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(54) **ENHANCED ANTISTATIC ADDITIVES FOR
HYDROCARBON FUELS & SOLVENTS**

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(57) **ABSTRACT**

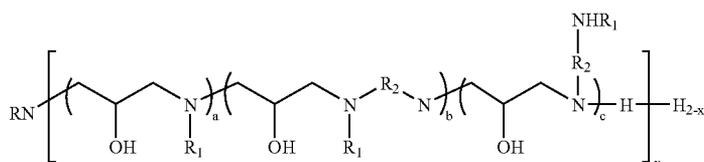
Described herein are enhanced performance of antistatic additive compositions for hydrocarbon fuels, the compositions comprising olefin-sulfur dioxide copolymers in combination with polymeric polyamines prepared using an ortho-xylene solvent.

ENHANCED ANTISTATIC ADDITIVES FOR HYDROCARBON FUELS & SOLVENTS

FIELD OF THE INVENTION

[0001] This invention concerns an improved two-component antistatic additive for hydrocarbon fuels and solvents to render them electrically conductive. One component is an olefin-sulfur dioxide copolymer (polysulfone copolymer)

having from about 4 to 24 carbon atoms, and from about 0 to 10 mol percent of units derived from an olefinic compound having the formula $\text{ACH}=\text{CHB}$ wherein A is a group having the formula $-(\text{C}_x\text{H}_{2x})-\text{COOH}$ wherein x is from 1 to about 23, and B is hydrogen or carboxyl, with the proviso that when B is carboxyl, x is 1, and wherein A and B together can be a dicarboxylic anhydride group, the antistatic composition comprises, in combination with said polysulfone component, a polymeric polyamide of the formula



prepared in orthoxylene, and the other component is a particular polymeric polyamine.

BACKGROUND OF THE INVENTION

[0002] Hydrocarbon fuels normally are very poor conductors of electricity. Electrical charges, therefore, tend to accumulate in the fuel and can be discharged as sparks thus creating the danger of an explosion or fire should such charges ignite hydrocarbon-air admixtures that may be present.

[0003] Numerous materials have been suggested in the art to increase the electrical conductivity of hydrocarbon fuels. Suggested materials include two-component additives where one component is a polysulfone and the other is a quaternary ammonium compound. Another suggested two-component additive comprises polysulfone as one component and polyvalent metal organic compounds of metals having an atomic number of from 22 to 29 as the other component.

[0004] An important aspect is the solvent used for the polymerization of the poly Sulfone component. Typically, solvents such as benzene, toluene, et al. have been employed. These solvents contain impurities which may result in a potentially toxic situation. Thus, there is a clear need to employ a safer solvent.

BRIEF SUMMARY OF THE INVENTION

[0005] The two-component antistatic additives of this invention are characterized by being highly effective at low levels of usage and by being ashless upon burning. These two-component antistatic additives are so efficient that even at relatively low concentrations they provide the desired conductivity (measured in picomhos per meter, or picoSiemens/meter) in nearly all hydro-carbon fuels. This performance is enhanced when the solvent for polymerization of the olefin and sulfur dioxide is ortho-xylene.

[0006] In the antistatic additive of this invention wherein the components are presented in a weight ratio of 100:1 to 1:100, and wherein one component is a polysulfone copolymer prepared in ortho-xylene solvent comprising about 50 mol percent of units from sulfur dioxide, about 40 to 50 mol percent of units derived from one or more 1-alkenes each

[0007] R^1 is an aliphatic hydrocarbyl group of 4 to 24 carbon atoms,

[0008] R^2 is an alkylene group of 2 to 6 carbon atoms,

[0009] R is R^1 , or, an N-aliphatic hydrocarbyl alkylene group of the formula R^1NHR^2 ,

[0010] a is an integer of 0 to 20,

[0011] b is an integer of 0 to 20,

[0012] c is an integer of 0 to 20, and

[0013] x is an integer of 1 to 2,

[0014] with the proviso that when R is R^1 then a is an integer of 2 to 20 and $b+c=0$, and when R is $\text{R}^1\text{NH}-\text{R}^2$ then a is 0 and $b+c$ is an integer of 2 to 20.

[0015] Particular embodiments of this invention are those wherein the polysulfone is composed solely of units derived from sulfur dioxide and units derived from at least one 1-alkene of from 4 to 24 carbon atoms. A particular embodiment is that wherein the 1-alkene is 1-decene and is prepared in an ortho-xylene solvent.

[0016] One embodiment, with reference to the polyamine component, is that where $\text{R}=\text{R}^1$, wherein R^1 is an aliphatic hydrocarbyl group of 4 to 24 carbon atoms, especially where R^1 is the aliphatic hydrocarbyl group of tallowamine.

[0017] Also, with reference to the polyamine component, are embodiments where R is R^1NHR^2 , wherein R^1 is an aliphatic hydrocarbyl group of 8 to 22 carbon atoms and R^2 is an alkylene group of 3 carbon atoms, especially where R^1 is the aliphatic hydrocarbyl group of tallowamine.

[0018] In one aspect of the invention, a polysulfone copolymer of the invention is 1-decene polysulfone having an molecular weight in the range of 10,000 to 1,500,000 amu and in a particular aspect, the polymeric polyamine is the polymeric 1:1.25 mol ratio reaction product of N-tallow-1, 3-diaminopropane with epichlorohydrin.

[0019] The weight ratio of polysulfone copolymer to polymeric polyamine in the invention composition ranges from about 100:1 to 1:100, in one aspect from about 50:1 to 1:1, and in another aspect from about 20:1 to 1:1.

