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(54) Title: POUR POINT DEPRESSANT ADDITIVES FOR OIL COMPOSITIONS

(57) Abstract: The present invention generally relates to oil compositions, primarily to fuel oil and petroleum compositions produced there from susceptible to wax formation at low temperatures, to polymeric amides for use with such fuel oil compositions, and to methods for their manufacture.



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Pour Point Depressant Additives for Oil Compositions

Field of the Invention

- 5 The present invention generally relates to polymeric amides useful as pour point depressants and their use in providing oils with improved low temperature flow properties.

Background of the Invention

- 10 The present invention generally relates to oil compositions, primarily to fuel oil and petroleum compositions produced therefrom susceptible to wax formation at low temperatures, to polymeric amides for use with such fuel oil compositions, and to methods for their manufacture.

- 15 Fuel oils and/or petroleum products, whether derived from petroleum or vegetable sources, contain components, e.g., paraffins, alkanes, etc. that at low temperature tend to precipitate as large crystals or spherulites of wax in such a way as to form a gel structure which causes the oil to lose its ability to flow. The lowest temperature at which the fuel will still flow is known as the pour point.

20

- As the temperature of the fuel falls and approaches the pour point, difficulties arise in transporting the fuel through lines and pumps. Further, the wax crystals tend to plug fuel lines, screens, and filters at temperatures above the pour point. These problems are well recognized in the art, and various additives have been proposed, many of which are in commercial use, for depressing the pour point of fuel oils. Similarly, other additives have been proposed and are in commercial use for reducing the size and changing the shape of the wax crystals that do form. Smaller size crystals are desirable since they are less likely to clog a filter. The wax from a diesel fuel, which is primarily an alkane wax, crystallizes as platelets; certain

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additives inhibit this and cause the wax to adopt an acicular habit, the resulting needles being more likely to pass through a filter than are platelets. The additives may also suspend in the fuel the crystals that have formed, the resulting reduced settling also assisting in prevention of blockages.

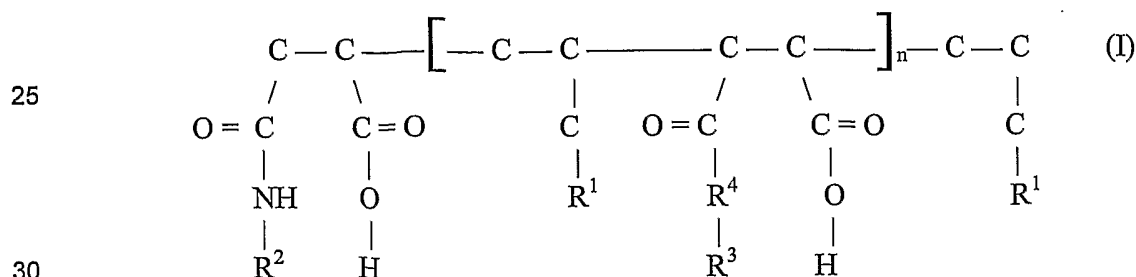
Effective wax crystal modification (as measured by cold filter plugging point (CFPP), (ASTM D97-66) and other operability tests, as well as simulated and field performance are known in the art. However, there is a continual need in the art to produce more effective polymers giving improved performance.

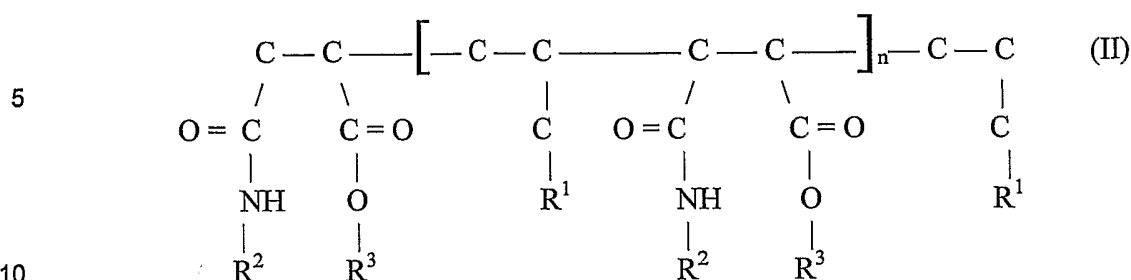
Surprisingly, the present inventors have found more effective and economical additives. In particular, applicant has found that certain polymeric amides can effectively and economically be employed as pour point depressants for various grades of crude and fuel oil.

Summary of the Invention

The present invention generally relates to an oil composition having improved low temperature properties comprising oil and an effective amount of a pour point depressant additive composition that comprises at least one pour point depressant additive of formula

(I) or (II):





wherein R^1 , R^2 and R^3 are independently selected from hydrocarbyl groups containing up to 50 carbon atoms, R^4 is selected from NH or O, and n is an integer of from 0 to 50.

