleamide, 8 parts by wt. of N,N'-disalicylidene-1,2-propanediamine and 42 parts by wt. of kerosine. This product was found to be a very effective stabilizer for catalytically cracked fuel oil, diesel fuel, and jet fuels and was emulsification inhibiting as indicated by the emulsification test described in Example I.

The concentrate of this example is a practical composition for commercial use in the hydrocarbon fuels described. N,N'-disalicylidene-1,2-propanediamine is present as a metal deactivator (for copper).

As many apparently widely different embodiments of this invention may be made without departing from the spirit and scope thereof, it is to be understood that this invention is not limited to the specific embodiments thereof except as defined in the appended claims.

I claim:

1. A petroleum base fuel oil containing (1) as a sludge inhibiting and dispersing agent at least 0.001% by weight of an oil-soluble, basic amino nitrogen-containing addition type copolymer containing in combined form as its essential monomeric components copolymerizable ethylenically unsaturated compounds each containing only one polymerizable ethylenic linkage, at least one of which component is amine-free and contains from 8 to about 18 carbon atoms in an aliphatic hydrocarbon chain which in the polymer is not part of the main chain, and one of the components as it exists in the polymer containing a basic amino nitrogen in the side chain, said copolymer containing 0.1% to 3.5% by weight of basic amino nitrogen and said copolymer having an inherent viscosity of 0.1 to 3.0 as determined at 0.1% weight/volume concentration in benzene at 25° C., and, (2) as an emulsion inhibitor about 0.00025 to 0.1% of a fatty acid amide of a polyamine taken from the group consisting of ethylene polyamine and propylene polyamine, said fatty acid amide having the general formula

$$Ac—NH—(C_nH_{2n}—NH)_m—C_nH_{2n}—NR_1R_2$$

wherein Ac is an aliphatic acyl group of from 8 to 18 carbon atoms; m is a whole number from zero to 3 inclusive; n is an integer from 2 to 3 inclusive; R_1 and R_2 are taken from the group consisting of hydrogen and a normal alkyl group of from 1 to 4 carbon atoms; and, each pair of nitrogen atoms is separated by at least 2 carbon atoms.

2. A fuel oil composition as set forth in claim 1 wherein said fuel oil comprises at least about 20%, by weight thereof, of catalytic cracked oil.

3. A fuel oil composition as set forth in claim 1 having incorporated therein (1) an oil-soluble, basic amino nitrogen-containing addition polymer consisting essentially of lauryl methacrylate and beta-diethylaminoethyl methacrylate, present in a proportion of 0.002% to 0.01% by weight of said fuel oil and (2) about 0.0004 to 0.005% by weight of said fuel oil of the oleic acid monoamide of diethylene triamine.

4. A fuel oil composition as set forth in claim 1 having incorporated therein (1) 0.002% to 0.01% by weight of said fuel oil of an oil-soluble, basic amino nitrogen-containing addition polymer consisting essentially of lauryl methacrylate and beta-diethylaminoethyl methacrylate and (2) about 0.0004 to 0.005% by weight of said fuel oil of an oleic acid monoamide of N,N-dimethyl-1,3-propylene diamine.

5. A fuel oil composition as set forth in claim 4 wherein the basic amino nitrogen-containing addition polymer is a tripolymer of octadecenyl methacrylate, styrene and beta-diethylaminoethyl methacrylate.

6. A fuel oil composition as set forth in claim 4 wherein the basic amino nitrogen-containing addition polymer is a tripolymer of octadecenyl methacrylate, styrene and beta-diethylaminoethyl methacrylate; the fatty acid amide is the oleic acid monoamide of N,N-diethyl-1,3-propylene diamine.

7. A petroleum base fuel oil containing (1) as a sludge inhibiting and dispersing agent at least 0.001% by weight of an oil-soluble, basic amino nitrogen-containing addition type copolymer containing in combined form as its essential monomeric components copolymerizable ethylenically unsaturated compounds, one of which is from the group consisting of acrylic and alkacrylic esters of aliphatic alcohols of from 8 to about 18 carbon atoms and one of the components is from the group consisting of alkyl and cycloalkyl substituted tertiary aminoalkyl and amino cycloalkyl esters of acrylic and alkacrylic acids, said copolymer containing 0.1% to 3.5% by weight of basic amino nitrogen and said polymer having an inherent viscosity of 0.1 to 3.0 as determined at 0.1% weight/volume concentration in benzene at 25° C. and (2) about 0.00025 to 0.1% of a fatty acid amide of a polyamine taken from the group consisting of ethylene polyamine and propylene polyamine, said fatty acid amide having the general formula