[0020] This invention also concerns the two-component additive as heretofore described together with a strong acid (oil-soluble sulfonic acid is suitable). Thus, a polyamine-sulfonic acid salt will be formed which has an improved resistance to precipitate-formation during long storage periods. This invention also concerns the additives in concentrate form in a solvent. One composition containing the antistatic additive, an acid to enhance precipitate-free storability, and a solvent, comprises, based on total weight:

[0021] i. from about 1 to 50 percent of the polysulfone, prepared in an ortho xylene solvent,

[0022] ii. from about 1 to 50 percent of the polymeric polyamine,

[0023] iii. from about 1 to 30 percent of oil-soluble sulfonic acid, and

[0024] iv. from about 3 to 97 percent of solvent.

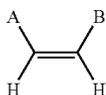
[0025] A suitable sulfonic acid (iii) is mono and di sulfonates of alky benzenes, and in one aspect is dodecylbenzene sulfonic acid, or dinonylnaphthyl sulfonic acid.

[0026] This invention also concerns a composition comprising a liquid hydrocarbon fuel boiling in the range of from about 20° to 375° C., and from about 0.01 ppm to 40 ppm of the two-component polysulfone-polyamine antistatic additive composition and the additive composition stabilized with a strong acid as described herein. Although more than 40 ppm of the additive can be used, no significant benefit is thereby derived. The additive composition can also be used in solvents, oils, and other mixtures such as paints and other formulations where improved conductivity is desired.

[0027] Certain co-additives which are known to provide good initial electrical conductivity in cooperation with the polysulfone copolymer component can also be included in the present invention composition. Included are quaternary ammonium compounds which are more fully described in coassigned U.S. Pat. No. 3,811,848 (the entire teaching of which is herein incorporated in its entirety by reference).

[0028] It has been found that improved three-component antistatic compositions can be obtained by combining the polymeric polyamine described herein with a two-component antistatic additive comprising:

[0029] (i) a polysulfone copolymer prepared in ortho-xylene comprising about 50 mol percent of units derived from sulfur dioxide from about 40 to 50 mol percent of units derived from 1-alkene of 4 to 24 carbon atoms and from 0 to about 10 mol percent of units derived from an olefin having the formula

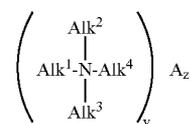


wherein

A is a group having the formula $-(C_xH_{2x})-COOH$ wherein x is from about 0 to about 17, and B is hydrogen or

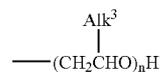
carboxyl, with the proviso that when B is carboxyl, x is 0, and wherein A and B together can be a dicarboxylic anhydride group and

[0030] (ii) a quaternary ammonium compound having the formula:



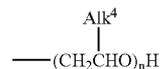
wherein

Alk¹ and Alk² are the same or different alkyl groups having from 1 to 22 carbon atoms, Alk³ is selected from the group consisting of alkyl groups of 1 to 22 carbon atoms and

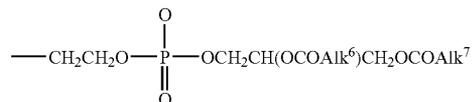


where Alk³ is hydrogen or methyl and n is 1 to 20,

Alk⁴ is selected from the group consisting of (a) an alkyl group having 1 to 22 carbon atoms, (b) an aralkyl group having from 7 to 22 carbon atoms, (c) a



group as defined above, (d) a



group wherein

Alk⁶ and Alk⁷ are the same or different alkyl groups having from 11 to 19 carbon atoms, and (e) an $-\text{Alk}^8-\text{CO}_2$ group wherein Alk⁸ is a hydrocarbyl group having from 1 to 17 carbon atoms, with the proviso that when Alk¹, Alk², Alk³ and Alk⁴ are each alkyl groups, at least one of them is an alkyl group having at least 8 carbon atoms,

[0031] A is an anion,

[0032] z is 0 or 1, z is 0 when Alk⁴ is (d) or (e), and

[0033] y is at least 1, y is equal to the ionic valence of anion A when z is 1.

[0034] The ratio of the components are such that for each part of polysulfone there is 0.01 to 100 parts of each of the polymeric polyamine and the quaternary ammonium compound.

[0035] A suitable quaternary ammonium compound is dicocodimethyl ammonium nitrite wherein "coco" refers to a mixture of C₈ to C₁₈ alkyl radicals of cocoamine. The quaternary ammonium compound can be present in the amounts of from about 1 part to 25 parts per 100 parts of polysulfone copolymer. The presence of a quaternary ammonium compound further enhances the electrical conductivity of the present invention composition in many hydrocarbon fuels and maintains the composition ash-free.

[0036] Another embodiment of the present invention is directed to a fuel oil composition. This fuel composition can comprise a suitable fuel component and a suitable additive component. In one aspect, the composition comprises from about 99.99% fuel and about 0.01% of additive to about 99.9999% fuel to about 0.0001% of additive. A suitable additive includes those described herein.

[0037] The term "hydrocarbyl" employed herein refers to straight and branched-chain groups containing only carbon and hydrogen. Such groups can be saturated, unsaturated or aromatic.

[0038] For a better understanding of the present invention, together with other and further objects thereof, reference is made to the accompanying drawings and detailed description and its scope will be pointed out in the appended claims.

DETAILED DESCRIPTION OF THE INVENTION

The Polysulfones:

[0039] The polysulfone copolymers often designated as olefin-sulfur dioxide copolymer, olefin polysulfones, or poly(olefin sulfone) are polymers wherein the structure is considered to be that of alternating copolymers of the olefins and sulfur dioxide, having a one-to-one molar ratio of the comonomers with the olefins in head to tail arrangement. The polysulfones used in this invention are readily prepared by the methods known in the art (cf. Encyclopedia of Polymer Science and Technology Vol. 9, Interscience Publishers, page 460 etc, the entire teaching of which is incorporated herein by reference).

