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Cloud point depressant composition.

A composition of a polymer of an 8 to 40 carbon hydrocarbyl ester of an ethylenically unsaturated acid, short chain ester-containing monomers, and short chain alkyl ether monomers ; and a mixture of hydrocarbyl-substituted polynuclear aromatic compounds, is effective to reduce the cloud point of paraffinic liquids.

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The present invention relates to a composition useful for reducing the cloud point of paraffinic liquids.

When diesel fuels, home heating oils, and other paraffinic liquids are cooled, solidification occurs progressively, normally over a range spanning some 10 to 15°C. This solidification is generally undesirable for materials which are normally handled in the liquid state, and efforts to measure and ameliorate this phenomenon have been pursued. Cloud point is the measurement of the temperature at which paraffin crystals first appear when such a material is cooled. This value is determined by standardized methods such as ASTM D 2500. The cloud point of a particular material depends on the paraffin (particularly n-paraffin) concentration in the liquid, on the molecular weight of the particular paraffins, and on the chemical nature of the non-paraffin component of the liquid. For instance, the presence of higher molecular weight paraffinic molecules generally leads to higher cloud points. At temperatures below the cloud point, the material becomes increasingly solid, until the pour point (ASTM D 97) is reached, that is, the temperature at which the material has essentially solidified. Although there are many materials which are known to be suitable as pour point depressants, a reduction of cloud point is considerably more difficult to achieve. The present invention provides for the reduction of the cloud point of paraffinic liquids, thus permitting the wider use of paraffinic liquids as fuel and lubricants, particularly at low temperatures.

A fuller discussion of the phenomenon of cloud point, including the measurement thereof by differential scanning calorimetry, is found SAE Technical Paper Series No. 861527, "New Additives for Diesel Fuels: Cloud-Point Depressants," Faure et al., October 6-9, 1986. This paper also discloses the use of copolymers of linear α -olefins with acrylic, vinylic and maleic unsaturated compounds as additives to reduce cloud point.

U.S. Patent 2,491,683, Munday et al., December 20, 1949, discloses a lubricant composition consisting of a major proportion of waxy mineral lubricating oil having dissolved therein about 0.07 to 0.20 % of a wax-naphthalene pour depressor (the condensation product of 100 parts chlorinated paraffin wax with naphthalene) and 0.05 to 0.25% of a polymerization product (e.g. a copolymer) of fumaric acid esters of mixed alcohols obtained by hydrogenation of coconut oil. Small amounts of the additive mixture give better results in depressing pour point than do either component individually.

U.S. Patent 3,475,321, Henselman et al., October 28, 1969, discloses solvent dewaxing using a synergistic dewaxing aid of a mixture of vinyl ester polymer and chlorinated wax-naphthalene Friedel-Crafts condensation product. The condensation product is prepared by the reaction of a halogenated paraffin with an aromatic hydrocarbon. The halogenated paraffin may, for example, contain from about 8 to about 60 carbon atoms. The aromatic hydrocarbon is preferably naphthalene. The vinyl ester polymer contains long chain vinyl esters monomers, e.g. containing substantially linear alkyl side chains of at least 11 carbon atoms.

U.S. Patent 4,439,308, Gudelis et al., March 27, 1984, discloses a process for solvent dewaxing of bright stock waxy raffinate oil. The dewaxing aid is a mixture of poly di-alkyl fumarate/vinyl acetate copolymers and a wax-naphthalene condensate. The condensate has a molecular weight of about 1,000 and greater.

The present invention provides a composition comprising (a) a polymer of (i) a hydrocarbyl ester of an ethylenically unsaturated acid of 3 to 6 carbon atoms, wherein the hydrocarbyl group contains about 8 to about 40 carbon atoms, (ii) an ester-containing monomer selected from the group consisting of alkyl esters of ethylenically unsaturated acids of 3 to 6 carbon atoms wherein the alkyl group contains fewer than 8 carbon atoms and vinyl alkanoates wherein the alkanoate group contains up to about 8 carbon atoms, and (iii) an alkyl ether monomer wherein the alkyl group contains up to about 8 carbon atoms; and

(b) a polynuclear aromatic material, substituted on at least one ring with at least one hydrocarbyl group having about 8 to about 20 carbon atoms and with at least one hydrocarbyl group having about 21 to about 40 carbon atoms, wherein the amounts of components (a) and (b) are such that the composition, when added to a paraffinic liquid, provides a reduction in the cloud point thereof.