$$Ac—NH—(C_nH_{2n}—NH)_m—C_nH_{2n}—NR_1R_2$$

wherein Ac is an aliphatic acyl group of from 8 to 18 carbon atoms; m is a whole number from zero to 3 inclusive; n is an integer from 2 to 3 inclusive; R_1 and R_2 are taken from the group consisting of hydrogen and a normal alkyl group of from 1 to 4 carbon atoms; and, each pair of nitrogen atoms is separated by at least 2 carbon atoms.

8. A petroleum base fuel oil containing (1) as a sludge inhibiting and dispersing agent at least 0.001% by weight of an oil-soluble, basic amino nitrogen-containing addition type copolymer containing in combined form as its essential monomeric components copolymerizable ethylenically unsaturated compounds, one of which is from the group consisting of acrylic and alkacrylic esters of aliphatic alcohols of from 8 to about 18 carbon atoms and one of the components is beta-diethylaminoethyl methylacrylate, said copolymer containing 0.1% to 3.5% by weight of basic amino nitrogen and said polymer having an inherent viscosity of 0.1 to 3.0 as determined at 0.1% weight/volume concentration in benzene at 25° C. and (2) about 0.00025 to 0.1% of a fatty acid amide of a polyamine taken from the group consisting of ethylene polyamine and propylene polyamine, said fatty acid amide having the general formula

$$Ac—NH—(C_nH_{2n}—NH)_m—C_nH_{2n}—NR_1R_2$$

wherein Ac is an aliphatic acyl group of from 8 to 18 carbon atoms; m is a whole number from zero to 3 inclusive; n is an integer from 2 to 3 inclusive; R_1 and R_2 are taken from the group consisting of hydrogen and a normal alkyl group of from 1 to 4 carbon atoms; and, each pair of nitrogen atoms is separated by at least 2 carbon atoms.

9. A stabilizing and non-emulsifying composition for petroleum base fuel oils comprising (1) an oil-soluble, basic amino nitrogen-containing addition type copolymer containing in combined form as its essential monomeric

components copolymerizable ethylenically unsaturated compounds each containing only one polymerizable ethylenic linkage, at least one of which component is amine-free and contains from 8 to about 18 carbon atoms in an aliphatic hydrocarbon chain which in the polymer is not part of the main chain, and one of the components as it exists in the polymer containing a basic amino nitrogen in the side chain, said copolymer containing 0.1% to 3.5% by weight of basic amino nitrogen and said copolymer having an inherent viscosity of 0.1 to 3.0 as determined at 0.1% weight/volume concentration in benzene at 25° C. and (2) a fatty acid amide of a polyamine taken from the group consisting of ethylene polyamine and propylene polyamine, said fatty acid amide having the general formula

$$Ac—NH—(C_nH_{2n}—NH)_m—C_nH_{2n}—NR_1R_2$$

wherein Ac is an aliphatic acyl group of from 8 to 18 carbon atoms; *m* is a whole number from zero to 3 inclusive; *n* is an integer from 2 to 3 inclusive; R_1 and R_2 are taken from the group consisting of hydrogen and a normal alkyl group of from 1 to 4 carbon atoms; and, each pair of nitrogen atoms is separated by at least 2 carbon atoms and an organic solvent therefor with a ratio of said oil-soluble, basic amino nitrogen-containing addition polymer to said monoamide between about 1:2.5 and 25:1.

10. A stabilizing and non-emulsifying composition for petroleum base fuel oils comprising (1) an oil-soluble, basic amino nitrogen-containing addition type copolymer containing in combined form as its essential monomeric components copolymerizable ethylenically unsaturated compounds, one of which is from the group consisting of acrylic and alkacrylic esters of aliphatic alcohols of from 8 to about 18 carbon atoms and one of the components is from the group consisting of alkyl and cycloalkyl substituted tertiary aminoalkyl and amino cycloalkyl esters of acrylic and alkacrylic acids, said copolymer containing 0.1% to 3.5% by weight of basic amino nitrogen and said polymer having an inherent viscosity of 0.1 to 3.0 as determined at 0.1% weight/volume concentration in benzene at 25° C. and (2) a fatty acid amide of a polyamine taken from the group consisting of ethylene polyamine and propylene polyamine, said fatty acid amide having the general formlua