[0040] The weight average molecular weights of the polysulfones are in the range from about 10,000 to about 1,500,000, in one aspect the range is from about 50,000 to about 900,000, and in another aspect the molecular weights range from about 100,000 to about 500,000. Olefin polysulfones whose molecular weights are below about 10,000, while effective in increasing conductivity in hydrocarbon fuels, do not increase the conductivity values as much as olefin polysulfones of higher molecular weights. Olefin polysulfones whose molecular weights are above about 1,500,000 are difficult to produce and are more difficult to handle.

[0041] The molecular weights of the olefin polysulfones can be determined by any of the well-known methods, such as the light scattering method. It is generally more convenient, however, to determine the inherent viscosity of the polymer to derive the approximate molecular weight range of the polysulfones therefrom. Inherent viscosity is defined as $\eta_{inh} = \ln \eta_{rel} / C$ wherein \ln is the natural logarithm, η_{rel} is a relative viscosity, i.e., ratio of the viscosity of the polymer solution to the viscosity of the polymer solvent and C is concentration of polymer g/100 mL. The units of inherent

viscosity are deciliters per gram (dl/g). The inherent viscosities of olefin poly-sulfones are conveniently measured in toluene at 30° C. as 0.5 weight percent solutions. It has been found by comparison with molecular weight determinations that polysulfones with inherent viscosities of between about 0.1 dl/g to 1.6 dl/g correspond to weight average molecular weights in the range of about 50,000 to 900,000.

[0042] The control of the molecular weights of the olefin polysulfones in the desired range is readily accomplished by those skilled in the art of polymer science by controlling the polymerization conditions such as the amount of initiator used, polymerization temperature and the like or by using molecular weight modifiers such as dodecyl mercaptan. The amount of molecular weight modifier required to obtain the desired molecular weight range will depend upon the particular 1-olefin being polymerized with sulfur dioxide, and can be determined easily with few experiments. Generally, the amount of modifier, such as dodecyl mercaptan, used to obtain the molecular weights in the range of 50,000 to 900,000 is in the range of up to about 0.007 mole per mole of 1-olefin.

[0043] The 1-alkenes useful for the preparation of the polysulfones are available commercially as pure or mixed olefins from petroleum cracking processes or from the polymerization of ethylene to a low degree. Included, but not limited to, are 1-hexene, 1-heptene, 1-octene, 1-nonene, 1-decene, 1-undecene, 1-dodecene, 1-tridecene, 1-tetradecene, 1-pentadecene, 1-hexadecene, 1-heptadecene, 1-octadecene, 1-nonadecene, 1-eicosene, 1-heneicosene, 1-docosene, 1-tricosene and 1-tetracosene. Poly unsaturated olefins such as butadiene and its analogs, and branched olefins and internal olefins are also utilizeable in the invention. Although branched-chain alkenes are useful, the straight-chain 1-alkenes are also useful whether pure or in admixture with other straight-chain 1-alkenes.

[0044] When the polysulfone copolymer contains up to 10 mol percent of the olefin AHC=CHB, as defined above, A and B can together form a dicarboxylic anhydride group. The dicarboxylic anhydride group is readily converted to two carboxyl groups by simple acid hydrolysis. The olefin, AHC=CH₂, is a terminally unsaturated alkenoic acid represented by CH₂=CH-(C_xH_{2x})-COOH. The alkylene group bridging the vinyl and the carboxyl groups can have from 1 to 24 carbon atoms or it can be absent, and such alkylene group when present can be a straight chain group or branched chain. The useful acids are alkenoic acids of 3 to 20 carbon atoms wherein the olefinic group is a terminal group. Representative but nonlimiting examples of alkenoic acids with a terminal olefinic group include acrylic acid, 3-butenic acid, 4-pentenoic acid, 5-hexenoic acid, 6-heptenoic acid, 7-octenoic acid, 8-nonenic acid, 9-decenoic acid, 10-undecenoic acid, 11-dodecenoic acid, 13-tetradecenoic acid, 15-hexadecenoic acid, 17-octadecenoic acid as well as branched chain alkenoic acids with terminal olefinic groups such as 2-ethyl-4-pentenoic acid, 2,2-dimethyl-4-pentenoic acid, 3-ethyl-6-heptenoic acid, 2-ethyl-6-heptenoic acid, 2,2-dimethyl-6-heptenoic acid, and the like. It should be understood that a mixture of alkenoic acids can be used.

[0045] The reaction leading to polysulfone formation is the art-known free-radical polymerization process. Nearly all types of radical initiators are effective in initiating

polysulfone formation. Radical initiators such as oxygen, ozonides, t-butylperoxy-pivalate, hydrogen peroxide, ascaridole, cumene peroxide, benzoyl peroxide, azobisisobutyronitrile are examples of some of the useful initiators. Free-radicals are generated from such radical initiators either thermally and/or by light activation in the presence of a mixture of sulfur dioxide and 1-alkene. The polymerization can be carried out in liquid phase, conveniently in a solvent such as benzene, toluene or xylene to facilitate the reaction. In one aspect of this invention, ortho-xylene ("o-xylene") is the solvent employed. Such solvent can be removed, e.g., by distillation, if desired, but it is generally more the convenient to use the polysulfone copolymer as a concentrate in such solvent. Generally, it is typical to use an excess of sulfur dioxide since any unreacted sulfur dioxide is readily removed as by passing nitrogen gas into the polymer solution. An excess of 1-alkene can be used, however, and the excess subsequently removed as by distillation.