The invention also relates to a pour point depressant additive composition, a pour point depressant additive concentrate composition and a method of improving the low temperature flow properties of a composition that comprises in major part at least one oil, said method comprising admixture of the composition comprising said at least one oil with an effective amount of the aforementioned pour point depressant additive and/or additive concentrate.

Detailed Description of the Invention

The present invention generally relates to a pour point depressant additive composition that comprises at least one polymeric amide as hereinafter described.

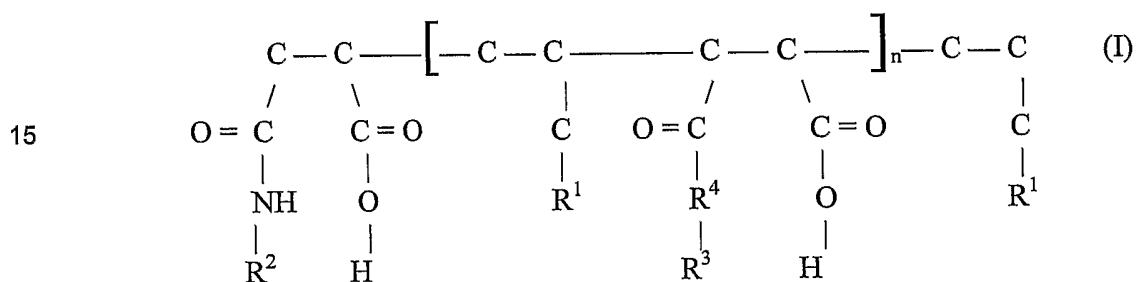
In a second aspect, this invention relates to a pour point depressant additive concentrate composition comprising the aforementioned pour point depressant additive and a compatible solvent thereof.

In a third aspect, the invention provides an oil composition with improved low temperature flow properties comprising oil and a amount of the aforementioned pour point depressant additive and/or additive concentrate.

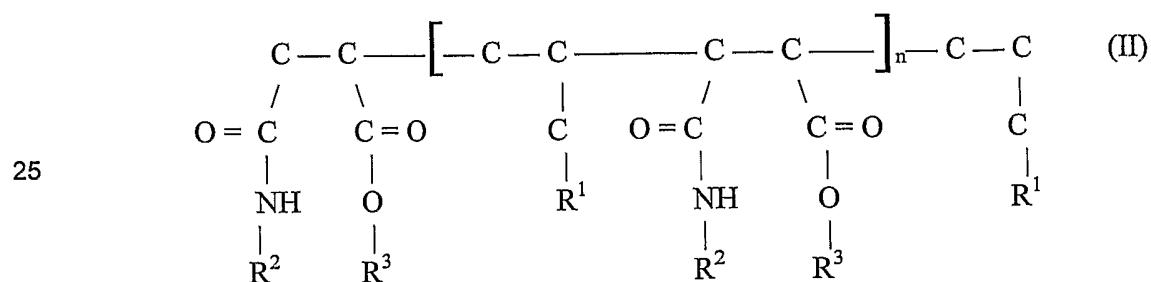
- 5 In a fourth embodiment the invention relates to a method of improving the low temperature flow properties of a composition that comprises in major part at least one oil, said method comprising admixture of the composition comprising said at least one oil with an effective amount of the aforementioned pour point depressant additive and/or additive concentrate.

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The pour point depressant additive of the present invention comprises at least one polymeric amide of General Formulae I or II:



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wherein R^1 , R^2 and R^3 are independently selected from hydrocarbyl groups containing up to 50 carbon atoms, R^4 is selected from NH or O and n is an integer of from 0 to 50.

As used herein the term "hydrocarbyl" refers to a group having a carbon atom directly attached to the rest of the molecule and having a hydrocarbon or predominantly hydrocarbon character. Among these, there may be mentioned hydrocarbon groups, including aliphatic, (e.g., alkyl), alicyclic (e.g., cycloalkyl),
5 aromatic, aliphatic and alicyclic-substituted aromatic, and aromatic-substituted aliphatic and alicyclic groups. Aliphatic groups can be saturated or unsaturated. These groups may contain non-hydrocarbon substituents provided their presence does not alter the predominantly hydrocarbon character of the group. Examples include keto, halo, hydroxy, nitro, cyano, alkoxy and acyl. If the hydrocarbyl group
10 is substituted, a single (mono) substituent is preferred. Examples of substituted hydrocarbyl groups include 2-hydroxyethyl, 3-hydroxypropyl, 4-hydroxybutyl, 2-ketopropyl, ethoxyethyl, and propoxypropyl. The groups may also or alternatively contain atoms other than carbon in a chain or ring otherwise composed of carbon atoms. Suitable hetero atoms include, for example, nitrogen, sulphur, and,
15 preferably, oxygen. Advantageously, the hydrocarbyl group contains at most 36, preferably at most 15, more preferably at most 10 and most preferably at most 8, carbon atoms.

