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**THICKENED FUEL COMPOSITIONS AND METHOD
AND MATERIAL FOR THICKENING SAME****William E. Cohrs, Midland, and Edward Stroiwas, Merrill,
Mich., assignors to The Dow Chemical Company, Mid-
land, Mich.****No Drawing. Continuation-in-part of application Ser. No.
792,848, Jan. 21, 1969. This application Nov. 24, 1969,
Ser. No. 879,552****Int. Cl. C10I 7/02****U.S. Cl. 44-7 D****17 Claims****ABSTRACT OF THE DISCLOSURE**

Aliphatic fuel compositions such as gasoline, jet (turbine) fuel, diesel fuel and the like are thickened to decrease flammability hazards employing soluble polymers containing minor amounts of polar materials such as acrylic acid. Such fuel does not induce sulfidation on combustion.

This application is a continuation-in-part of our co-pending application Ser. No. 792,848, filed Jan. 21, 1969.

This invention relates to thickened aliphatic hydrocarbons, and more particularly relates to liquid aliphatic hydrocarbons thickened with a minor proportion of a polymeric additive.

It is desirable for many purposes to thicken liquid aliphatic hydrocarbons. One particularly advantageous application of such thickened hydrocarbons is in fuel for combustion engines such as aircraft engines, automobile engines and the like. The use of a thickened fuel markedly reduces the fire hazard when a fuel tank is ruptured by impact such as in the event of a crash or damage sustained from gun fire. The requirements of such a thickened fuel are somewhat contradictory in that an ideal crash-safe fuel would be a solid coherent material which did not fragment or spread on impact. However, in order for the fuel to be fed to an engine, it is necessary that it be pumped and drained from a fuel tank under the influence of gravity. Thus, a suitable fuel should have a viscous or gelatinous nature when not subject to shear and behave essentially as a liquid when subjected to shear such as shear imposed by a fuel pump. Beneficially, the thickened fuel under the influence of gravity should flow in the manner of a liquid at a rate sufficient to permit the material to be withdrawn from a fuel tank at a rate at least equal to the rate of fuel consumption. It is highly desirable that minimal quantities of such thickening agents be employed and that all components of the fuel mixture be volatile under combustion conditions and that the system be substantially free from metal ions which induce sulfidation in internal combustion engines. Such fuels are generally hydrocarbon compositions, and beneficially aliphatic hydrocarbon compositions. Hereinafter, the term "aliphatic hydrocarbon(s)" shall include aliphatic hydrocarbons, cycloaliphatic hydrocarbons and mixtures thereof.

Aliphatic hydrocarbons operable in the invention include compounds that may be either branched or linear such as propane, butane, pentane, hexane, heptane, octane, nonane, decane, dodecane, propene, butene, 1,3-butadiene, isoprene and the like saturated and unsaturated aliphatic hydrocarbons. Exemplary of the cycloaliphatic hydrocarbons that can be gelled or thickened in accordance with the present invention are cyclopentane, 1,1-dimethyl cyclopentane, 1,3 - dimethyl cyclopentane, cyclohexane, methyl cyclohexane, ethyl cyclohexane, 2,4-dimethyl cyclohexane and the like cycloaliphatic hydrocarbons.

Materials which may be gelled by practice of the present invention are those which have solubility parameters

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varying from about 6.8 to 11. Solubility parameters are described by Hildebrand and Scott in "The Solubility of Nonelectrolytes," Reinhold, 1949, and by H. Burrell in "Solubility Parameters," Interchemical Review, vol. 14, pages 3 and 31, 1955. Solubility parameters of various hydrocarbons are hereinafter set forth:

Hydrocarbon:	Parameters
Low odor mineral spirits	6.9
Apco 140	7.3
TS-28 solvent	7.4
Apco 18	7.5
VM&P naphtha	7.6
Socal solvent 3	7.7
Apcothinner	7.8
Socal solvent 2	7.9
Socal solvent 1	8.1
Turpentine	8.1
Terpene B	8.4
Solvesso 150	8.5
Dipentene	8.5
Solvesso 100	8.6
Pine oil	8.6
Carbon tetrachloride	8.6
Hiflash naphtha	8.7
Xylene	8.8
Toluene	8.9
Benzene	9.2
Monochlorobenzene	9.5
Tetralin	9.5
Isobutylene	6.7
Pentane	7.0
Hexane	7.3
Heptane	7.4
Octane	7.6
Kerosene	8.2
Ethylbenzene	8.8
Methylcyclohexane	7.8
Cyclohexane	8.2

Other hydrocarbons which may be employed are mixtures comprising essentially one or more materials of the foregoing classes of hydrocarbons such as may be obtained by the distillation or alkylation of petroleum stocks. Examples of such are petroleum ether, gasoline, kerosene, benzene, ligroin, motor oil and the like.

Also useful in the practice of the present invention are the aromatic hydrocarbons such as benzene, toluene, xylene and the like, either alone or in admixture with each other, or aliphatic hydrocarbons. Of particular interest are such petroleum distillates as are commercially available for fuels such as those sold under the trade designation "Jet-A" and "Jet-B," both with and without deicing additives, and like turbine fuels. The hydrocarbon materials to be thickened should not be dehydrated, but should contain the customary traces of water present in commercial grade material.

Such hydrocarbon materials in accordance with the present invention are thickened by uniformly incorporating within the hydrocarbon body from about 0.2 to about 10 percent of a synthetic organic polymer soluble in the hydrocarbon, advantageously the polymer having present in at least 0.2 percent to 3 percent thereof an oxygen-containing polar compound selected from the group consisting of olefinically unsaturated copolymerizable (a) acids containing up to 6 carbon atoms, such as acrylic acid, methacrylic acid, itaconic acid, citraconic acid; (b) amides containing up to 4 carbon atoms, such as acrylamide, and mixtures thereof; (c) hydroxy acrylic esters such as 2-hydroxyethyl methacrylate, 2-hydroxypropyl methacrylate, 3-hydroxypropyl methacrylate, 2-hydroxyethyl acrylate, 2-hydroxypropyl acry-

late, 3-hydroxypropyl acrylate; (d) sulphonic acids such as 2-sulphoethyl methacrylate, 2-sulphoethyl acrylate, 3-vinylbenzenesulphonic acid, 2-benzenesulphonic acid and the like.