[0046] Using ortho-xylene has several advantages. For example, the use of o-xylene as a solvent leads to increased conductivity, an increase of approximately 15% was observed when o-xylene was used (See Tables I and II, infra.) Ortho-xylene also facilitates the removal of toxins, e.g., ethyl benzene. One also observes an increase in flash point using o-xylene, as compared to toluene. This is mainly due to the difference in the flash points between o-xylene (86° C.) and Toluene (40° C.)

TABLE I

Comparison of the conductivity enhancement of a Static Dissipater formulation where the poly Sulfone polymer in the formulation was prepared in o-xylene, to that which was prepared in Toluene.		
Formulation	Conductivity pS/m	Conductivity pS/m
1 PSI w/o-xylene	369	425
2 PSI w/o-xylene	342	388
3 PSI w/toluene	303	345

[0047]

TABLE II

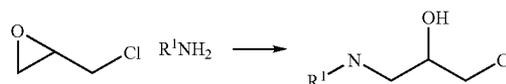
Conductivity of a Static Dissipater formulations where the poly Sulfone polymer in the formulation was prepared in Toluene.	
Formulation	Conductivity
1	361 pS/m
2	338 pS/m
3	287 pS/m
4	347 pS/m
5	296 pS/m
6	274 pS/m
7	272 pS/m
8	242 pS/m
9	300 pS/m

[0048] The particular ratio of 1-alkene to sulfur dioxide appears to be immaterial since the resultant polysulfone copolymer contains 1-alkene and sulfur dioxide in 1:1 molar ratio regardless of the particular ratio used. However, for efficiency in utilization of the reactants and of the equipment, a slight excess of sulfur dioxide is often employed. The polymerization can be carried out at atmospheric or super-atmospheric pressures, the polymerization reaction

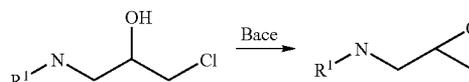
being independent of the pressure. The polymerization temperature can be any convenient temperature below the ceiling temperature of the particular 1-alkene employed. Ceiling temperature is the temperature at which the rates of polymerization and depolymerization are equal so that no polymer formation takes place. The above mention "Encyclopedia of Polymer Science and Technology" on page 466 lists ceiling temperatures for various 1-alkenes. Generally, the convenient polymerization temperature range is from about 0° to about 50° C.

The Polymeric Polyamines:

[0049] The polyamine component of the antistatic composition of the present invention is a polymeric reaction product of epichlorohydrin with an aliphatic primary monoamine or N-aliphatic hydrocarbyl alkylene diamine. The polymeric reaction products are prepared by heating an amine with epichlorohydrin in the molar proportions of from about 1:1-1.5 in the temperature range of about 50° to about 100° C. Generally, with aliphatic monoamines, R¹NH₂, the molar ratio is about 1:1. The initial reaction product is believed to be an addition product as illustrated below with a primary monoamine, R¹NH₂,

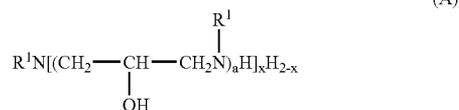


[0050] The aminoalcohol (I) upon reaction with an inorganic base then forms an aminoepoxide.



[0051] The aminoepoxide (II), which contains a reactive epoxide group and a reactive amino-hydrogen, undergoes polymerization to provide a polymeric material containing several amino groups. The ratio of epichlorohydrin to amine and the reaction temperature used are such that the polymeric reaction product contains from 1 to 20 recurring units derived from the aminoepoxide represented by II.

[0052] The polymeric reaction product derived from epichlorohydrin and an aliphatic primary monoamine as defined is represented by subgeneric formula (A),



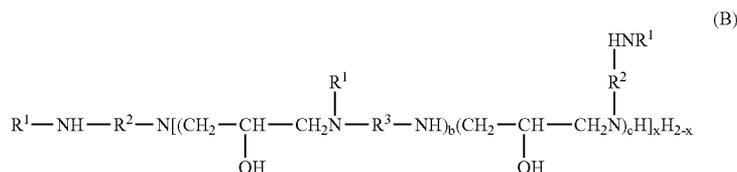
[0053] where a is an integer from 1 to 20 and x is an integer of 1 to 2.

[0054] The aliphatic primary monoamines that can be used to prepare the polymeric reaction products with epichlorohydrin can be straight chain or branched chain and include,

inter alia, octylamine, nonylamine, decylamine, undecylamine, dodecylamine, tridecylamine, tetradecylamine, pentadecylamine, hexadecylamine, heptadecylamine, octadecylamine, nonadecylamine, eicosylamine, heneicosylamine, docosylamine, tricosylamine, tetracosylamine and the corresponding alkenyl analogs. The aliphatic primary amine should have at least about 4 carbon atoms, in one aspect, about 12 to 24 carbon atoms to provide polymeric reaction products of sufficient solubility in hydrocarbon fuels. While aliphatic primary amines containing more than about 24 carbon atoms are useful, such amines are of limited availability.

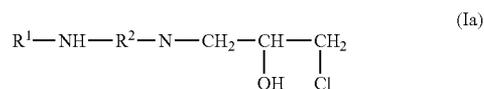
[0055] Mixtures of aliphatic primary amines can also be used, and are typical since mixtures of primary amines derived from tall oil, tallow, soybean oil, coconut oil, cotton seed oil and other oils of vegetable and animal origin are commercially available and at lower cost than individual amines. The above mixtures of amines generally contain alkyl and alkenyl amines of from about 12 to 18 carbon atoms, although sometimes an individual amine mixture, depending upon the source, contains small amounts of primary amines having fewer or more carbon atoms. An example of a commercially available mixture of primary monoamines is hydrogenated tallow amine which contains predominantly hexadecyl- and octadecylamines with smaller amounts of tetradecylamine.

