United States Patent Office

2,978,302

Patented Apr. 4, 1961

2,978,302

STABILIZED DISTILLATE FUELS

Joel R. Siegel, Irvington, and John V. Clarke, Jr., Cranford, N.J., assignors to Esso Research and Engineering Company, a corporation of Delaware

No Drawing. Filed Feb. 28, 1958, Ser. No. 718,120

17 Claims. (Cl. 44—62)

The present invention relates to improvements in the stability of hydrocarbon oil products and more particularly relates to improved petroleum distillate fuels boiling in the range between about 300° F. and about 900° F. which have been stabilized against deterioration during storage by the incorporation therein of small amounts of certain alkyl and acyl derivatives of hydrazine.

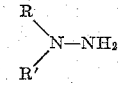
Petroleum distillate fuels boiling in the range between about 300° F. and about 900° F. such as heating oils, diesel engine fuels and fuels for turbo-jet aircraft engines, particularly distillate fuels derived in part from thermal or catalytically cracked petroleum fractions, generally contain unsaturated hydrocarbons and other relatively unstable compounds. During the storage of such fuels these unstable constituents often undergo oxidation, polymerization or other reactions and form sludge and sediment which, upon subsequent introduction of the fuels into engines and burner systems, may lead to the plugging and fouling of fuel lines, filters and orifices.

These difficulties attributable to the presence of unstable constituents in petroleum distillate fuels are particularly pronounced in the case of fuels used in turbo-jet aircraft engines. Because of the high temperatures at which turbo-jet engines operate, it is necessary to continuously cool the lubricating oil used in order to prevent its thermal degradation. Conventionally this is accomplished by providing such engines with heat exchangers through which the fuel and the lubricating oil are circulated. The fuel is thus employed as a cooling medium for the oil and may be subjected to temperatures as high as 400° F. for extended periods of time before it is actually burned. This prolonged exposure to high temperatures accelerates reaction of the unstable constitutents in the fuel and leads to a buildup of varnish and deposits upon the heat exchanger surfaces and the formation of increased quantities of sludge and sediment. Decreased cooling of the lubricating oil, reduced fuel flow and engine power, and in extreme cases flameouts may thus occur as a direct result of turbo-jet fuel instability. The serious consequences which may ensue are obvious.

Because of the growing demand for turbo-jet fuels and similar fuels products and the necessity for using increasing quantities of cracked petroleum fractions in order to supply that demand, there has been a great deal of activity in the development and use of additives for stabilizing purposes. The additives most widely used to date have metallic compounds such as calcium and barium sulfonates and naphthenates. Such additives are reasonably effective in reducing sludge and sediment formation to acceptable levels under ordinary storage conditions but they are not satisfactory for use under very severe conditions such as those encountered in turbo-jet engines and do not overcome the problem of heat exchanger tube deposits in such engines. Moreover, such additives are undersirable because they leave a residue when burned and hence cause a buildup of carbonaceous deposits in engine combustion chambers and upon burner nozzles. Such deposits are very undesirable in jet engines because they disrupt the desired fuel spray pattern in the combustors, cause warping of the liners and thus reduce the thrust which can be generated. Similarly adverse effects are experienced in diesel engines and in heating systems. Various ashless compounds, particularly certain polymeric dispersant compositions, have been suggested for use as stabilizing additives but it has been found that these are not wholly effective and that they do not lend sufficient stability to petroleum distillate fuels for use in turbo-jet aircraft engines to overcome the problem of varnish and deposit formation.

The present invention provides a new and improved class of additives which may be incorporated into petroleum distillate fuels boiling in the range between 300° and about 900° F. in order to improve the stability of such fuels. It has now been discovered that the addition of small amounts of certain alkyl or acyl derivatives of hydrazine to such fuels either alone or in combination with certain polymeric dispersant compositions permits their storage for extended periods of time at high temperatures or under other adverse conditions without the formation of appreciable quantities of sludge, sediment and varnish such as are otherwise encountered. It has been found that combinations of the hydrazine derivatives and polymeric stabilizing additives exhibit a synergistic effect and at a given concentration produce a more stable fuel than can be obtained by using either the hydrazine derivatives or the dispersant polymers alone. The invention thus provides a new and improved class of stabilizing additives for use in petroleum distillate fuels boiling between about 300° and about 900° F. which are surprisingly more effective than additive materials which have been employed heretofore.