Oil soluble polymers useful in the present invention include alkylstyrene polymers which are readily obtained by polymerization of alkylstyrene monomers, with the oxygen-containing polar compound, the alkylstyrenes have alkyl groups containing from 3 to 20, and preferably from 4 to 12, carbon atoms, and mixtures of styrene monomers containing an average of at least 3, and no more than 20, preferably from 4 to 12, aliphatic carbon atoms per aromatic ring. Effective thickening alkylstyrene polymers include: polymers of tertiary-alkylstyrenes such as p-tertiary-butylstyrene, p-tertiary-amylstyrene, p-tertiary-hexylstyrene, p-tertiary-octylstyrene, p-tertiary-dodecylstyrene, p-tertiary-octadecylstyrene and p-tertiary-eicosylstyrene; polymers of n-alkylstyrenes such as n-butylstyrene, n-amylstyrene, n-hexylstyrene, n-octylstyrene, n-dodecylstyrene, n-octadecylstyrene and n-eicosylstyrene; polymers of sec-alkylstyrenes such as sec-butylstyrene, sec-hexylstyrene, sec-octylstyrene, sec-dodecylstyrene, sec-octadecylstyrene and sec-eicosylstyrene; polymers of isoalkylstyrenes such as isopropylstyrene, isobutylstyrene, isohexylstyrene, isooctylstyrene, isododecylstyrene, isooctadecylstyrene and isoeicosylstyrene and copolymers thereof, as well as copolymers of such alkylstyrenes with styrene and vinyl toluene, for example, such as a copolymer of p-tertiary-butylstyrene and styrene in at least a 75:25 mole ratio containing polymerized therein 1 percent acrylic acid; a copolymer of n-amylstyrene and styrene in at least a 60:40 mole ratio containing polymerized therein 1 percent itaconic acid; a copolymer of n-hexylstyrene and styrene in at least a 50:50 mole ratio containing polymerized therein 1 percent citraconic acid; a copolymer of sec-dodecylstyrene and styrene in at least a 25:75 mole ratio containing polymerized therein 1 percent acrylamide; a copolymer of isoeicosylstyrene and styrene in at least a 15:85 mole ratio and 1 percent itaconic acid; a copolymer of p-tertiary-butylstyrene and vinyl toluene in at least a 67:33 mole ratio and 1 percent acrylic acid; a copolymer of sec-amylstyrene and vinyl toluene in at least a 50:50 mole ratio and 2 percent methacrylic acid; a copolymer of n-octylstyrene and vinyl toluene in at least a 29:71 mole ratio and 3 percent methacrylic acid; a copolymer of n-dodecylstyrene and vinyl toluene in at least a 19:81 mole ratio and 0.5 percent acrylic acid, and a copolymer of sec-octadecylstyrene and vinyl toluene in at least a 12:88 mole ratio and 1.5 percent citraconic acid, alkyl acrylates such as lauryl acrylate, di-2-ethylhexyl acrylate, stearyl acrylate either as homopolymers or copolymerized with an alkylstyrene. When employing alkylstyrenes, it is particularly beneficial to have included therein up to about 500 parts of isopropenylvinylbenzene per million parts of the alkylstyrene, and most beneficially, about 300 parts of isopropenylvinylbenzene per million parts of the alkylstyrene. The presence of the isopropenylvinylbenzene in the alkylstyrene prior to polymerization enhances the gelling or thickening properties of the resultant polymer. Suitable polar compounds include acrylic acid, methacrylic acid, acrylamide, itaconic acid employed in a proportion of from about 0.2 to 3 weight percent of the polymerizable components charged to the reactor. If, with the alkylstyrene, less than 0.2 percent is employed, suitable thickening is not obtained. If the level of the polar compound is above about 3 percent, thickening is also impaired. The most beneficial range for the polar compound is from about 0.5 to 1.5 weight percent. Such polymers beneficially are prepared by emulsion polymerization employing conventional emulsion polymerization procedures. However, it is critical that in the preparation of such polymers no surface active agent, catalyst or other additive be employed which introduces a metallic ion into the system. Therefore, it is preferred to

employ ammonium or amine salts of sulfonated fatty alcohols, alkylaryl sulfonates, long chain fatty acids such as lauric acid, palmitic acid, stearic acid and the like.

It is critical in the preparation of thickened fuels in accordance with the present invention that the inclusion of non-volatile components be rigorously avoided. By "non-volatile components" are meant components which boil as components, or thermal decomposition products which on oxidation boil above about 400° C. For instance, it is essential and critical that the inclusion of functional quantities of materials containing sodium, calcium, iron and like metallic elements, which on oxidation tend to form solid deposits, be rigorously avoided. The gelation or thickening characteristics of the polymer are enhanced by the addition of ionic material, but the cation and the anion of the ionic material should volatilize when the fuel is oxidized. Consequently, base materials such as ammonium hydroxide and organic base materials such as tetramethylammonium hydroxide or other organic bases such as amines containing up to about 10 carbon atoms, including primary, secondary and tertiary amines, and quaternary ammonium salts such as methyl amine, ethyl amine, butyl amine, dimethyl amine, ethylene amine, n-octyl amine, aniline, N-methyl aniline, guanidine, are found to be eminently satisfactory. Addition of the base materials to polymers containing acidic or hydroxyl groups generally prevents or markedly reduces variation of viscosity with time. When it is desired to add deicer compositions, such as ethylene glycol, the addition of a base material will provide maximum thickening characteristics. Usually, the base is added to provide a concentration of from 2.5×10^{-4} to 0.5 molar solution of the base in the thickened hydrocarbon. Generally, optimum thickening is obtained when the base concentration is from about 10^{-3} to 10^{-4} molar when employing aqueous ammonia.