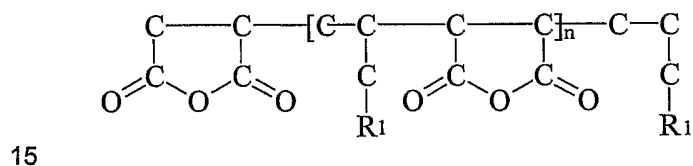
In one embodiment R^1 is a C_6 - C_{40} saturated or unsaturated substituted or
20 unsubstituted alkyl group; R^2 is a C_6 - C_{30} saturated or unsaturated substituted or unsubstituted alkyl group; and n is an integer of from 1-30. In another embodiment R^1 is a C_8 - C_{24} saturated or unsaturated substituted or unsubstituted alkyl group; R^2 is a C_8 - C_{24} saturated or unsaturated substituted or unsubstituted alkyl group; and n is an integer of from 1-20. In still another embodiment R^1 is a C_{12} - C_{22} saturated or
25 unsaturated substituted alkyl group; R^2 is a C_{12} - C_{22} saturated or unsaturated substituted or unsubstituted alkyl group; and n is an integer of from 1-10.

The products of the present invention are generally prepared by reacting an (a) alpha olefin with (b) maleic anhydride in the presence of a free radical initiator such

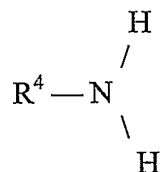
as, for example, tert-butyl peroxybenzoate (other free radical initiators useful in the context of the present invention are known to those skilled in the art) in order to form (c) a high molecular weight copolymer. This copolymer is then reacted with an (d) amine optionally in the presence of an alcohol, glycol, or a compound that yields an alcohol or glycol in situ (for example an epoxide) in order to form the compound of formula (I).

It is understood that any alpha olefin of varying carbon chain length can be employed in order to make the products of the invention. In one embodiment the a) alpha olefin is a C₆ - C₂₄ alpha olefin; in another embodiment it is a C₁₂-C₂₄ alpha olefin and still another it is a C₂₀-C₂₄ alpha olefin.

In one embodiment the high molecular weight copolymer is of the formula:



The amines employable in the reaction with the high molecular weight copolymer can be any amine commercially available that reacts with such copolymer, including but not limited to primary, secondary and tertiary amines. Preferably, the amine is of the formula:



where R^4 is an alkylene group of from 6 to 30 carbon atoms. Nonlimiting examples of amines suitable for use include but are not limited to tallowamine, hydrogenated tallowamine, cocoamine, soyamine, oleylamine, octadecylamine, hexadecylamine, dodecylamine, 2-ethylhexylamine, dicocoamine, ditallowamine, dehydrogenated
 5 tallowamine, didecylamine, dioctadecylamine, N-coco-1,3-diaminopropane, N-tallow-1,3-diaminopropane, N,N,N-trimethyl-N-tallow-1,3-diaminopropane, N-oleyl-1,3-diaminopropane, N,N,N-trimethyl-N-9-octadecenyl-1,3-diaminopropane, 3-tallowalkyl-1,3-hexahydropyrimidine and mixtures thereof.

10 The reaction of the high molecular weight copolymer and amine is generally conducted in the presence of at least one alcohol and/or glycol and/or a substance that yields an alcohol and/or glycol in situ, for example, an epoxide. Alcohols and/or glycols generally contain from 1 up to 50 carbon atoms. In one embodiment of the invention, alcohols/glycols that can usefully be employed include, but are not
 15 limited to methanol, ethanol, propanol, isopropanol, butanol, isobutanol $C_{10} - C_{20+}$ alcohol blends, $C_{12} - C_{36}$ Guerbet alcohols, Behenyl alcohols and mixtures thereof.

The polymer may be made by any of the methods known in the art, e.g., by solution polymerization with free radical initiation, or by high pressure
 20 polymerization, conveniently carried out in an autoclave or a tubular reactor.

Advantageously, polymerization is effected in the following manner. In order to prepare the amide of structure (I), the alcohol is mixed with the amine at any molar ratio to form a mixture of amide and ester. The amount of attachment may vary
 25 from 0.1 to 1.0 moles of combined alcohol and amine for each mole of maleic anhydride employed. These half ester structures are then made by mixing the high molecular weight copolymer with amine/alcohol mixture. This mixture is normally heated to 100-200° C to form the half ester. As an example, one could react 0.5 moles of tallowamine and 0.5 moles of behenyl alcohol for each mole of maleic

anhydride in order to get the polymer of formula (I). In one embodiment, examples of preferred amides that can be usefully employed in the context of the present invention include, but are not limited to amides derived from the reaction of at least one of the following amines with maleic anhydride: tallowamine, hydrogenated
5 tallowamine, cocoamine, soyamine, oleylamine, octadecylamine, hexadecylamine, dodecylamine, 2-ethylhexylamine, dicocoamine, ditallowamine, dehydrogenated tallowamine, didecylamine, dioctadecylamine, N-coco-1,3-diaminopropane, N-tallow-1,3-diaminopropane, N,N,N-trimethyl-N-tallow-1,3-diaminopropane, N-oleyl-1,3-diaminopropane, N,N,N-trimethyl-N-9-octadecenyl-1,3-diaminopropane, 3-
10 tallowalkyl-1,3-hexahydropyrimidine and mixtures thereof.