The hydrazine derivatives which are employed as stabilizing additives for petroleum distillate fuels in accordance with the present invention are compounds having the general formula



where R and R′ are selected from the group consisting of hydrogen, and alkyl and acyl groups containing from about 1 to about 18 carbon atoms, there being at least one carbon atom attached to the primary nitrogen atom. The additive compounds suitable for use in accordance with the invention thus include mono-substituted, and N-N di-substituted hydrazine and hydrazides. Preferred compounds for purposes of the invention because of their superior stabilizing properties are the mono- and N,N-dialkyl hydrazines and hydrazides. The N,N-dialkyl hydrazines having alkyl groups of from about 1 to about 6 carbon atoms and the mono-substituted hydrazides derived from straight chain fatty acids having from about 8 to about 18 carbon atoms per molecule are particularly preferred.

Specific examples of hydrazine derivatives coming within the above definitions and suitable for use as distillate fuel stabilizing additives in accordance with the present invention include methyl hydrazine, ethyl hydrazine, propyl hydrazine, butyl hydrazine, hexyl hydrazine, decyl hydrazine, octadecyl hydrazine, N,N-dimethyl hydrazine, N-ethyl-N-butyl hydrazine, acetic hydrazide, decanoic hydrazide, octadecanoic hydrazide, and butyric hydrazide.

The hydrazine derivatives represented by the above formula may be prepared in a number of different ways by reactions familiar to those skilled in the art of nitrogen chemistry. The monalkyl hydrazines such as methyl

and ethyl hydrazine may be prepared, for example, by means of the Hofmann reaction wherein an N-alkyl urea is treated with sodium hypochlorite. Dimethyl hydrazine and other N,N-dialkyl compounds can be prepared by reducing the corresponding nitrosamines with zinc and acetic acid or a similar reducing agent. The hydrazides can be prepared by a number of the methods used for preparing amides by merely substituting hydrazine in place of the ammonia used to form the amides. The action of hydrazine on acid chlorides, esters and anhydrides, for example, yields the corresponding hydrazides. The above are all well known reactions and need not be discussed in detail for purposes of this invention. Descriptions of these and other methods for preparing hydrazine derivatives may be readily found in the chemical and patent literature.

A number of polymeric dispersant additives suitable for stabilizing petroleum distillate fuels are available commercially or known to those skilled in the fuels art and may be employed in conjunction with the hydrazine derivatives in accordance with the present invention.

A preferred class of such polymeric stabilizing additives for use with the hydrazine derivatives are those prepared by the copolymerization of an alkyl chloropropyleneoxy mixed ester of an unsaturated conjugated dibasic acid with a polymerizable organic monomer containing a vinylidene linkage. The alkyl chloropropyleneoxy mixed esters used as one of the components of such copolymers are prepared by first reacting a C_4 to C_5 unsaturated conjugated dibasic acid such as maleic acid, fumaric acid, citraconic acid, mesaconic acid or a mixture of such acids or their anhydrides, when they exist, with a long chain saturated aliphatic alcohol to produce a half ester. Suitable alcohols for this purpose are those containing from about 8 to about 24 carbon atoms per molecule, preferably about 8 to 18 carbon atoms per molecule. Straight chain primary alcohols such as dodecyl, cetyl, eicosyl and docosyl alcohols are preferred but branched chain alcohols such as 2-ethylhexanol-1 and C_8 oxo-alcohols, secondary alcohols such as capryl alcohol and mixtures of straight and branched-chain alcohols may also be used. Commercially marketed mixtures of alcohols of the requisite chain length, such as those obtained by the hydrogenation of coconut oil, may also be used.

The half ester produced in the above manner is then reacted with epichlorohydrin in the presence of either an acidic or a basic catalyst such as boron fluoride or sodium hydroxide to produce the mixed ester. The ratio of the half ester to epichlorohydrin in the reaction mixture may range from about 1:1 to 1: 4. Addition of the epichlorohydrin takes place through the epoxy group and the chlorine atom is unaffected. The mixed ester may thus contain from 1 to about 3 chlorine atoms.