[0056] When the amine reacted with epichlorohydrin is an N-hydrocarbylalkyl-enediamine as defined, the polymeric reaction product is represented by subgeneric formula (B),

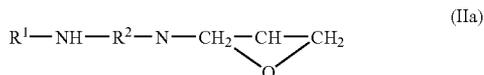


[0057] where R^1 is an aliphatic hydrocarbyl group of 4 to 24 carbon atoms, R^2 is an alkylene group of 2 to 6 carbon atoms, b and c are integers of 0 to 20 and $b+c$ is an integer of 2 to 20 and x is 1 to 2.

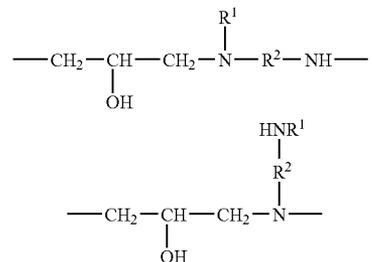
[0058] In the reaction of epichlorohydrin with an N-aliphatic hydrocarbylalkyl-enediamine, it is believed (because of the known greater reactivity of primary amino hydrogen over secondary amino hydrogen) that the initially formed aminochlorohydrin is of the formula



and the subsequently formed aminoepoxide is of the formula



[0059] When IIa undergoes further condensation, the recurring units in the product may be



or both, since (IIa) contains two reactive secondary amino-hydrogens. Thus, in subgeneric formula (B), above, b is from 0 to 20, c is from 0 to 20 and $b+c$ is from 2 to 20.

[0060] Illustrative examples of useful N-aliphatic hydrocarbyl alkylene diamines include, but not limited to, N-octyl, N-nonyl, N-decyl, N-undecyl, N-dodecyl, N-tridecyl, N-tetradecyl, N-pentadecyl, N-hexadecyl, N-heptadecyl, N-octadecyl, N-nonadecyl, N-eicosyl, N-uneicosyl, N-docosyl, N-tricosyl, N-tetracosyl, as well as the corresponding N-alkenyl derivatives of ethylenediamine, propylenediamine, butylenediamine, pentylenediamine and hexylenediamine. In one aspect, the N-aliphatic hydrocarbyl-alkylenediamine is N-aliphatic hydrocarbyl-1,3-propylenediamine. The N-aliphatic hydrocarbyl-1,3-propylenediamines are

commercially available and are readily prepared from aliphatic primary monoamines such as those described above by cyanoethylation with acrylonitrile and hydrogenation of the cyanoethylated amine. Mixtures of N-aliphatic hydrocarbyl-1,3-propylenediamines can also be advantageously used. A typical mixture is N-tallow-1,3-propylenediamine which is commercially available as "Duomeen T" wherein "tallow" represents predominantly mixtures of alkyl and alkenyl groups of 16 to 18 carbon atoms which can contain small amounts of alkyl and alkenyl groups of 14 carbon atoms.

[0061] The reaction between the amines (as defined) and epichlorohydrin is advantageously carried out in the presence of a solvent such as benzene, toluene, xylene, orthoxylene, or other higher boiling mixtures of aromatic solvents, such as Aromatic 100 or Aromatic 150 which can also contain some hydroxylic component such as ethanol, propanol, butanol and the like.

[0062] After the initial reaction between the amine and epichlorohydrin to form an aminochlorohydrin intermediate as illustrated above by Products I and Ia, the reaction mass is treated with an inorganic base, such as sodium, potassium

or lithium hydroxide, to form an aminoepoxide as represented by Products II and IIa above, which under continued heating undergoes polymerization to yield the desired product represented above by the generic formula and subgenerics A and B. Inorganic chloride formed in the reaction is removed by filtration. The solvent used to facilitate the reaction can be removed if desired, e.g., by distillation, but generally it is more convenient to use the polymeric polyamine as a solution.

[0063] The above-described reactions of epichlorohydrin with amines to form polymeric products are well known and find extensive use in epoxide resin technology (cf. "Epoxy Resins", Henry Lee and Kris Neville, The McGraw-Hill Book Co., 1957, the entire teaching of which is incorporated herein by reference). The polymeric reaction products of epichlorohydrin and amines are complex mixtures but it is believed that the above formulas of the polymeric polyamines fairly represent the composition and structures that are obtained.

[0064] The normally liquid hydrocarbon fuels to which the additives are added to render such hydrocarbon fuels electrically conductive are those boiling in the range of about 20° to about 375° C. and include such commonly designated fuels as aviation gasoline, motor gasoline, jet fuels, naphtha, kerosene, diesel fuel and distillate burner fuel oil. The additive composition can be added in any conventional manner. Each individual component of the composition can be added to the hydrocarbon fuel separately or the composition can be added as a simple mixture or as a solution in a solvent, such as benzene, toluene, xylene, o-xylene, isopropanol, cyclohexane, Aromatic 100 and Aromatic 150 fuel oil, or in a mixture of such solvents. It is convenient to prepare both the polysulfone copolymer and the polymeric polyamine in a solvent, such as one or more of those mentioned above. Thus, it is typical to use such solutions of polysulfone and polymeric polyamine and to combine them. The combination, which can be termed a concentrate, can then be added to the hydrocarbon fuel. Such concentrate conveniently contains from about 1 to 40% by weight of polysulfone copolymer, from about 1 to about 40% by weight of polymeric polyamine and from about 20 to 98% by weight of a solvent or a mixture thereof as described. In one aspect, the concentrate will contain from about 5 to 25% by weight of polysulfone copolymer, from about 5 to 25% by weight of polymeric polyamine and from about 50 to 90% by weight of solvent.