While obtaining gelation or thickening by the inclusion of such materials as sodium hydroxide, sodium lauryl sulphate and the like provides compositions of acceptable rheological characteristics, such fuels tend to form deposits within an internal combustion turbine engine, such as a jet engine, and after a relatively short period of time, the engine becomes unsatisfactory because of sulfidation, more commonly referred to as "Black Plague," and requires servicing. Minute amounts of water added to a thickened composition of hydrocarbon and polymer provide enhanced thickening. However, such enhancement disappears after a period of time, most frequently in about 24 hours.

The catalysts employed in the polymerization reaction advantageously are materials such as ammonium persulfate and the like which result in volatile oxidation products when oxidized in the presence of a liquid hydrocarbon. Similarly, the catalysts used in such a polymerization beneficially are ammonium persulfates and perborates, hydrogen peroxide, organic peroxides and hydroperoxides such as benzoyl peroxide, t-butylhydroperoxide, t-butylperbenzoate and the like. Azo catalysts are also suitable such as azobisisobutyronitrile. Catalysts are generally employed at a level from about 0.05 to about 1 percent based on the weight of the monomer, and beneficially from about 0.1 to 0.5 percent. Emulsion polymerization is conveniently carried out by heating a suitable admixture of monomer catalyst and water to a desirable polymerization temperature, beneficially from about 40° to 100° C. The solids level for the latex advantageously is maintained at from 30 to 50 percent, and beneficially about 40 weight percent. Advantageously, the polymerization is carried out in a medium at a pH between about 3 and 6. Generally, it is advantageous to adjust the pH with a volatile alkali such as ammonia, either aqueous or anhydrous, to a value of about 4.2. Alternately, quaternary ammonium salts such as tetramethylammonium hydroxide are employed with benefit, or ammonium salts such as ammonium carbonate, ammonium bicarbonate are also satisfactory.

The polymers of the present invention are highly effective thickeners for the previously specified aliphatic hydrocarbons. Such aliphatic hydrocarbon and thickener combinations can be employed to great advantage in compositions where viscosity control or gelation is desired. A particular application in which the present composition can be employed with great advantage is in the manufacture of greases, which application, depending upon the purpose for which the greases are formulated, presents a wide variety of thickening requirements. Another application is in the gelling of liquid rocket fuels to provide some of the advantages inherent only in solid rocket fuels.

The polymers of the present invention are employed with particular benefit in the thickening of liquid hydrocarbon fuels. Mobile volatile hydrocarbon fuels such as jet or turbine fuel, diesel fuel, gasoline and other like hydrocarbon fuels may be converted into viscous liquids by the incorporation of from about 0.2 to 5 to 3 to 5 weight percent of the polymers in accordance with the present invention. Beneficially, it is often desirable to employ 0.5 to 3 weight percent, and advantageously from about 0.75 to 2.5 weight percent, of the polymers in accordance with the present invention. Increasing the viscosity of such fuels contributes significantly to their resistance to ignition in a crash or collision wherein the fuel tank is ruptured. The precise mechanism of such a flammability reduction is not fully understood—whether this occurs because of the high viscosity of the liquid and its resistance to forming small droplets, or whether this is a reduction in the vapor pressure of the liquid fuel, a reduction in the rate of vaporization, or a combination of all factors, or a combination of all factors and other unknown factors. The flash point of the fuel composition appears to be raised when the thickening agents of the present invention are employed. The thickened fuels in accordance with the present invention are liquids which can be pumped and transported in conventional fuel storage and supply means of vehicles or fixed storage. The more highly thickened fuels of the present invention are fuels which are thixotropic clear to slightly cloudy liquids which, when subjected to shear, exhibit almost instantaneous reduction in viscosity, and on removal of shearing force exhibit an almost instantaneous recovery of the apparent viscosity measured. The more highly thickened fuels of the present invention are apparently gels often times of a stringy and coherent nature. If the thickened solutions exhibit any true gel structure, they have a yield point which is too weak to resist the force of gravity for extended periods of time. A more highly thickened solution in accordance with the present invention when disturbed, such as by being shaken in a closed container, exhibits a lumpy surface, portions of the fuel clinging in a somewhat irregular manner to the sides of the container. The solution also exhibits characteristics such as stringiness or fibrousness which can be attributed to a gel. However, on standing for a relatively short period of time, the solution has the general appearance of a liquid. Repeated inversion of a container having such a solution therein to entrap air bubbles in the solution gives the impression that the material is a gel; the bubbles slowly rise to the surface and the contents of the container resume their liquid-like appearance. Rapid rotation of the container through about a one quarter turn and a rapid stop indicates that the material is viscoelastic in nature. Generally circular oscillation of the fluid occurs after the container has been brought to rest. A bubble rising through the thickened material oftentimes will proceed at an irregular rate which suggests coherent regions within the solution. Portions of the liquid removed from the container and placed on a flat surface appear to be a gel; however, on standing form a puddle of liquid within relatively few minutes. Such phenomena is concentration- and time-dependent; as the concentration decreases, that is, approaches 1 percent, the gel-like characteristics tend to

disappear; whereas, when the concentration of the polymers is increased in the hydrocarbon, such characteristics become more obvious. Viscosity of such solutions as measured by a Brookfield Viscometer provides a linear plot when viscosity is plotted against the log of the shear rate indicating that the solution is a liquid and not a gel. Less highly thickened liquids in accordance with the present invention range from viscous to liquid when concentrations of polymer are used approaching the minimum values and have the general appearance and characteristics of a true gel. As the concentration of the thickening agent is increased, there is a gradual transition from what appears to be a pure liquid to a more highly thickened solution with the hereinbefore described properties.