The mixed ester prepared as described above is then copolymerized with from about ½ to about 20 parts of an unsaturated organic monomer containing a vinylidene group in the presence of gamma radiation, a peroxide type catalyst such as benzoyl peroxide, or an azo catalyst such as alpha-alpha azo-bisisobutyronitrile. Suitable monomers containing vinylidene groups include hydrocarbons such as styrene, isobutylene and butadiene; esters such as vinyl propionate and methyl methacrylate; ethers such as divinyl ether; and nitriles such as acrylonitrile and vinyl-acetronitrile. Mixtures of such monomers containing vinylidene groups with other copolymerizable materials, long chain alcohol esters of unsaturated conjugated dibasic acids such as lauryl maleate and tallow fumarate for example, may also be used. Vinyl esters of short chain fatty acids, particularly vinyl acetate and mixtures of such esters with fumarate or maleate esters of long chain aliphatic alcohols containing from about 8 to about 20 carbon atoms per molecule are preferred monomers for preparation of the copolymers with the mixed esters.

The resulting copolymers are oil-soluble and preferably have molecular weights between about 6000 and about 20,000 Staudinger. Such copolymers are described in copending application S.N. 673,156, filed July 22, 1957.

A second class of dispersant polymeric additives which are preferred for use with the hydrazine derivatives in accordance with the invention are the oil-soluble, nitrogen-containing addition type copolymers prepared by copolymerizing an amine-free monomer containing one polymerizable ethylenic linkage and an aliphatic hydrocarbon chain of from 8 to 18 carbon atoms with a monomer containing a nitrogen atom and one polymerizable ethylenic linkage. Such copolymers may be prepared, for example, by the copolymerization of an acrylic or alpha-substituted acrylic ester of an aliphatic alcohol containing an average of from 8 to 18 carbon atoms, such as lauryl methacrylate, with an ethylenically unsaturated compound containing a basic amino group, such as beta dimethylamino-ethyl methacrylate. Other specific examples of the amine-free monomers containing a polymerizable ethylenic linkage and a C_8–C_{18} aliphatic chain include the tridecyl, cetyl and octadecyl esters of acrylic and methacrylic acids. Also suitable are esters of these acids prepared from mixtures of alcohols such as those containing primary alcohols of from 10 to 18 carbon atoms derived by the hydrogenation of coconut oil and sold under the trade name "Lorol." A typical mixture consists chiefly of lauryl alcohol having 12 carbon atoms per molecule and has the following approximate composition:

Alcohol constituent	Weight percent
$C_{10}H_{21}OH$	4.0
$C_{12}H_{25}OH$	55.5
$C_{14}H_{29}OH$	22.5
$C_{16}H_{33}OH$	14.0
$C_{18}H_{37}OH$	4.0

The polymerizable ethylenically unsaturated compounds containing a nitrogen-containing group which are used in forming the second class of preferred copolymers suitable for use in accordance with the invention include the basic tertiary amino-alkyl acrylates, such as the dialkyl amino-alkyl acrylates and alpha hydrocarbon-substituted acrylates, beta dimethylaminoethyl acrylate and methacrylate, and their homologs and analogs. The nitrogen may be a member of a heterocycle where the polymerizable ethylenic unsaturation is extranuclearly bonded to the heterocycle, such as the vinyl pyridines, vinyl pyrrolidone.

Limited amounts of other copolymerizable monomers in addition to those described above may be incorporated into the copolymers of the second preferred class as filler materials. Such filler materials include vinyl and allyl formates, acetates, propionates; isobutylene; styrene; methyl methacrylate; ethyl vinyl ether and the like. The final copolymer may contain from about 20% to about 99% of the nitrogen-free monomer, from about 0.5% to 50% of the nitrogen-containing monomer, and from about 0 to about 79% of the monomer used as a filler material. Many of the polymeric additives falling within the second preferred class described above are described in detail in U.S. Patent No. 2,737,452, issued March 6, 1956.