The invention further provides a method for reducing the cloud point of a paraffinic liquid, comprising adding thereto an effective amount of such compositions; and further such compositions such additives in paraffinic liquids.

Various preferred features and embodiments of the invention will be described below by way of non-limiting illustration.

The first important component (a) of the present invention is a polymer of a hydrocarbyl ester of an ethylenically unsaturated acid. This is a polymer which has a substantially carbon chain backbone derivable from the addition polymerization of an ethylenically unsaturated acid and other comonomers, described below. The polymerized acid groups are at least partly and preferably substantially completely in the form of hydrocarbyl esters; reference herein to polymerization of acids is not intended to be limiting to the use of the actual acid in the polymerization reaction, but encompasses polymerization of esters and other materials which can be converted into esters, including anhydrides and acid halides.

The acids which are capable of polymerization are generally those ethylenically unsaturated acids having 3 to 6 carbon atoms, including those with α,β -ethylenic unsaturation. Specific materials include acrylic acid,

crotonic acid, methacrylic acid, ethacrylic acid, fumaric acid, maleic acid, itaconic acid, and citraconic acid and their reactive equivalents. The diacids are preferred, and of these fumaric acid is most preferred; the corresponding dialkyl ester is a dialkyl fumarate. It is understood that maleic acid and fumaric acid become substantially equivalent after they are polymerized, since their double bond becomes a single bond during the polymerization reaction. However, details of the stereochemistry of the resulting polymer may in some cases differ depending on whether maleic (cis) or fumaric (trans) monomer is used. In some instances it may be more convenient to use one material rather than the other; maleic acid, for example, can form a cyclic anhydride which can be polymerized as such, while fumaric acid cannot. Generally, however, references herein to polymers of fumaric acid or fumaric esters are intended to include polymers similarly derived from maleic acid, maleic anhydride, or maleic esters.

The polymer can be prepared directly from the ester of the acid, or it can be prepared from the acid itself or (in the case of certain diacids) the anhydride or other reactive monomers. If the polymer is prepared from one of the materials other than the ester it can be converted into the ester form by reaction of the polymer with a suitable alcohol or by other well-known reactions.

The alcohol with which the acid monomer or the polymeric acid functionality is reacted to form the ester is an alcohol with a hydrocarbyl chain containing 8 to 40 carbon atoms, more preferably 10 to 28 carbon atoms, and most preferably 12 to 14 carbon atoms. The hydrocarbyl group need not be derived from a single alcohol of a single chain length, however, but can be derived from a mixture of alcohols if desired, provided that at least some of the chain lengths of the alcohol portion are within the desired range. Moreover, the specific chain length of the hydrocarbyl groups can be selected to correspond to the type of paraffinic fluid in which the polymer is employed, as described in more detail below.