Of particular advantage are thickened liquid combustible fuels which comprise a major portion of an oxidizable liquid hydrocarbon having uniformly dispersed there-through a polymeric thickening agent, the composition being within the viscosity set forth in Table I below when measured by a Brookfield Viscometer Model RVT at 73° F. $\pm 1.5^\circ$ F.

TABLE I

R.p.m.	Number 4 Spindle		R.p.m.	Number 6 Spindle	
	Maximum viscosity, centipoise	Minimum viscosity, centipoise		Maximum viscosity, centipoise	Minimum viscosity, centipoise
5	50,000	2,000	5	500,000	10,000
20	20,000	8,000	2.5	130,000	5,000
100	5,000	1,000	10	50,000	2,500

Especially advantageous for general service in internal combustion engines, particularly turbo jet engines, are compositions having an apparent viscosity of from about 7500 to about 20,000 centipoise as measured at 10 revolutions per minute with a number 6 spindle with a Brookfield Viscometer Model RVT at 73° F. $\pm 1.5^\circ$ F. The composition is capable of flow under the force of gravity and is substantially free of ionic materials which result in non-gaseous combustion products when the composition is oxidized in air. Advantageously, the fuel composition contains from 0.5 to 5 weight percent of the polymeric thickening agent, and beneficially from 0.75 weight percent to about 2.5 weight percent.

Thickened hydrocarbons in accordance with the present invention are readily prepared by dispersing polymers of the present invention within the hydrocarbon. Generally it is desirable to disperse the polymer within the liquid hydrocarbon employing high shear agitation such as is obtained in a colloid mill or a high shear agitator such as a centrifugal pump, gear pump, propeller-type mixer, serrated edge disc mixer and the like. If desired, solution or dispersion may be hastened by heating. Under agitation, the dispersion or solution appears liquid. However, when agitation is discontinued, the gel-like characteristics become apparent. Therefore, for many applications, it is desired to supply the thickening polymer in the form of fine particles or agglomerations of fine particles such as are obtained by spray drying or drying a latex or aqueous suspension of the polymer at a temperature below the film forming temperature of the polymer in a tray dryer, drum dryer and the like.

If a small amount of water is permissible in a particular application for a thickened hydrocarbon, a latex of the polymer may be directly incorporated into the hydrocarbon by agitation. The thickening effect does not appear to be significantly impaired. Generally when incorporating a latex of a thickening polymer into a hydrocarbon, high speed vigorous agitation is employed with benefit. The water-containing mixture usually has a distinct cloudy appearance rather than the clear to slightly cloudy appearance of solutions or dispersions prepared with a dry

thickening polymer. If desired, the de-watering of the thickened material is accomplished by subjecting the dispersion of latex and hydrocarbon to a reduced pressure and fractionally distilling water from the system. Generally it is undesirable to raise the temperature above about 80° C., as the thickening effect is reduced which may be due to the dehydration of the system and removal of trace amounts of water normally found in hydrocarbons of commercial purity.

Usually, optimum thickening is obtained by preparing a concentrated dispersion of the polymer in hydrocarbon and subsequently diluting to the desired solids concentration with additional hydrocarbon material. Addition of alcohols such as methanol, butanol, ethylene-glycol and like hydroxylated compounds reduces the apparent viscosity of the thickened hydrocarbons and alters the flow characteristics thereof. Usually such an addition of alcohols to a gel-like thickened hydrocarbon results in Newtonian or more Newtonian flow.

The following examples illustrate the manner in which the principles of the invention are applied but are not to be construed as limiting the scope of the invention. Unless otherwise noted, viscosities are measured with a Brookfield Model RVT Viscometer 24 hours after solution is complete at a temperature of 73° F.±1.5° F.

EXAMPLE 1

An agitated and jacketed reactor is charged with 82 parts by weight of deionized water, 0.0264 part by weight of ethylenediaminetetraacetic acid. The reactor is closed, gases evacuated until an absolute pressure of about 127 milliliters of mercury is obtained. While maintaining agitation, the pressure on the reactor is returned to atmospheric by adding nitrogen. This procedure is repeated to remove air from the reactor. 0.164 part by weight of 28 percent aqueous ammonium hydroxide is added to the reactor and nitrogen added until the pressure within the reactor reaches about 5 pounds per square inch gauge. The contents of the reactor are heated to 98° C. and 56 parts by weight of a monomer mixture are added. The monomer mixture is prepared by mixing 65.4 parts by weight t-butylstyrene with 0.1 part by weight methacrylic acid. A catalyst mixture is prepared by dissolving 0.354 part by weight ammonium persulfate and 6 parts water. Two parts by weight of the catalyst mixture are added to the reaction mixture. The reaction mixture is maintained at 98° C. by steam and water applied to the jacket of the vessel. An exothermic reaction is indicated by a drop in temperature of the water in the jacket. After a period of about 45 minutes when the temperature of the water in the jacket has risen to 98° C., 0.5 part by weight of the ammonium persulfate solution is added to the reaction mixture and the reaction continued until the jacket cooling water and reaction mixture are both indicating 98° C. The reactor is vented to the atmosphere. The reaction mixture is a latex having a solids content of about 40 weight percent and a particle size of about 2600 angstroms. The reaction mixture is cooled to about 30° C., filtered to remove coagulum and the resultant polymer recovered by tray-drying at a temperature of 60° C. The tray-dried material is a fragile cake which is readily crushed to a fine powder. Portions of the polymer are dissolved with vigorous agitation in a hydrocarbon mixture commercially available as a jet aircraft engine fuel under the designation of "Jet-A." A 2 weight percent solution of the polymer in Jet-A jet or turbine fuel gives a viscous stringy gel-like solution having a viscoelastic appearance which has a viscosity as measured on a Brookfield Viscometer employing a No. 6 spindle at 10 revolutions per minute, of 15,000 to 25,000 centipoises; employing a 3 weight percent solution of the polymer in Jet-A jet fuel, the solution has a viscosity of 40,000 to 50,000 centipoise. The viscosity ranges indicate the ranges obtained by employing various batches of Jet-A jet fuel.