The copolymers described above and the hydrazine derivatives may each be employed in petroleum distillate fuels in concentrations ranging between about 0.001% and about 2% by weight. The ratio of the copolymer to the hydrazine derivative will preferably range between about 1 : 5 to 1 : 0.5. A ratio of 1 to 1 is particularly preferred.

The petroleum distillate fuels in which the additive materials are employed in accordance with the invention consist of a major proportion, at least 95%, of liquid

hydrocarbons boiling at temperatures in the range between about 300° F. and about 900° F. They are derived from petroleum crude oil by a number of processing operations including straight distillation, catalytic and thermal cracking, catalytic and thermal reforming, hydrofining and the like. They include aviation turbo-jet fuels boiling between about 250 and about 550° F., such as JP–4, JP–5 and JP–6; diesel fuels for use in stationary, marine and automotive type diesel engines; and heating oils suitable for use in both domestic and industrial heating systems. Aviation turbo-jet engine fuels as referred to in connection with the invention are defined by U.S. Military Specifications MIL–F–5624C, MIL–F–25524A and MIL–F–25558A and are used in both military and commercial aircraft. Diesel fuels as contemplated herein are defined by ASTM Specification D–975–53T and fall into Grades 1D, 2D and 4D, in all of which the additive materials of the invention may be used. Typical of the heating oils in which the additives may be employed are those covered by ASTM Specification D–396–48T and falling within Grades 1 and 2 thereof.

The additive materials of the invention are effective when incorporated into fuels such as those described above in concentrations ranging from about 0.001% to about 2% by weight. Concentrations between about 0.005% and about 1% by weight are usually sufficient for stabilizing most petroleum distillate fuels and are therefore preferred. The additives may in most cases be incorporated directly into the fuels but in some cases it may be preferred to first dissolve them in a suitable solvent such as hexane, benzene, toluene or xylene and then add the solution to the fuels in quantities sufficient to give the desired additive concentration. The additives may be employed in conjunction with other additive agents commonly used in distillate fuels boiling between about 300° F. and about 900° F., including rust inhibitors, anti-emulsifying agents, anti-static additives, dyes, dye stabilizers and the like. If desired a concentrate of these additives and the additives of the invention may be prepared and then added to the fuels.

The invention may be further illustrated by the following examples.

Example 1

Stearic hydrazide prepared by heating together equal molar quantities of aqueous hydrazine hydrate and the methyl ester of stearic acid was added in a concentration of 0.0075% to a heating oil consisting of about 50 percent of virgin distillate and about 50 percent of catalytically cracked stock. Typical properties of such a heating oil are as follows:

Distillation, API:	
Initial boiling point, ° F	334
10% point, ° F	418
50% point, ° F	506
90% point, ° F	582
Final boiling point, ° F	648
Gravity, API	32.9
Color, Tag-Robinson	13
Flash, ° F	152
Sulfur, percent	0.8
Aniline point, ° F	139

Samples of this heating oil containing the stearic hydrazide and samples of the same base heating oil without stearic hydrazide were then subjected to an Accelerated Storage Stability Test in order to determine their relative stabilities. The test comprised heating the samples for a period of 16 hours at a temperature of 210° F. in order to accelerate the formation of sediment due to the presence of unstable constituents and then filtering each sample through a sintered glass filter. The sediment collected from each sample was weighed and the light transmission of each sample was determined. The following results were obtained.

Sample	Sediment, mg./600 g. oil	Percent Light Transmission (Untreated Base=100%)
Base Heating Oil	14.3	72
Base Heating Oil+0.0075% Stearic Hydrazide	0.8	84

As shown by the above data, the addition of the stearic hydrazide to the unstable heating oil substantially reduced the amount of sediment formed during the accelerated storage period and thus transformed it it into a considerably more stable product. The percentage of light transmitted through the oil, indicative of the amount of suspended material and soluble color bodies present in the oil, was similarly improved by the addition of the stearic hydrazide.