The polymer of component (a) also contains other monomers derived from ethylenically unsaturated compounds. These comonomers are, first, short chain ester-containing monomers. Examples of short chain ester-containing monomers include vinyl alkanoates where the alkanoate moiety contains up to 8 carbon atoms and preferably up to 4 carbon atoms, such as vinyl acetate, vinyl propionate, and vinyl butyrate. Other examples are short chain esters of unsaturated acids, having fewer than 8 carbon atoms, and preferably up to 4 carbon atoms in the alcohol-derived moiety. Such short chain esters include methyl acrylate, methyl methacrylate, ethyl acrylate, ethyl methacrylate, propyl acrylate or methacrylate, and n-butyl, t-butyl, and isobutyl acrylate or methacrylate. Secondly, the polymer of component (a) contains short chain alkyl ether comonomers, where the alkyl group has up to 8 carbon atoms and preferably up to 4 carbon atoms. Examples are the alkyl vinyl ethers such as ethyl vinyl ether, propyl vinyl ether, and the butyl vinyl ethers. Examples of suitable polymers include terpolymers of fumaric esters with vinyl acetate and ethyl vinyl ether, terpolymers of fumaric esters with vinyl propionate and propyl vinyl ether, terpolymers of fumaric esters with methyl acrylate and ethyl vinyl ether, and terpolymers of fumaric esters with n-butyl acrylate and propyl vinyl ether. Preferred polymers are terpolymers of fumaric esters with vinyl acetate and ethyl vinyl ether, the latter comonomers being in relative molar amounts of 1:9 to 9:1. Preferably each of the latter comonomers will comprise a minor portion of the polymer, typically 1 to 15 percent by weight and preferably 3 to 10 percent. Particularly preferred polymers are described in greater detail in U.S. Patent 3,250,715.

The polymer of component (a) may also contain other copolymerizable monomers such as the α -olefins, including ethylene, propylene, or styrene, as well as carbon monoxide or sulfur dioxide. The amount of these and other supplemental comonomers, if any, is preferably sufficiently low that the polymer substantially retains its character as a hydrocarbyl alkenoate polymer, modified by the presence of the above-defined comonomers.

The polymers of component (a) can be prepared by known methods. In a preferred case di-(C₁₂-C₁₄) fumarate is mixed with an appropriate amount of vinyl acetate and ethyl vinyl ether. The polymerization is carried out by mixing and heating the reactants with or without a solvent or diluent in the presence of a small amount of an initiator at a temperature of from 25°C to 150°C, preferably up to 100°C. Since the polymerization is exothermic, cooling may be required to maintain the reaction mixture at the desired temperature. It is often convenient to add one of the reactants to the other reactant or reactants over a period of time in order to control the rate of the reaction.

The polymerization can be carried out in the presence of a small amount of an initiator such as an organic peroxide or azo-bis-isobutyronitrile. Organic peroxides such as benzoyl peroxide are especially useful. Generally 0.01 to 1.5% of the initiator is used.

The reaction time will vary from 1 to 30 hours depending on the temperature, reactivity of the monomers, and other reaction conditions. The polymerization can be run continuously or batchwise. Details of such polymerizations are well known to those skilled in the art and are reported in greater detail in U.S. Patent 3,250,715.

The molecular weight of the resulting polymer will depend on a variety of factors under the control of the skilled operator, including concentrations of monomers and catalyst. The polymer of the present invention ordinarily has a weight average molecular weight of 3,000 to 300,000, generally 5,000 to 100,000, preferably

about 20,000.

The second important component (b) of the present invention is a compound with fused aromatic rings, that is, polynuclear aromatic compounds in which the aromatic rings share at least one side. The polynuclear aromatic compound is substituted on at least one such ring with at least one hydrocarbyl group having chain length defined below. Typical fused ring aromatic systems include naphthalene, with two rings, anthracene and phenanthrene, with three rings, and naphthacene, chrysene, triphenylene, and pyrene with four rings. Naphthalene is the preferred fused ring aromatic hydrocarbon.

The polynuclear aromatic compound is substituted on at least one ring by at least one hydrocarbyl group having 8 to 40 carbon atoms. The overall composition of component (b) is such that it contains a mixture of hydrocarbyl substituents of different lengths. The different hydrocarbyl substituent may appear on a single aromatic molecule or on different molecules within the mixture. Alternatively, component (b) can be a mixture of different types of molecules, some having one type of hydrocarbyl substitution, some having another, and some having mixed types of substitution on the same molecule.