EXAMPLE 2

The polymerization procedure of Example 1 is repeated with the exception that 2 parts of the catalyst solution are added to the reactor immediately prior to the addition of 56 parts of monomer mixture. Polymer is recovered by tray-drying and evaluated for thickening characteristics by dissolving the polymer in various samples of Jet-A jet fuel. Viscosities of 15,000 to 20,000 centipoise are obtained measured in accordance with the procedure of Example 1 using a No. 6, spindle at 10 revolutions per minute.

EXAMPLE 3

The jacketed agitated reactor is charged with 856 parts by weight of deionized water. The reactor is closed, evacuated to a pressure of about 130 milliliters of mercury absolute, filled with nitrogen until atmospheric pressure is obtained and the purging procedure with nitrogen repeated twice more. The water in the reactor is heated to 98° C. with agitation and 1.2 parts by weight of ammonium persulfate, 1.8 parts by weight of 28 percent aqueous ammonia are added. The monomer is immediately charged to the vessel. The monomer charge is a mixture of 596 parts by weight tertiary-butylstyrene and 0.67 part by weight methacrylic acid. The reactor contents are maintained at 98° C. for a period of 15 minutes after the jacket temperature rises to 98° C. The reaction mixture is cooled and vented to the atmosphere. The reaction mixture is in the form of a latex having a particle size of about 1400 angstroms. The conversion of monomer to polymer is 95 percent. The polymer is recovered by tray-drying. A 3 weight percent solution of the resultant polymer is prepared employing Jet-A jet fuel as a solvent. The solution forms a stringy gel-like liquid having a viscosity of about 31,000 centipoise using a No. 6 spindle at 10 revolutions per minute.

EXAMPLE 4

The procedure of Example 3 is repeated with the exception that after heating the water to 98° C., 0.6 part of a 14 percent by weight ammonium lauryl sulfate solution in water is applied. The tertiary-butylstyrene contains 300 parts per million isopropenylvinylbenzene. Conversion of monomer to polymer is 95 percent. The latex particles have a diameter of about 1400 angstroms. A Brookfield Model RVT Viscometer with a No. 6 spindle is employed to determine the viscosity of various concentrations of the polymer in Jet-A jet fuel. The results are set forth in Table II.

TABLE II

Concentration	Revolutions per minute	Viscosity in centipoise
Percent:		
1.25-----	0.5	40,000
	1	29,000
	2.5	14,600
	5	9,000
	10	5,500
	20	3,200
	50	1,500
	100	950
1.5-----	.5	64,000
	1	52,000
	2.5	28,500
	5	17,500
	10	10,500
	20	6,000
	50	2,900
	100	1,800
1.75-----	.5	116,000
	1	82,000
	2.5	43,200
	5	27,200
	10	15,000
	20	8,500
	50	4,300
	100	2,300

TABLE II—Continued

Concentration	Revolutions per minute	Viscosity in centipoise
Percent:		
2.0	.5	124,000
	1	80,000
	2.5	50,000
	5	30,400
	10	18,600
	20	10,300
	50	4,440
	100	2,450

EXAMPLE 5

The procedure of Example 3 is repeated with the exception that the monomer mixture is pumped into the reactor over a period of about 12 minutes. The resultant latex particle size is in excess of 3000 angstroms. Evaluation of the tray-dried polymer at 3 weight percent solution in Jet-A jet fuel gives a gel-like solution with a viscosity of 28,000 centipoise at 10 revolution per minute using a No. 6 spindle.

EXAMPLE 6

An agitated jacketed vessel is charged with 1800 parts by weight deionized water. A sparger tube is positioned at the bottom of the vessel and the vessel sparged for 10 minutes with nitrogen. The vessel is closed, heated to 80° C. 3.6 parts by weight ammonium persulfate are added. A monomer mixture of 10.8 parts by weight acrylic acid and 1789 parts by weight t-butylstyrene are pumped at a constant rate into the vessel for a period of about 1½ hours. The reaction mixture is maintained at a temperature of about 80° C. with agitation for a further period of about 1½ hours. The conversion of monomer to polymer is 95 percent. The particle size of the latex is 7000 angstroms. The polymer is recovered by spray drying and 3 weight percent solution in Jet-A jet fuel gives a gel-like solution having a viscosity of 18,000 centipoise using a No. 6 spindle at 10 revolutions per minute.

EXAMPLE 7

Employing the reactor of Example 6, 400 parts by weight of deionized water are placed in the reaction vessel with agitation and heated to 98° C. and sparged with nitrogen. Two solutions are prepared: (1) a water solution of 450 parts by weight water, 0.6 part by weight ammonium persulfate and 1.8 parts by weight of a 28 weight percent aqueous solution of ammonia; (2) a monomer solution which consists of 3 parts by weight methacrylic acid 597 parts by weight 1-butylstyrene. The two solutions are simultaneously added to the vessel over a period of about 3 hours and the reaction mixture maintained at 98° C. for a period of about 15 minutes after addition of both streams is complete. A latex is obtained which is about 41 percent solids representing a monomer to polymer conversion of 95 percent. The polymer is recovered by tray drying and evaluated for thickening characteristics by preparing a 3 weight percent solution in Jet-A jet fuel. The solution has a viscosity of 16,000 centipoise using a No. 6 spindle at 10 revolutions per minute.