Example 2

To separate samples of the base heating oil employed in Example 1 were added stearic hydrazide, a stabilizing additive of the dispersant polymer type, and a combination of equal parts of the stearic hydrazide and the polymeric additive. The polymeric additive employed was a copolymer of 20 parts of vinyl acetate, 40 parts of a C_{16}–C_{17} alkyl maleofumarate (mixture of C_{16}–C_{17} alkyl esters of maleic and fumaric acid), 10 parts of an isooctyl ethyleneoxy maleate and 30 parts of di C_8 oxo maleofumarate. The polymeric additive was diluted with an equal quantity of a petroleum distillate having an API gravity of 56. A total additive concentration of 0.000625 weight percent was used in each instance. These samples were then subjected to the Accelerated Storage Stability Test as described in the proceding example. The results obtained were as follows:

Sample	Sediment, g./600 gms. oil	Percent Light Transmission (Untreated Oil=100)
Base Oil+0.000625% Polymeric Additive	8.6	58
Base Oil+0.000625% Stearic Hydrazide	13.6	70
Base Oil+0.0003125% Polymeric Additive+0.0003125% Stearic Hydrazide	6.2	55

The above test was carried out at additive concentrations well below the range in which the additives are preferably used in petroleum distillate fuels. At the very low concentration of 0.000625% the stearic hydrazide actually caused an increase in sediment. Despite the extremely low concentration, however, when the stearic hydrazide and the polymeric additive were used in combination a synergistic effect occurred. The sediment formed when the combination of additives was used was less than that formed when the individual additives were employed at the same total concentration. The addition of the hydrazide to the polymeric additive produced little change in the light transmission, although the hydrazide alone substantially improved the transmission of light through the oil.

Example 3

Samples of a turbo-jet aircraft engine fuel were subjected to a fuel stability test in order to determine the effects of various additives upon fuel stability. Inspections of the fuel were as follows:

Gravity, API	41.9
Viscosity, centistokes at 100° F	1.89
Freezing point, ° F	−30

ASTM distillation:	
Initial boiling point, ° F	338
10% point, ° F	376
50% point, ° F	450
90% point, ° F	510
Final boiling point, ° F	540
Smoke point, mm	22
Olefins, vol. percent	1.7
Aromatics, vol. percent	11.3
Sulfur, wt. percent	0.073
Flash point, ° F	130
Heat content, B.t.u./lb	18551

To samples of this fuel were added the following dispersant polymer additives:

Additive A.—A copolymer consisting of one part of vinyl acetate, 0.25 part of isooctyl chloropropyleneoxy maleate and 0.75 part of mixed C_{16}–C_{18} alkyl fumarate.

Additive B.—A nitrogen-containing copolymer used commercially as a stabilizer for distillate fuels consisting of 8 parts of Lorol methacrylate and 2 parts of beta diethylaminoethyl methacrylate.

Additive C.—A copolymer used commercially as a stabilizer for distillate fuels consisting of a methacrylate copolymer containing nitrogen in a neutral, i.e. non-basic form.

The fuel stability tests were carried out in apparatus closely resembling a scaled-down turbo-jet fuel system, the CFR Fuel Coker. The fuel samples, containing each of the above polymeric additives, were pumped from a supply tank through a screen and rotameter to an annular aluminum he at exchanger where they were heated to a temperature of 400° F. They were then passed through a sintered metal filter held at a temperature of 500° F. Fuel performance was measured by the time required for the pressure drop across the filter to increase by 25 inches of mercury or by the pressure increase which occurred in 300 minutes, depending upon which took place first. Upon the basis of the pressure drop and the length of the run, a merit rating was assigned to each fuel sample. A merit rating of 500 in this standardized test is equivalent to a pressure drop of 12 inches of mercury across the filter in 300 minutes and has been established by actual service tests as an acceptable stability level for turbo-jet fuels for aircraft.

The percentage of the heat exchanger tubes covered by varnish deposits and the color of the deposits at the conclusion of each test were also noted, since this serves as an indication of the extent to which similar deposits will be formed in an actual turbo-jet engine.