[0065] When formulating concentrates, it is typical that the polymeric polyamine be present as a salt, particularly a sulfonic acid salt, for improved resistance to precipitate formation in storage. For example, when a concentrate as described comprising polymeric polyamine in the free base form is stored at elevated temperatures of about 44° C. for a period of time of about 4 weeks, a small amount of precipitate sometimes forms. The presence of small amounts of precipitate in the concentrates have little or no effect on the usefulness of the present compositions as antistatic additives but are undesirable if only from an aesthetic point of view. It has been found that strong acids such as hydrochloric, sulfuric or a sulfonic acid can be used to limit precipitate formation in the concentrates. Oil-soluble sulfonic acids are typical because they effectively inhibit precipitate formation without substantial deleterious effect upon the electrical conductivity property of the composition.

Any oil-soluble sulfonic acid such as an alkanesulfonic acid or an alkarylsulfonic acid can be used. A useful sulfonic acid is petroleum sulfonic acid resulting from treating oils with sulfuric acid.

[0066] Generally, the amount of sulfonic acid incorporated in the concentrate is an equivalent amount, that is, sufficient amount of sulfonic acid to neutralize all the amine groups of the polymeric polyamine, although lesser or greater than the equivalent amount can be used. Thus, one form of the concentrate of the present invention will contain from about 5 to 25% by weight of polysulfone copolymer, from about 5 to 30% by weight of polymeric polyamines, from about 5 to 30% by weight of, say, dodecylbenzenesulfonic acid, and from about 20 to 85% by weight of solvent. Typically an equivalent amount of dodecylbenzenesulfonic acid or dinonylnaphthyl sulfonic acid is used.

[0067] When a three-component additive is employed (where a quaternary ammonium compound is the third component), the concentrate composition will comprise, based on total weight of the composition: from about 5 to 25% of polysulfone, from about 5 to 25% of polyamine, from about 0.5 to 5% of quaternary ammonium compound, from about 5 to 25% of a sulfonic acid, say, dodecylbenzene sulfonic acid, and from about 20 to 84.5% of solvent.

[0068] The utility of the present invention composition as a highly effective antistatic additive for hydrocarbon fuels is demonstrated by the fact that the incorporation into hydrocarbon fuels of as little as 0.00003% by weight (0.3 part per million, ppm) of polysulfone copolymer and 0.00002% by weight (0.2 ppm) of polymeric polyamine is sufficient, in nearly all hydrocarbon fuels investigated, to provide electrical conductivities of at least 100 C.U. (conductivity units). In certain responsive fuels, as little as 0.000018 weight % (0.018 ppm) polysulfone copolymer and 0.000013 weight % (0.013 ppm) polymeric polyamine provide a conductivity of at least 100 C.U. Thus, the present invention provides a highly effective ashless antistatic additive composition which confers increased electrical conductivity to hydrocarbon fuels at very low usage levels.

[0069] The antistatic effectiveness of the present invention composition is unexpected as the polysulfone product prepared in o-xylene and the correspondent composition derived from said polysulfone is superior to a similar composition derived from polysulfone prepared from toluene.

[0070] The hydrocarbon fuels into which the present composition is incorporated exhibit satisfactory water interaction properties as evidenced by satisfactory results in the water separation test according to ASTM D-2250-66T. The hydrocarbon fuel composition containing the composition of the invention can also contain conventional additives used in hydrocarbon fuels such as antiknock compounds, antioxidants, corrosion inhibitors, metal deactivators, rust preventatives, dyes, anti-icing agents and the like.

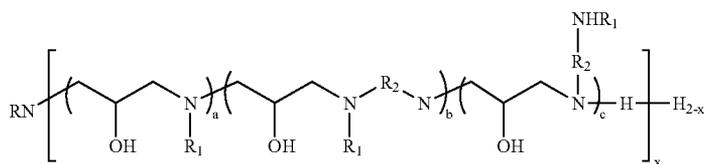
[0071] The polysulfones, and poly amines evaluated in the present invention were prepared according to procedures outlined in U.S. Pat. No. 3,917,466. The examples cited therein are not intended to be a limit of the scope of the invention.

[0072] Another embodiment of the present invention is directed to a fuel oil composition. This fuel oil composition

can comprise a suitable fuel oil component and a suitable additive component. In one aspect, the composition comprises from about 99.99% fuel and about 0.01% additive to about 99.9999% fuel to about 0.0001% additive. In one aspect, a suitable additive includes those described herein. The fuel oil can be a petroleum-based fuel oil, suitably a gasoline or middle distillate fuel oil. The fuel oils can comprise atmospheric or vacuum distillate, contain cracked gas oil in or a blend of any proportion of straight run or thermally or catalytically cracked distillates, and in many cases are hydrogen-treated or otherwise processed to improve properties.

units derived from one or more 1-alkenes each having from about 4 to 24 carbon atoms, and from about 0 to 10 mol percent of units derived from an olefinic compound having the formula $\text{ACH}=\text{CHB}$ wherein A is a group having the formula $-\text{C}_x\text{H}_{2x}-\text{COOH}$ wherein x is from about 0 to about 17, and B is hydrogen or carboxyl, with the proviso that when B is carboxyl, x is 0, and wherein A and B together can be a dicarboxylic anhydride group,

said polymeric polyamine of (ii) having the formula



[0073] Gasolines are low boiling mixtures of aliphatic, olefinic, and aromatic hydrocarbons, and optionally alcohols or other oxygenated components, boiling in the range from room temperature up to 225° C. Other fuel oils are kerosine, jet fuels, diesel fuel oils and home heating fuel oils (such as, middle distillate heating fuels), generally having flash points greater than 380° C. These fuels are higher boiling mixtures of aliphatic, olefinic, and aromatic hydrocarbons having a boiling point up to 350° C.