EXAMPLE 8

A heated agitated vessel is charged with 856 parts by weight water, purged with nitrogen while heating to 95° C. When the purge is complete, the following materials are charged as rapidly as possible: 0.6 parts by weight ammonium persulfate, 1.8 parts by weight of 28 percent aqueous ammonia solution and a monomer mixture of 600 parts by weight t-butylstyrene containing 600 parts per million of t-butylcatechol and 4 parts by weight methacrylic acid. The temperature is controlled at 90° C. and after a period of 2 hours, the reaction mixture is cooled, filtered and spray dried to recover a polymer of fine white powder. The conversion of monomer to polymer is 95 percent. The particle size of the latex in the reaction vessel is 1400 angstroms. A 2 weight percent solution in Jet-A jet fuel is prepared. On standing,

the solution appears to form a gel-like liquid which has a viscosity of 11,000 centipoise using a No. 6 spindle at 10 revolutions per minute.

EXAMPLE 9

The procedure of Example 6 is repeated with the exception that 10.8 parts by weight of acrylamide are employed instead of acrylic acid. The viscosity of a 3 weight percent solution is 6000 centipoise using a No. 6 spindle at 10 revolutions per minute.

EXAMPLE 10

The procedure of Example 6 is repeated with the exception that the monomer mixture is a 1:1 mixture of 2-ethylhexyl acrylate and t-butylstyrene. When 3 weight percent polymer is dissolved in Jet-A jet fuel, the viscosity of the solution is 4000 centipoise using a No. 6 spindle at 10 revolutions per minute.

EXAMPLE 11

In order to illustrate the effect of various non-metallic cations on the thickening characteristics of polymers prepared in accordance with the invention, a plurality of solutions are prepared wherein a thickening additive is employed. The solutions are prepared by adding the thickener to the fuel with agitation. Where a deicer additive is employed, the additive is mixed with a predetermined quantity of thickened Jet-A jet fuel. The solutions are then permitted to stand for 24 hours and the viscosity measured employing a Brookfield Viscometer Model LVF at 6 revolutions per minute and spindle as indicated in Table III. The asterisks appearing after the numbers in the column titled "Polymer Sample" indicate the example from which the polymer is selected for evaluation. The chemical composition of the additive is indicated under "Type Additive." The column headed "Additive Quantity" indicates the percentage of additive based on the quantity of thickening polymer, and the column "Percent Gellant Polymer" indicates the weight percent of polymer in the Jet-A jet fuel.

TABLE III

Polymer Sample	Percent gellant polymer	Type additive	Additive quantity ¹	Viscosity, cps.	Spindle Number
Example 1:					
1	1.25	None	Control	5,000	3
2	1.25	NH ₄ OH	0.11	8,500	3
3	1.25	NH ₄ OH	0.22	15,000	3
4	1.25	NH ₄ OH	0.33	14,000	3
5	1.25	NH ₄ OH	0.36	15,000	4
6	1.25	NH ₄ OH	0.72	14,000	4
7	1.0	None	Control	100	1
8	1.0	NH ₄ OH	0.6	5,000	3
9	2.0	None	Control	18,000	3
10	2.0	NH ₄ OH	0.50	32,000	4
Example 2:					
11	1.25	None	Control	50	1
12	1.25	Water	1.8	50	1
13	1.25	NH ₄ OH	0.50	12,000	4
Example 1; 14	1.25	Anhy. NH ₃	(*)	6,000	3
Example 2:					
15	1.5	None	Control	2,000	4
16	1.5	TMAH ²	0.16	14,000	4
17	1.5	TMAH	0.32	16,000	4
18	1.5	TMAH	0.64	17,000	4
19	1.5	TMAH	0.80	22,000	4
20	1.5	TMAH ³	1.28	15,000	4
21	1.5	TMAH	1.60	6,000	4
22	1.25	TMAH	0.50	13,000	4
23	1.25	TMAH ³	0.53	3,000	4
24	1.25	TMAH	1.06	10,000	4
25	1.25	TMAH	1.59	10,000	4
26	1.25	NaOH	2.7	60	1
27	1.25	H ₂ O	1.8	120	1
Example 1:					
28	1.25	NaOH	0.9	10,000	4
29	1.25	LiOH	2.7	1,000	2
30	1.25	H ₂ O	1.8	50	1
31	1.25	Ca(OH) ₂	2.7	600	1
32	1.25	Mg(OH) ₂	2.7	200	2
33	1.25	CaCl ₂	1.0	50	1
34	1.25	Al(OH) ₃	2.7	50	1
35	1.25	Al(OH) ₃	2.7	2,000	3

¹ Percent by weight, based on polymer gellant.

² Tetramethylammonium hydroxide (used as a 60% solution of the pentahydrate).

³ Tetramethylammonium hydroxide pentahydrate (solid).

⁴ Sparged.

In the preceding examples, the jet fuels contain no deicer additives. When the polymers alone are added to jet fuels containing deicer additives, initial thickening will occur, but the viscosity rapidly decreases in value. After one hour, a 2 percent solution of the polymer of Example 1 has a viscosity of 800 centipoise, and after 2 days, a viscosity of 300 centipoise. A 2 weight percent solution of the polymer of Example 1 is prepared in Jet-B jet fuel (which contains a deicer additive) plus 0.5 percent by weight, based on the polymer, of 28 percent ammonium hydroxide. After 2 days, the viscosity of the solution is 14,000 centipoise; after 7 days, the viscosity is 15,000 centipoise. Adding tetramethylammonium hydroxide pentahydrate, the viscosity after 7 days is 16,000 centipoise. A 2 percent solution in Jet-B jet fuel without deicer has a viscosity of 12,000 centipoise. Similar results are obtained when diesel fuel and gasoline with and without deicer additives are employed.

EXAMPLE 12

A latex is prepared in accordance with Example 2 and divided into a plurality of samples. Table IV indicates the type of material added to the latex, the amount and the weight percent of resin in Jet-A jet fuel and the viscosity of the resultant solutions. The various latexes are dried in an oven at a temperature of about 60° C. for a period of 18 hours, the remaining dried polymer ground in a mortar and added to Jet-A jet fuel.