Following tests of the fuels containing the polymeric additives as described above, N,N-dimethyl hydrazine and the same polymeric additives were added to samples of the same fuel and the tests were repeated. The results obtained in these tests were as follows:

Fuel	Merit Rating [1]	Preheater Tube Deposits [2]
Base Fuel	100	50/8
Base Fuel+0.005% of Additive A	710	75/5
Base Fuel+0.01% of Additive A	740	35/7
Base Fuel+0.01% N,N-Dimethyl Hydrazine	370	[5] 30/8
Base Fuel+0.005% of Additive A+0.005% N,N-Dimethyl Hydrazine	765	15/5
Base Fuel+0.0025% of Additive B	770	50/7
Base Fuel+0.01% of Additive B+0.01% N,N-Dimethyl Hydrazine	890	10/2
Base Fuel+0.01% of Additive C	255	[3] 60/8
Base Fuel+0.01% of Additive C+0.01% N,N-Dimethyl Hydrazine	320	[4] 15/2

[1] 500 is considered passing. 900 is the upper limit in the test and incremental improvements become more difficult to attain as this limit is approached.

[2] First number is percent of tube covered; second number is color of deposits: 0=clear; 2=very light tan; 4=tan; 6=brown; 8=dark brown; 10=black.

[3] Deposits rated after 150 minutes of operation. Full 300 minute test could not be run since filter had plugged.

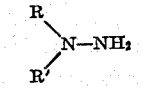
[4] Deposits rated after 200 minutes of operation. See [3].

[5] Deposits rated after 235 minutes of operation. See [3].

The data obtained in these tests clearly show the effect of the hydrazine derivatives upon the stability of petroleum distillate fuels containing polymeric type stabilizing additives. In every case, even where a poor polymeric additive, Additive C, was employed, the addition of the hydrazine derivative brought about an appreciable increase in merit rating and a surprising decrease in tube deposits. The advantages of using such hydrazine derivatives in combination with polymeric stabilizing additives in turbo-jet aircraft engine fuels are thus apparent.

What is claimed is:

1. A petroleum distillate fuel boiling in the range between about 300° F. and about 600° F. containing from about 0.001% to about 2% by weight of an oil-soluble polymeric dispersant selected from the group consisting of (*a*) a 6000 to 20,000 molecular weight copolymer of a C_8 to C_{24} alkyl aliphatic oxy mixed ester of an unsaturated conjugated C_4 to C_5 dibasic acid and a vinyl ester of a short chain fatty acid wherein said aliphatic groups are selected from the class consisting of a C_2 to C_3 alkylene and a C_2 to C_3 halogenated alkylene, and (*b*) a copolymer of from 20 to 99% by weight of a C_8 to C_{18} aliphatic alcohol ester of an acid selected from the group consisting of acrylic acid and an alpha substituted acrylic acid in which the alpha substituent is a lower alkyl group, from 0.5 to 50% by weight of a basic tertiary amino alkyl acrylate, and from 0 to 79% by weight of a copolymerizable olefinically unsaturated organic monomer and from about 0.001% to about 2% by weight of a hydrazine derivative having the formula



where R and R′ are selected from the group consisting of hydrogen, alkyl radicals containing from 1 to about 6 carbon atoms and acyl groups derived from fatty acids containing from about 8 to 18 carbon atoms, there being at least one carbon atom attached directly to the primary nitrogen atom.

2. A fuel as specified in claim 1 wherein said dispersant and said hydrazine derivative are present in a ratio of from 1 : 5 to 1 : 0.5 parts by weight.

3. A fuel as specified in claim 1 wherein said dispersant and said hydrazine derivative are each present in a concentration of from about 0.005 to about 1% by weight.

4. A fuel as specified in claim 1 wherein said dispersant is a copolymer of one part of, isooctyl chloropropyleneoxy maleate and from ½ to 20 parts of a mixture of vinyl acetate and C_{16}–C_{18} alkyl fumarate, said copolymer having a molecular weight of from about 6000 to about 20,000.

5. A fuel as specified in claim 1 wherein said dispersant is a copolymer of mixed C_{10}– to C_{18}– alkyl methacrylate and beta-diethylaminoethyl methacrylate, said copolymer being made up of from 0.5 to 50 wt. percent of beta-diethylaminoethyl methacrylate.