The substitution of the material of component (b) comprises a fraction of relatively shorter chain hydrocarbyl groups, containing 8 to 20 carbon atoms, and a second fraction of relatively longer chain hydrocarbyl (or hydrocarbylene) groups, containing 21 to 40 carbon atoms. The longer chain groups are preferably derived from chlorinated hydrocarbons or are materials of similar structure although derived from precursors other than chlorinated hydrocarbons. Chlorinated hydrocarbons typically contain at least a fraction of molecules which are polychlorinated, which fraction can result in hydrocarbylene substitution on the aromatic molecules, that is, formation of hydrocarbylene linkages among aromatic nuclei. (As used herein, the term "hydrocarbyl" is to be construed to include hydrocarbylene). Formation of hydrocarbylene linkages increases the effective molecular weight of the molecules. In the preferred material at least a portion of the aromatic nuclei are so linked. The polyfunctional reactants which lead to hydrocarbylene groups and the linkage of aromatic moieties preferably contain at least about 14 carbon atoms, and more preferably at least about 22 carbon atoms. That is, preferably the polyfunctional reactants constitute the longer chain fraction of the hydrocarbyl substituents.

The relative weight ratios of the shorter chain hydrocarbyl substituents to the longer chain hydrocarbyl substituents are preferably 10:1 to 1:1, and more preferably 5:1 to 3:1.

The hydrocarbyl group or groups are preferably alkyl (or alkylene) groups. Alkyl or alkylene groups can be attached to an aromatic ring by any of a variety of methods, the commonest being known as the Friedel-Crafts reaction. A chlorinated alkane or a chlorinated wax, for example, can be condensed with the aromatic ring in the presence of an appropriate amount of inert solvent, using a small amount of a catalyst such as aluminum chloride. A chlorinated material with a single chlorine atom will provide an alkyl chain; a material with multiple chlorine atoms will provide alkylene substitution and linkage of multiple aromatic rings into an oligomeric or polymeric structure. Alternatively, the starting material can be an olefin which is reacted with aluminum chloride in situ. The reaction can be started at room temperature and, after the catalyst and reactants have all been mixed, the reaction mixture can be heated to a final temperature of 30 to 100°C. After the reaction has been completed (generally requiring 1/2 hour to 10 hours) residual catalyst can be hydrolyzed by adding water and base and the catalyst removed by an appropriate method such as filtration or washing with water. The product can be purified if desired by known methods, although this may not be necessary.

In a preferred embodiment, an alkylation of naphthalene is conducted using a chlorinated alkane having a molecular weight of about 242, that is, having a carbon chain length of about 24, followed by a commercial mixture of C₁₆ to C₁₈ α -olefins. The product is naphthalene having mixed 16-18 and about 24 carbon alkyl substitution and is believed to be a mixture of mono- and poly-alkylated materials. It is further believed that the product also contains a fraction of material with naphthalene nuclei which are bridged by alkylene chains derived from alkylation of the naphthalene by di- or polychlorinated alkanes. Such bridged materials may be considered polymeric materials, the term being interpreted broadly to include oligomeric materials containing e.g. 2 or 3 or several aromatic groups as well as structures with higher molecular weights. Such materials are included within the definition of hydrocarbyl-substituted aromatic compounds, and in such cases the hydrocarbyl substituents are to be construed to contain the number of carbon atoms contained in the chlorinated alkane, that is, discounting the effects of the polymerization.

The relative amounts of components (a) and (b) are such that the combination, when added to a paraffinic liquid, provides a reduction in the cloud point of the liquid. In practice it has been found preferable in some cases to use a modest excess of the hydrocarbyl-substituted aromatic compound. Thus generally components (a) and (b) are used in relative amounts of 90:10 to 5:95 by weight; preferably the relative amounts of components (a) and (b) are 80:20 to 10:90, and most preferably the relative amounts are 50:50 to 20:80.

Components (a) and (b) (and any further optional components, described below) can be combined by any convenient means, or they can be added separately to a paraffinic liquid. Combining of the components can be effected by blending at ambient temperatures with moderate mixing for 10 minutes to 2 hours, typically about

30 minutes. Gentle heating, to e.g. 50-80°C (preferably about 65°C) often improves the ease of mixing.