TABLE IV

Formulant	Percent active formulant ¹	Percent polymer in fuel	Viscosity, cps. ²
None.....	Control	1.25	60
NH ₄ OH.....	0.05	1.25	100
	0.14	1.25	100
	0.28	1.25	400
	0.56	1.25	300
TMAH ³	0.10	1.25	2,000
	0.20	1.25	2,000
TMAH.....	0.40	1.25	7,000
	0.60	1.25	7,000

¹ Based on polymer.

² Number 6 spindle at 10 revolutions per minute.

³ Tetramethylammonium hydroxide.

EXAMPLE 13

Polymer prepared in the foregoing example has a solubility parameter of about 8.45. Portions of the polymer prepared in accordance with Example 1 are employed to make 3 weight percent solutions employing a variety of solvents. The results are set forth in Table V.

TABLE V

Solvent	α_n ¹	Viscosity ²	Description
Trimethyl pentane.....	6.85	4,000	Apple sauce gel. ³
n-Pentane.....	7.0	6,500	Solid gel.
n-Hexane.....	7.3	27,000	Do.
n-Heptane.....	7.45	36,000	Do.
n-Octane.....	7.55	48,000	Do.
Isooctane.....	7.55	22,000	Do.
Necane.....	7.7	35,000	Do.
Cyclohexane.....	8.2	55,000	Solid gel—slightly viscoelastic.
Toluene.....	8.93	35,000	Viscoelastic.
Benzene.....	9.15	35,000	Do.
o-Dichlorobenzene.....	10.0	70,000	Do.
Nitromethane.....	12.7	(4)	Polymer doesn't disperse.

¹ Solubility parameter.

² Brookfield Viscometer Model LVF #4 spindle at 6 revolutions per minute.

³ Having the appearance of apple sauce as commercially available.

⁴ No thickening.

EXAMPLE 14

Employing the apparatus and general procedure of Example 1, a latex is prepared employing as a charge 107 parts by weight of deionized water, 0.15 part by weight ammonium persulfate, 0.25 part by weight of a 28 percent aqueous solution of ammonia, 0.75 part by weight methacrylic acid, 75 parts by weight lauryl acrylate, 20 parts by weight acetone and 4 parts by weight of a 28 percent active aqueous solution of ammonium lauryl sulfate. The contents of the reactor are heated to 80° C. and main-

tained at this temperature for 4 hours. The reaction product is recovered by tray drying in the form of a fine white powder. A 3 weight percent solution of the polymer obtained by tray drying is formed in Jet-A jet fuel. The solution has a viscosity of 5000 centipoise as measured at 10 revolutions per minute with a No. 4 spindle.

EXAMPLE 15

A flammability evaluation apparatus is employed. The apparatus comprises a gun, the barrel of which is 40 feet in length and 8 inches in diameter. The sample to be evaluated is placed in a cylinder of foamed polystyrene having one inch thick walls. The fuel to be evaluated in turn is placed in a double-walled polyethylene bag and placed in the foam cylinder. The fuel to be evaluated in the foam cylinder are placed in the breech of the gun. The gun is pointed in a horizontal direction at a vertically disposed steel grating positioned about 20 feet from the muzzle of the gun. Remote from the gun and adjacent to the grating are five pans about one foot in width, 2 feet in length and 4 inches deep filled with Jet-B jet fuel. The pans are arranged in a rectangle with one pan centrally disposed; one edge of the rectangle is parallel to the grating. The rectangle is about 10 feet on a side. The closest pan is about 10 feet from the grating. The Jet-B jet fuel is ignited. The foam container is then fired into the grating at a muzzle velocity of about 90 miles per hour and the ignition characteristic of the resultant fuel spray is visually observed and rated in the following manner:

- (1) 100 percent reduction of explosion—no flaming;
- (2) 80 to 90 percent reduction of explosion—very slight flaming;
- (3) 50 to 60 percent reduction of explosion—slight flaming;
- (4) 20 to 30 percent reduction of explosion—there is a definite explosion with a small fire ball;
- (5) 0 to 20 percent reduction of explosion—there is a large explosion and fire ball.

Jet-A jet fuel and Jet-B jet fuel with polymer as prepared in Example 1 are evaluated and the results are set forth in Table VI.

TABLE VI

Polymer concentration Jet-A jet fuel, weight percent:	Brookfield viscosity at 10 r.p.m., cps.	Explosion rating
1.....		5
1.5.....	3,500	4
1.75.....	5,000	3
2.....	14,000	2-1
2.5.....	22,000	1
Polymer concentration Jet-B jet fuel, weight percent:		
2.....	10,200	4
2.5.....	14,000	3

NOTE.—Jet-A jet fuel is less volatile than Jet-B jet fuel.

EXAMPLE 16

The procedure of Example 15 is repeated employing polymer prepared in accordance with Example 4 wherein a 2 percent solution of the polymer is prepared in Jet-A jet fuel and portions of this solution diluted to obtain concentrations of 1, 1.25 and 1.5 percent. The results are set forth in Table VII.

TABLE VII

Polymer concentration Jet-A jet fuel, weight percent:	Brookfield viscosity at 10 r.p.m., cps.	Explosion rating
0.....		5
1.....	2,000	4
1.25 ¹	4,500	3
1.5 ¹	12,000	2
2.....	23,000	1

¹ Prepared by dilution of 2% solution with fuel.

EXAMPLE 17

A sample of Jet-A jet fuel is thickened with 2 weight percent of the polymer of Example 1 and is pumped to a J-47 jet (turbine) engine. The engine operates satisfactorily on a stationary test stand on the thickened fuel and no malfunction or sulfidation is observed.

EXAMPLE 18

A portion of the polymer of Example 1 is dissolved at various concentrations in Jet-A jet fuel and 24 hours after solution is complete the viscosity of the solutions is measured at varying shear rates at about 25° C. with a No. 6 spindle. The results are set forth in Table VIII.