6. A petroleum distillate fuel boiling in the aviation turbo-jet fuel, diesel fuel and heating oil boiling range having incorporated therein from about 0.001% to about 2% by weight of an unsymmetrical dialkyl hydrazine having alkyl groups of from about 1 to 6 carbon atoms in length and from about 0.001% to about 2% by weight of a 6000 to 20,000 molecular weight copolymer of a C_8– to C_{18}– alkyl chloropropyleneoxy ester of a C_4 to C_5 unsaturated conjugated dibasic acid with a vinyl ester of a short chain fatty acid, said chloropropyleneoxy ester comprising about 1/20 to about ⅓ of the total monomers making up said copolymer.

7. A fuel as specified in claim 6 wherein said hydrazine is N,N-dimethyl hydrazine.

8. A fuel as specified in claim 6 wherein said copolymer is copolymer of about 0.25 part of isooctyl chloropropyleneoxy maleate, about 1 part of vinyl acetate, and about 0.75 part of mixed C_{16}–C_{18} alkyl fumarates.

9. A petroleum distillate fuel boiling in the aviation turbo-jet fuel, diesel fuel and heating oil boiling range having incorporated therein from about 0.001% to about 2% by weight of an unsymmetrical dialkyl hydrazine having alkyl groups of from about 1 to 6 carbon atoms in length and from about 0.001% to about 2% by weight of an oil-soluble copolymer of from 20 to 99% by weight of a C_8^- to C_{18}^- aliphatic alcohol ester of methacrylic acid, from 0.5 to 50% by weight of a basic tertiary amino alkyl methacrylate, and from 0 to 79% by weight of a copolymerizable olefinically unsaturated organic monomer.

10. A fuel as specified in claim 9 wherein said copolymer is a copolymer of about 80% of mixed C_{10}^- to C_{18}^- alkyl methacrylates and about 20% of beta-diethylaminoethyl methacrylate.

11. A fuel as specified in claim 10 wherein said hydrazine is N,N-dimethyl hydrazine.

12. A fuel as specified in claim 1 wherein said hydrazine is N,N-dimethyl hydrazine.

13. A fuel as specified is claim 1 wherein said hydrazine is stearic hydrazine.

14. A fuel as specified in claim 1 wherein said dispersant is a copolymer of one part of isooctyl ethyleneoxy maleate and from ½ to 20 parts of a mixture of vinyl acetate and a C_{16} to C_{17} alkyl maleofumarate, said copolymer having a molecular weight of from about 6000 to about 20,000.

15. A petroleum distillate fuel boiling in the aviation turbo-jet fuel, diesel fuel and heating oil boiling range having incorporated therein from about 0.001% to about 2% by weight of an unsymmetrical mono-substituted hydrazine having acyl groups derived from fatty acids of from about 8 to 18 carbon atoms in length and from about 0.001% to about 2% by weight of a 6000 to 20,000 molecular weight copolymer of a C_8^- to C_{18}^- alkyl ethyleneoxy ester of a C_4 to C_5 unsaturated conjugated dibasic acid with a vinyl ester of a short chain fatty acid, said ethyleneoxy ester comprising about 1/20 to about 1/3 of the total monomers making up said copolymer.

16. A fuel as specified in claim 15 wherein said copolymer is a coploymer of about 20 parts of vinyl actate, about 40 parts of a C_{16} to C_{17} alkyl maleofumarate, about 10 parts of an isooctyl ethyleneoxy maleate, and about 30 parts of a di C_8 oxo maleofumarate.

17. A fuel as specified in claim 15 where said hydrazide is stearic hydrazide.

References Cited in the file of this patent

UNITED STATES PATENTS

1,906,044	Burk	Apr. 25, 1933
2,027,394	McMullan	Jan. 14, 1936
2,607,761	Seymour	Aug. 19, 1952
2,615,845	Lippincott	Oct. 28, 1952
2,729,690	Oldenburg	Jan. 3, 1956
2,737,452	Catlin et al.	Mar. 6, 1956
2,808,416	Bell et al.	Oct. 1, 1957

OTHER REFERENCES

"The Chemistry of Hydrazine," by Audrieth and Ogg; John Wiley and Sons Inc., 1951, pages 225, 226, and 227.

Ind. and Eng. Chem., vol. 42, September 1950, "Hydrazine in Organic Chemistry," by Byrkit and Michalek, pages 1862 to 1875.