Components (a) and (b) are added to a paraffinic liquid and serve to reduce its cloud point. Paraffinic liquids include refined and unrefined petroleum, including condensate crude oils (oils obtained from gas wells, comprising predominantly low molecular weight materials with a high molecular weight fraction). Crude petroleum contains a wide variety of components, in particular alkanes having up to about 28 carbon atoms and above. Among the fractions derived from crude oil by distillation are middle distillates, loosely characterized by normal boiling points of 177-454°C (350-850°F), and diesel fuels, loosely characterized by normal boiling points of 177-343°C (350-650°F). These boiling points correspond roughly to those of alkanes in the C₁₂ to C₁₈ range for middle distillates and the C₁₂ to C₁₆ range for diesel fuels.

The present invention is also applicable to lighter distillation cuts including gasoline or naphtha, as well as to synthetic oils which have a paraffinic component. Such synthetic oils include those made by polymerization of olefins or other unsaturated aliphatic olefins. The invention is applicable to paraffinic liquids which can be used as lubricants, as fuels, as functional fluids (including hydraulic fluids), or for any other use.

The chain lengths of the substituents of components (a) and (b) are preferably selected to correspond, at least approximately, to the length of the carbon chains in the paraffinic liquid. That is, when the composition is used as a cloud point depressant in a diesel fuel, the hydrocarbyl or alkyl groups in the alcoholic-derived moiety of the ester group preferably contain 10 to 16, and more preferably 12 to 14 carbon atoms. When the composition is used in other middle range distillates, the alcohol-derived moieties can preferably contain 12 to 20, and more preferably 14 to 18 carbon atoms. For higher boiling fractions, the alcohol-derived moieties can contain 18 to 28 carbon atoms. The hydrocarbyl or alkyl groups on the polynuclear aromatic material can be similarly selected. Suitable selection of hydrocarbyl chain length provides optimum solubility and compatibility properties.

The amount of the total additive composition (a) plus (b) is an amount sufficient to cause a reduction of the cloud point of the paraffinic liquid to which it is added. Often this amount is 50 to 2000 parts per million, preferably 100 to 600 parts per million (i.e. 0.01 to 0.6 percent by weight of the composition).

Components (a) and (b) can also be used in the form of a concentrate in a diluent oil or other suitable medium. When this is the case the absolute amounts of the individual component will be much higher than their concentration in the final composition. Typically a concentrate will contain up to 50% or more by weight of a diluent oil. Calculation of the appropriate concentrations of active ingredients in a concentrate for any given application is well within the abilities of those skilled in the art.

Other customary additives can also be present in the compositions of the present invention. When the composition is used as a fuel or a lubricant it can contain such materials as octane improvers, cetane improvers, antioxidants such as 2,6-di-tertiary-butyl-4-methylphenol, rust inhibitors such as alkylated succinic acids and anhydrides, bacteriostatic agents, gum inhibitors, metal deactivators, and dispersants such as esters of a mono- or polyol and a high molecular weight mono- or polycarboxylic acid acylating agent, especially those containing at least 30 carbon atoms in the acyl moiety. Other additives which can be present include detergents, antiwear agents, extreme pressure agents, emulsifiers, demulsifiers, friction modifiers, and dyes.

Although the compositions of the present invention have been discussed and described principally as cloud point depressant, they are also themselves effective as pour point depressants. Thus the addition of an effective amount of the combination of components (a) and (b) will not only reduce the cloud point of a paraffinic liquid, but will normally also reduce the pour point. This further increases the utility of the present compositions, since they can be used not only to inhibit the onset of paraffin crystal formation, but also to retard the general solidification of the liquid.