TABLE VIII

Concentration	Revolutions per minute	Viscosity in centipoises
Percent:		
1.25-----	2.5	3,100
	5	2,600
	10	2,000
	20	1,600
	50	800
	100	500
1.5-----	.5	15,000
	1	10,000
	2.5	8,000
	5	6,800
	10	3,200
	20	2,100
	50	1,100
	100	650
2-----	.5	52,000
	1	37,000
	2.5	33,000
	5	25,000
	10	14,000
	20	8,500
	50	3,800
	100	2,100
2.5-----	.5	120,000
	1	80,000
	2.5	54,000
	5	35,000
	10	22,000
	20	12,500
	50	5,800
	100	3,200
3-----	.5	260,000
	1	190,000
	2.5	110,000
	5	72,000
	10	46,000
	20	25,000
	50	11,500
	100	6,000

EXAMPLE 19

A plurality of 150 gram samples of a solution of 1.25 weight percent of the polymer of Example 1 is treated with varying quantities of aqueous ammonium hydroxide and a viscosity response which occurs is measured. No significant alteration in viscosity is observed from about 2 microliters per 150 grams to about 200 microliters at 10 revolutions per minute with a No. 6 spindle. About 2.5 microliters of 28 percent aqueous ammonium appears to be optimum, and quantities from 0.2 microliters and higher appear eminently satisfactory. The increase in viscosity is most noted at low shear rates; that is, shear rates corresponding to 5 revolutions per minute and less where maximum viscosities are observed at a concentration of about 3 microliters per 150 grams of 1.5 weight percent of polymer dissolved in Jet-A jet fuel.

Similar results are obtained when the procedures of the foregoing examples are repeated employing p-tertiary-amylstyrene, m-n-hexylstyrene, p-tertiary-hexylstyrene and mixtures thereof in place of p-tertiary-butylstyrene.

As is apparent from the foregoing specification, the present invention is susceptible of being embodied with various alterations and modifications which may differ particularly from those that have been in the preceding specification and description. For this reason, it is to be fully understood that all of the foregoing is intended to be merely illustrative and is not to be construed or in-

terpreted as being restrictive or otherwise limiting of the present invention.

What is claimed is:

1. A thickened hydrocarbon comprising a hydrocarbon body containing uniformly incorporated therein from about 0.2 to about 10 weight percent of a synthetic organic alkyl styrene or lauryl acrylate latex polymer soluble in the hydrocarbon body, the polymer having at least 0.2 to 3 weight percent, based on the weight of the polymer, of an oxygen-containing polar compound selected from the group consisting of olefinically unsaturated copolymerizable (a) acids containing up to 6 carbon atoms, and (b) amides containing up to 4 carbon atoms such as acrylamide, and mixtures thereof; (c) hydroxy acrylic esters such as 2-hydroxyethyl methacrylate, 2-hydroxypropyl methacrylate, 3-hydroxypropyl methacrylate, 2-hydroxyethyl acrylate, 2-hydroxypropyl acrylate, 3-hydroxypropyl acrylate; (d) sulphonic acids such as 2-sulphoethyl methacrylate, 2-sulphoethyl acrylate, 3-vinylbenzenesulphonic acid, 2-benzenesulphonic acid and the like.

2. The composition of claim 1 wherein the polymer is a polymer of an alkylstyrene.

3. The composition of claim 1 including a metal-free base wherein the base is ammonia.

4. The composition of claim 1 wherein the polymer is present in a proportion of from about 1 to about 4 weight percent of the composition.

5. The composition of claim 4 wherein the polymer is present in a proportion of from about 1.25 weight percent to about 2.5 weight percent.

6. The composition of claim 1 wherein the polymer is a polymer of t-butylstyrene.

7. The composition of claim 6 wherein the polymer is a polymer of t-butylstyrene and methacrylic acid.

8. A hydrocarbon fuel composition suitable for internal combustion engines such as turbo jet engines, the fuel composition being a pumpable liquid having the appearance of a viscoelastic fuel, the fuel composition comprising a major portion of liquid combustible hydrocarbons and from 0.2 to 5 weight percent of a polymeric thickening agent, the polymeric thickening agent being an alkyl styrene or lauryl acrylate latex polymer containing from about 0.5 to about 3 weight percent, based on the weight of the polymeric thickening agent, of an oxygen-containing polar compound polymerized therein, the polar compound being an acid containing up to 6 carbon atoms or an amide containing up to 4 carbon atoms, the composition being substantially free of materials which induce sulfidation in a turbo jet internal combustion engine.

9. The composition of claim 8 wherein the hydrocarbon fuel is jet fuel.

10. The composition of claim 9 wherein the polymeric thickening agent is a polymer of an alkylstyrene and a carboxylic acid.

11. The composition of claim 10 wherein the polymeric thickening agent is a polymer of t-butylstyrene and methacrylic acid.

12. The composition of claim 10 wherein the polymeric thickening agent is a polymer of t-butylstyrene and acrylic acid.

13. The composition of claim 8 including a volatile base.

14. The composition of claim 13 wherein the volatile base is ammonia.

15. A method for the preparation of a thickened hydrocarbon, the steps of the method comprising:

providing a liquid combustible hydrocarbon fuel,

providing a synthetic organic polymeric thickening agent, the polymeric thickening agent being an alkyl styrene or lauryl acrylate latex polymer having polymerized therein from about 0.5 to about 3 weight percent, based on the weight of the polymer, of an oxygen-containing polar compound, the polar com-

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pound being an unsaturated copolymerizable acid or amide containing up to 5 carbon atoms, admixing the polymeric thickening agent and the liquid fuel until the thickening agent is generally uniformly incorporated throughout the combustible hydrocarbon, 5

discontinuing mixing, thereby providing a pumpable viscous fuel composition having the appearance of a viscoelastic gel.

16. The method of claim 15 including the step of 10 incorporating a minor amount of a base therein.

17. The method of claim 16 wherein the base, polymer and liquid hydrocarbon are simultaneously admixed.

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