$$Ac—NH—(C_nH_{2n}—NH)_m—C_nH_{2n}—NR_1R_2$$

wherein Ac is an aliphtic acyl group of from 8 to 18 carbon atoms; *m* is a whole number from zero to 3 inclusive; *n* is an integer from 2 to 3 inclusive; R_1 and R_2 are taken from the group consisting of hydrogen and a normal alkyl group of from 1 to 4 carbon atoms; and, each pair of nitrogen atoms is separated by at least 2 carbon atoms, and an organic solvent therefore with a ratio of said oil-soluble, basic amino nitrogen-containing addition polymer to said monoamide between about 1:2.5 and 25:1.

11. A stabilizing and non-emulsifying composition for petroleum base fuel oils comprising (1) an oil-soluble, basic amino nitrogen-containing addition type copolymer containing in combined form as its essential monomeric components copolymerizable ethylenically unsaturated compounds, one of which is lauryl methacrylate and one of which is beta-diethyl-aminoethyl methacrylate, said copolymer containing 0.1 to 3.5% by weight of basic amino nitrogen and said copolymer having an inherent viscosity of 0.1 to 3.0 as determined at 0.1% weight/volume concentration in benzene at 25° C. and (2) the oleic acid amide of diethylene triamine and an organic solvent therefor with a ratio of said oil-soluble, basic amino nitrogen-containing addition polymer to said amide between about 1:2.5 and 25:1.

12. A stabilizing and non-emulsifying composition for petroleum base fuel oils comprising (1) an oil-soluble, basic amino nitrogen-containing addition type copolymer containing in combined form as its essential monomeric components copolymerizable ethylenically unsaturated compounds, one of which is lauryl methacrylate and one of which is beta-diethyl-aminoethyl methacrylate, said copolymer containing 0.1 to 3.5% by weight of basic amino nitrogen and said copolymer having an inherent viscosity of 0.1 to 3.0 as determined at 0.1% weight/volume concentration in benzene at 25° C. and (2) the oleic acid amide of N,N-dimethyl-1,3-propylene diamine and an organic solvent therefor with a ratio of said oil-soluble, basic amino nitrogen-containing addition polymer to said amide between about 1:2.5 and 25:1.

13. A stabilizing and non-emulsifying composition for petroleum base fuel oils comprising (1) an oil-soluble, basic amino nitrogen-containing addition type tripolymer of a 50/40/10 tripolymer of octadecenyl methacrylate, styrene and diethylaminoethyl methacrylate contained in combined form as the essential monomeric copolymerizable ethylenically unsaturated compounds, said tripolymer containing 0.1 to 3.5% by weight of basic amino nitrogen and said tripolymer having an inherent viscosity of 0.1 to 3.0 as determined at 0.1% weight/volume concentration in benzene at 25° C., (2) N-(3-dimethylaminopropyl) oleamide, (3) N,N'-disalicylidene-1,2-propane diamine, and, kerosine, with a ratio of said tripolymer to said amide, to said diamine and to said kerosine being about 1:1:0.32:1.68 parts by weight respectively.

14. A stabilizing and non-emulsifying composition for petroleum base fuel oils comprising (1) an oil-soluble, basic amino nitrogen-containing addition type tripolymer of a 50/40/10 tripolymer of octadecenyl methaycrylate, styrene and diethylaminoethyl methacrylate contained in combined form as the essential monomeric copolymerizable ethylenically unsaturated compounds, said tripolymer containing 0.1 to 3.5% by weight of basic amino nitrogen and said tripolymer having an inherent viscosity of 0.1 to 3.0 as determined at 0.1% weight/volume concentration in benzene at 25° C. and (2) the oleic acid amide of N,N-dimethyl-1,3-propylene diamine and an organic solvent therefor with a ratio of said oil-soluble, basic amino nitrogen-containing addition polymer to said amide between about 1:2.5 and 25:1.

References Cited in the file of this patent

UNITED STATES PATENTS

2,622,018	White et al.	Dec. 16, 1952
2,718,503	Rocchini	Sept. 20, 1955
2,737,452	Catlin et al.	Mar. 6, 1956