It is preferred, however, that, along with the combination of components (a) and (b) and any optional customary ingredients, there is also present an effective amount of an (additional) polymeric pour point depressant. The combination of the present additives with certain supplemental pour point depressants exhibit especially superior properties of pour point reduction. Materials which are useful as pour point depressants are well known and include such materials as alkyl acrylate polymers, alkyl methacrylate polymers, esters of olefin-maleic anhydride polymers (including esters of ethylene/maleic anhydride copolymers and styrene/maleic anhydride copolymers), and in particular ethylene vinyl acetate (EVA) copolymers.

EVA copolymers are well known materials, typically made by free-radial polymerization of vinyl acetate and ethylene, optionally with other comonomers. Preferred materials for use in the present invention are binary copolymers which contain 15 to 40 weight percent, and more preferably 33 to 38 weight percent copolymerized vinyl acetate. The number average molecular weight of the supplemental polymeric pour point depressant is not particularly critical but for EVA copolymers is preferably 1000 to 10,000, more preferably 1500 to 2600.

The desirable amount of the supplemental polymeric pour point depressant is that amount which will produce the desired reduction in pour point and will vary with the chemical nature of the polymer and of the paraffinic liquid in which it is to be employed. Effective amounts are typically 0.1 to 10 times the amount of the

total of components (a) and (b), and preferably 0.5 to 2 times the amount. In a more absolute sense the amount of the supplemental polymeric pour point depressant typically comprises 100 to 2000 parts per million by weight of the final composition, preferably 200 to 400 parts per million. This supplemental material can also be present in a concentrate along with components (a) and (b) and other additives, if any; if this is the case the absolute amount of the material will be adjusted accordingly.

Each of the materials used in the present invention may be available as the pure chemical or may be present as a concentrate with a diluent such as mineral oil. The choice of form of the constituent materials is generally irrelevant to the present invention, so long as the amount of diluent is taken into consideration in selecting the amount of active agent employed.

As used herein, the term "hydrocarbyl substituent" or "hydrocarbyl group" is used in its ordinary sense, which is well-known to those skilled in the art. Specifically, it refers to a group having a carbon atom directly attached to the remainder of the molecule and having predominantly hydrocarbon character. Such groups include hydrocarbon groups, substituted hydrocarbon groups, and hetero groups, that is, groups which, while primarily hydrocarbon in character, contain atoms other than carbon present in a chain or ring otherwise composed of carbon atoms.

EXAMPLES

Examples 1-10. Compositions are prepared of a standard diesel fuel (Amoco™ Whiting base fuel) containing various amounts of the composition of the present invention and, for comparison, no additive. The additive representative of the present invention is a mixture of a C₁₂₋₁₄ fumarate/vinyl acetate/ethyl vinyl ether copolymer (5.5% vinyl acetate moiety content and 3.1% ethyl vinyl ether content, by weight, weight average molecular weight about 20,000) and an alkylated naphthalene, in the parts by weight indicated. The alkylated naphthalene is substituted by a mixture of alkyl and alkylene groups and is prepared by alkylation of 1 part of naphthalene first with 1.9 parts by weight of a chlorinated hydrocarbon mixture having on average about 24 carbon atoms per molecule and having on average about 2 chlorine atoms per hydrocarbon chain, and thereafter with 7.4 parts by weight of a mixture of C₁₆-C₁₈ olefins, using 0.2 parts by weight AlCl₃ catalyst. Some of the listed components are available as concentrates containing a certain amount (up to 37%) of diluent oil. The compositions are reported in Table I on an active chemical basis (i.e. excluding the diluent oil) and are tested by the procedure of ASTM D 2500 "Cloud point of petroleum oils." Results of the test are reported to the nearest 3°C, the temperature reported being the lowest temperature at which the sample is clear; at a temperature 3° colder, crystal formation is observed:

TABLE I

Ex.	Fumarate copolymer ppm	Alkylated naphthalene, ppm	Cloud point, °C
1	0	0	-12,
			-15
2	63	150	-18
3	76	180	-18
4	101	240	-18
5	126	300	-18
6	189	450	-18
7	252	600	-18
8	97	96	-18
9	194	192	-18
10	630	500	-15