[0074] Conductivity of fuels and solvents comprising static dissipators are commonly measured using ASTM D 2624 or IP 274, a technically equivalent method. See, ASTM D 2624-02, the entire teaching of which is incorporated herein by reference. For comparative purposes, compositions can be tested according to the method described in ASTM in fuels, or in a standard solvent such as Isopar M. Isopar M is a high-flash solvent marketed by Exxon Mobil and is highly paraffinic. Results from testing in this solvent are directionally similar to those obtained in fuels such as motor gasoline, aviation gasoline, aviation turbine fuel, diesel fuels of various sulfur contents, and home heating fuels.

[0075] Although the invention has been described with respect to various embodiments, it should be realized this invention is also capable of a wide variety of further and other embodiments within the spirit and scope of the appended claims.

What is claimed is:

1. An antistatic additive composition for hydrocarbon fuels comprising, based on total weight,

- i. from about 1 to 50 percent of polysulfone,
- ii. from about 1 to 50 percent of polymeric polyamine,
- iii. from about 1 to 30 percent of oil-soluble sulfonic acid, and
- iv. from about 3 to 97 percent of solvent,

said polysulfone of (i) comprising about 50 mol percent of units from sulfur dioxide, about 40 to 50 mol percent of

wherein

R¹ is an aliphatic hydrocarbyl group of 8 to 24 carbon atoms,

R² is an alkylene group of 2 to 6 carbon atoms,

R is R¹, or, an N-aliphatic hydrocarbyl alkylene group of the formula R¹NHR²,

a is an integer of 0 to 20,

b is an integer of 0 to 20,

c is an integer of 0 to 20, and

x is an integer of 1 to 2,

with the proviso that when R is R¹ then a is an integer of 2 to 20 and b=c=0, and when R is R¹NH—R² then a is 0 and b+c is an integer of 2 to 20,

said oil-soluble sulfonic acid of (iii) being dodecylbenzenesulfonic acid, and

said solvent of (iv) being ortho-xylene.

2. The composition of claim 1, wherein said polysulfone has a molecular weight ranging from about 10,000, to about 1,500,000 amu.

3. The composition of claim 1, wherein said polysulfone is selected from the group consisting of 1-hexene, 1-heptene, 1-octene, 1-nonene, 1-decene, 1-undecene, 1-dodecene, 1-tridecene, 1-tetradecene, 1-pentadecene, 1-hexadecene, 1-heptadecene, 1-octadecene, 1-nonadecene, 1-eicosene, 1-heneicosene, 1-docosene, 1-tricosene, and 1-tetracosene.

4. The composition of claim 3, wherein said polysulfone is 1-decene.

5. The composition of claim 1, wherein said polymeric polyamine is a polymeric reaction product of epichlorohydrin with an aliphatic primary monoamine or N-aliphatic hydrocarbyl alkylene diamine.

6. The composition of claim 5, wherein said aliphatic primary monoamine is selected from the group consisting of octylamine, nonylamine, decylamine, undecylamine, dodecylamine, tridecylamine, tetradecylamine, pentadecylamine, hexadecylamine, heptadecylamine, octadecyl-

lamine, nonadecylamine, eicosylamine, heneicosylamine, docosylamine, tricosylamine, and tetracosylamine.

7. The composition of claim 5, wherein said N-aliphatic hydrocarbyl alkylene diamine is selected from the group consisting of N-octyl, N-nonyl, N-decyl, N-undecyl, N-dodecyl, N-tridecyl, N-tetradecyl, N-pentadecyl, N-hexadecyl, N-heptadecyl, N-octadecyl, N-nonadecyl, N-eicosyl, N-uneicosyl, N-docosyl, N-tricosyl, N-tetracosyl, as well as the corresponding N-alkenyl derivatives of ethylenediamine, propylenediamine, butylenediamine, pentylenediamine, and hexylenediamine

8. The composition of claim 1, wherein a weight ration of said polysulfone to said polyamine ranges from about 100:1 to about 1:100.

9. The composition of claim 1, wherein a weight ration of said polysulfone to said polyamine ranges from about 50:1 to about 1:1.

10. The composition of claim 1, wherein a weight ration of said polysulfone to said polyamine ranges from about 20:1 to about 1:1.

11. The composition of claim 1, wherein said sulfonic acid is either a mono or di sulfonate of alkyl benzene.

12. The composition of claim 11, wherein said sulfonic acid is either dodecylbenzene sulfonic acid or dinonylnaphthyl sulfonic acid.

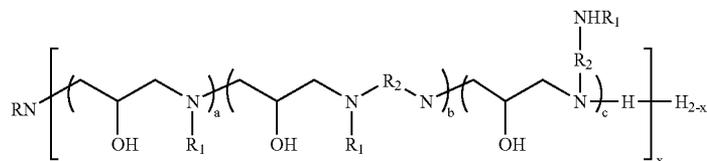
13. A hydrocarbon fuel boiling range of from about 200 to about 375° C. having from about 0.01 ppm to about 40 ppm of said composition defined in claim 1.