Examples 11-28. Examples 1-10 are substantially repeated in a diesel fuel from Star Enterprise. The concentrations and results are shown in Table II:

TABLE II

Ex.	Fumarate copolymer ppm	alkylated naphthalene, ppm	Cloud point, °C
11	0	0	-6
12	630	1000	-9
13	630	1000	-9
14	756	1000	-9
15	882	1000	-9
16	1008	1000	-9
17	630	800	-9
18	630	600	-9
19	194	192	-6
20	388	385	-9
21	582	577	-6
22	776	769	-9
23	970	962	-9
24	1164	1154	-9
25	1552	1538	-9
26	1940	1923	-9
27	252	600	-9
28	126	300	-9

Example 29. The above procedure is repeated in a diesel fuel designated DDR-490, which has a cloud point of -6°C. (a) Addition of 386 to 773 ppm of the additive combination of Example 8 reduces the cloud point to -9°C. (b) Addition of 213 to 639 ppm of the additive combination of Example 2 does not lead to a measurable change in cloud point at a measurement interval of 3C°. More precise measurements, made using an interval of less than 3C° or using a differential scanning calorimetry method, will detect the reduction in cloud point.

Examples 30-33. The oil of Example 1 is treated with the following materials, defined as for Example 2, and the cloud point is determined:

TABLE III

Ex.	Fumarate copolymer, ppm	Alkylated naphthalene, ppm
30	15	35
31	45	105
32	1800	200
33	200	1900

Example 34. Example 33 is repeated except that the alkylated naphthalene is replaced in turn by a corresponding amount of the following materials:

- naphthalene, mono- and di-alkylated by a mixture of C-12 alkyl groups and C-22 to C-30 alkyl and alkylene groups.
- naphthalene, predominantly monoalkylated by a mixture of C-10 and C-30 alkyl groups.

c. 1-nonylanthracene, reacted with chlorinated C-24 paraffin wax.

Example 35. Example 33 is repeated except that the fumarate copolymer is replaced in turn by a corresponding amount of the following materials:

- a. a C₁₂₋₁₄ alkyl fumarate/vinyl acetate/ethyl vinyl ether/ethylene tetrapolymer (5.5% vinyl acetate moiety content, 3.1% ethyl vinyl ether content, and 2% ethylene moiety content, by weight), weight average molecular weight about 4000.
- b. a polymer of (di-(C₁₂ to C₁₄ alkyl)) fumarate, n-butyl acrylate, and propyl vinyl ether, in relative weight percentages of 96.5%, 1.5%, and 2%, weight average molecular weight 8,000.
- c. methyl acrylate/vinyl acetate/ethyl vinyl ether/di(C₁₆ to C₁₈ alkyl)fumarate tetrapolymer, having about 10 percent by weight copolymerized methyl acrylate, 2 percent by weight vinyl acetate, and 1 percent by weight ethyl vinyl ether, weight average molecular weight 60,000. In a separate example, this additive composition is added to a middle distillate of predominantly C-14 - C-20 hydrocarbons.

Example 36. A composition is prepared of 60 parts of the alkylated naphthalene and 40 parts of the alkyl fumarate/vinyl acetate/ethyl vinyl ether copolymer of claim 1. To the diesel oil of Example 1 is added a total of 213 parts per million of the above alkylated naphthalene/fumarate composition and 125 parts per million of an ethylene vinyl acetate copolymer (33.5 weight percent vinyl acetate monomer, number average molecular weight 1900 - 2500).

Example 37. Example 36 is repeated except that the amount of the alkylated naphthalene/fumarate composition is 426 parts per million and the amount of the EVA copolymer is 250 parts per million.

Each of the documents referred to above is incorporated herein by reference. Except in the Examples, or where otherwise explicitly indicated, all numerical quantities in this description specifying amounts of materials, reaction conditions, molecular weights, number of carbon atoms, and the like, are to be understood as modified by the word "about." Unless otherwise indicated, each chemical or composition referred to herein should be interpreted as being a commercial grade material which may contain the isomers, by-products, derivatives, and other such materials which are normally understood to be present in the commercial grade. However, the amount of each chemical component is presented exclusive of any solvent or diluent oil which may be customarily present in the commercial material, unless otherwise indicated. As used herein, the expression "consisting essentially of" permits the inclusion of substances which do not materially affect the basic and novel characteristics of the composition under consideration.

Claims

1. A composition comprising:
 - (a) a polymer of:
 - (i) a hydrocarbyl ester of an ethylenically unsaturated acid of 3 to 6 carbon atoms, wherein the hydrocarbyl group contains 8 to 40 carbon atoms,
 - (ii) an ester-containing monomer selected from the group consisting of alkyl esters of ethylenically unsaturated acids of 3 to 6 carbon atoms wherein the alkyl group contains fewer than 8 carbon atoms and vinyl alkanoates wherein the alkanoate group contains up to 8 carbon atoms, and
 - (iii) an alkyl ether monomer wherein the alkyl group contains up to 8 carbon atoms; and
 - (b) a polynuclear aromatic material, substituted on at least one ring with at least one hydrocarbyl group having 8 to 20 carbon atoms and with at least one hydrocarbyl group having 21 to 40 carbon atoms, wherein the amounts of components (a) and (b) are such that the composition, when added to a paraffinic liquid, provides a reduction in the cloud point thereof.
2. The composition of claim 1 wherein the polymer of (a) comprises 1 to 15 percent by weight of the ester-containing monomer (ii) and 1 to 15 percent by weight of the alkyl ether monomer (iii).
3. The composition of claim 1 or claim 2 wherein the polymer is a polymer of a dialkyl fumarate or a dialkyl maleate, a vinyl alkanoate, and an alkyl vinyl ether.
4. The composition of any preceding claim wherein the weight ratio of the hydrocarbyl groups in (b) of 8 to 20 carbon atoms to the hydrocarbyl groups of 21 to 40 carbon atoms is 10:1 to 1:1.
5. The composition of any preceding claim wherein the polynuclear aromatic hydrocarbon is naphthalene.
6. The composition of claim 5 wherein the substitution on the naphthalene component comprises at least

in part alkylene groups of at least 14 carbons atoms, which alkylene groups link at least a portion of the naphthalene moieties into a polymeric structure.

- 5 7. The composition of any preceding claim wherein components (a) and (b) are present in relative amounts of 90:10 to 5:95 by weight.
8. The composition of any preceding claim further comprising a pour point depressant in an amount sufficient to reduce the pour point of a paraffinic liquid.
- 10 9. The composition of any preceding claim further comprising a concentrate-forming amount of an organic hydrocarbon liquid.
10. A composition of a paraffinic liquid and an amount of the composition of any preceding claim sufficient to reduce the cloud point of said paraffinic liquid.
- 15 11. The composition of claim 10 wherein the total amount of (a) and (b) is 50 to 2000 parts per million.
12. The composition of claim 10 or claim 11 further comprising an amount of an ethylene/vinyl acetate copolymer sufficient to reduce the pour point of the composition.
- 20 13. A process for reducing the cloud point of a paraffinic liquid, comprising adding thereto an effective amount of a combination of:
 - (a) a polymer of (i) a hydrocarbyl ester of an ethylenically unsaturated acid of 3 to 6 carbon atoms, wherein the hydrocarbyl group contains 8 to 40 carbon atoms, (ii) ester-containing monomers selected from the group consisting of alkyl esters of ethylenically unsaturated acids of 3 to 6 carbon atoms where-
25 in the alkyl group contains fewer than 8 carbon atoms and vinyl alkanoates wherein the alkanoate group contains up to 8 carbon atoms, and (iii) alkyl ether monomers wherein the alkyl group contains up to 8 carbon atoms; and
 - (b) a polynuclear aromatic material, substituted on at least one ring with at least one hydrocarbyl group having 8 to 20 carbon atoms and with at least one hydrocarbyl group having 22 to 40 carbon atoms.

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