14. An antistatic additive composition comprising, based on total weight,

- i. from about 1 to 50 percent of polysulfone,
- ii. from about 1 to 50 percent of polymeric polyamine, and
- iii. from about 3 to 97 percent of solvent,

said polysulfone of (i) comprising about 50 mole percent of units derived from sulfur dioxide, about 40 to 50 percent of units derived from one or more 1-alkenes each having from about 4 to 24 carbon atoms, and from about 0 to 10 mol percent of units derived from an olefinic compound having the formula $\text{ACH}=\text{CHB}$ wherein A is a group having the formula $-\text{C}_x\text{H}_{2x}-\text{COOH}$ wherein x is from 0 to about 17, and B is hydrogen or carboxyl, with the proviso that when B is carboxyl, x is 0, and wherein A and B together can be a dicarboxylic anhydride group,

said polymeric polyamine of (ii) having the formula



wherein

R^1 is an aliphatic hydrocarbyl group of 8 to 24 carbon atoms,

R^2 is an alkylene group of 2 to 6 carbon atoms,

R is R^1 , or, an N-aliphatic hydrocarbyl alkylene group of the formula R^1NHR^2 ,

a is an integer of 0 to 20,

b is an integer of 0 to 20,

c is an integer of 0 to 20, and

x is an integer of 1 to 2,

with the proviso that when R is R^1 then a is an integer of 2 to 20 and $b=c=0$, when R is $\text{R}^1\text{NH}-\text{R}^2$ then a is 0 and $b+c$ is an integer of 2 to 20, and

said solvent of (iii) being ortho-xylene.

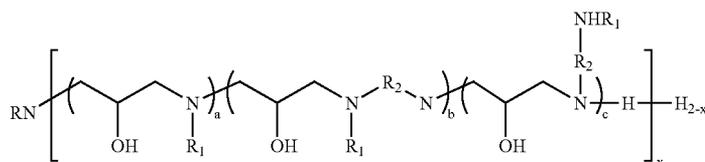
15. An antistatic additive composition comprising, based on total weight,

- i. from about 1 to 50 percent of polysulfone,
- ii. from about 1 to 50 percent of polyamine,
- iii. from about 0.5 to 5 percent of quaternary ammonium compound,
- iv. from about 1 to 30 percent of oil-soluble sulfonic acid, and
- v. from about 3 to 97 percent of solvent,

said polysulfone of (i) comprising about 50 mol percent of units derived from sulfur dioxide, from about 40 to 50 mol percent of units derived from 1-alkene of 4 to 24 carbon atoms and 0 to about 10 mol percent of units derived from an olefin having the formula, $\text{ACH}=\text{CHB}$, wherein A is a group having the formula $-\text{C}_x\text{H}_{2x}-\text{COOH}$ wherein

x is from 0 to about 17, and B is hydrogen or carboxyl, with the proviso that when B is carboxyl, x is 0, and wherein A and B together can be a dicarboxylic anhydride group,

said polyamine of (ii) having the formula



wherein

R¹ is an aliphatic hydrocarbyl group of 8 to 24 carbon atoms,

R² is an alkylene group of 2 to 6 carbon atoms,

R is R¹, or, an N-aliphatic hydrocarbyl alkylene group of the formula R¹NHR²,

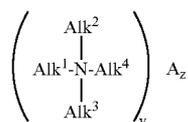
a is an integer of 0 to 20,

b is an integer of 0 to 20,

c is an integer of 0 to 20, and

x is an integer of 1 to 2,

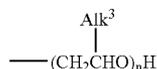
with the proviso that when R is R¹ then a is an integer of 2 to 20 and b=c=0, and when R is R¹NH—R² then a is 0 and b+c is an integer of 2 to 20, the quaternary ammonium compound of (iii) having the formula



wherein

Alk¹ and Alk² are the same or different alkyl groups having from 1 to 22 carbon atoms,

Alk³ is selected from the group consisting of alkyl groups of 1 to 22 carbon atoms and



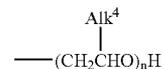
where Alk³ is hydrogen or methyl and n is 1 to 20,

Alk⁴ is selected from the group consisting of

(a) an alkyl group having 1 to 22 carbon atoms,

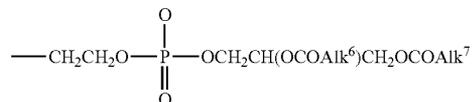
(b) an aralkyl group having from 7 to 22 carbon atoms,

(c) a



group as defined above,

(d) a



group, wherein

Alk⁶ and Alk⁷ are the same or different alkyl groups having from 11 to 19 carbon atoms, and

(e) an —Alk⁸—CO₂ group wherein Alk⁸ is a hydrocarbyl group having from 1 to 17 carbon atoms, with the proviso that when Alk¹, Alk², Alk³ and Alk⁴ are each alkyl groups, at least one of them is an alkyl group having at least 8 carbon atoms,

A is an anion,

z is 0 or 1, z is 0 when Alk⁴ is (d) or (e), and

y is at least 1, y is equal to the ionic valence of anion A when z is 1,

said composition comprises, in combination therewith,

said oil-soluble sulfonic acid of (iv) being dodecylbenzenesulfonic acid, and

said solvent of (v) being ortho-xylene.

16. The composition of claim 15, wherein said quaternary ammonium is dicocodimethyl ammonium nitrite.

17. A composition comprising a major proportion of a suitable fuel oil and a minor portion of a suitable additive.

18. The composition of claim 17, wherein said suitable fuel oil is selected from the group consisting of a petroleum-based fuel, kerosene, jet fuel oil, middle distillate heating oils, and diesel fuel oil.

19. The composition of claim 18, wherein said petroleum-based fuel is a gasoline or middle distillate fuel oil.

20. The composition of claim 17, wherein said suitable additive is an additive defined by claim 1.

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