In order to prepare the amide ester of formula (II), the alcohol is mixed with the amines at any alcohol/amine ratio to form a mixture of amide + ester. The amount of attachment may vary from 0.1 to 2.0 moles of combined alcohol and amine for
15 each mole of maleic anhydride employed. The full ester structure is then made by reacting the copolymer with the amine/alcohol which can be run at any water-producing temperature with or without solvent. Some imide may also be formed by this process. In one embodiment, examples of preferred amides + esters that can be usefully employed in the context of the present invention include, but are not
20 limited to amides + esters derived from the reaction maleic anhydride with at least one of the following amines: tallowamine, hydrogenated tallowamine, cocoamine, soyamine, oleylamine, octadecylamine, hexadecylamine, dodecylamine, 2-ethylhexylamine, dicocoamine, ditallowamine, dehydrogenated tallowamine, didecylamine, dioctadecylamine, N-coco-1,3-diaminopropane, N-tallow-1,3-
25 diaminopropane, N,N,N-trimethyl-N-tallow-1,3-diaminopropane, N-oleyl-1,3-diaminopropane, N,N,N-trimethyl-N-9-octadecenyl-1,3-diaminopropane, 3-tallowalkyl-1,3-hexahydropyrimidine and mixtures thereof in combination with the alcohols: methanol, ethanol, propanol, isopropanol, butanol, isobutanol C₁₀ - C₂₀+ alcohol blends, C₁₂ -C₃₆ Guerbet alcohols, Behenyl alcohols and mixtures thereof.

As indicated above, the polymeric amides of the invention may contain a mixture of different species. It is also within the scope of the invention to provide a composition comprising a mixture of two or more of said polymers.

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The pour point depressant additive of the present invention is especially useful in crude and/or fuel oils having a relatively high wax content, e.g., a wax content of 0.1 to 20% by weight per weight of fuel, preferably 3.0 to 4.5, such as 3.5 to 4.5% wt, measured at 10° C. below wax appearance temperature (WAT).

10

The polymer is preferably soluble in the oil to the extent of at least 10,000 ppm by weight per weight of oil at ambient temperature. However, at least some of the additive may come out of solution near the cloud point of the oil and function to modify the wax crystals that form.

15

The pour point depressant additive of the present invention can be employed alone, or it may be combined with other additives for improving low temperature flowability and/or other properties, which are in use in the art or known from the literature. The pour point depressant additive composition may also comprise additional cold flow improvers, including but not limited to comb polymers, polar nitrogen compounds, compounds containing a cyclic ring system, hydrocarbon polymer, polyoxyalkylene compounds, mixtures thereof and the like.

20

Comb polymers - are polymers in which branches containing hydrocarbyl groups are pendant from a polymer backbone, and are discussed in "Comb-Like Polymers. Structure and Properties", N. A. Plate and V. P. Shibaev, J. Poly. Sci. Macromolecular Revs., 8, p 117 to 253 (1974), which is incorporated herein by reference.

25

Generally, comb polymers have one or more long chain hydrocarbyl branches, e.g., oxyhydrocarbyl branches, normally having from 10 to 30 carbon atoms, pendant from a polymer backbone, said branches being bonded directly or indirectly to the backbone. Examples of indirect bonding include bonding via
5 interposed atoms or groups, which bonding can include covalent and/or electrovalent bonding such as in a salt.

Advantageously, the comb polymer is a homopolymer or a copolymer having at least 25 and preferably at least 40, more preferably at least 50, molar per cent of
10 the units of which have side chains containing at least 6, and preferably at least 10, atoms.

These comb polymers may be copolymers of maleic anhydride or fumaric or itaconic acids and another ethylenically unsaturated monomer, e.g., an alpha-olefin, including styrene, or an unsaturated ester, for example, vinyl acetate or
15 homopolymer of fumaric or itaconic acids. It is preferred but not essential that equimolar amounts of the comonomers be used although molar proportions in the range of 2 to 1 and 1 to 2 are suitable. Examples of olefins that may be copolymerized with e.g., maleic anhydride, include 1-decene, 1-dodecene, 1-tetradecene, 1-hexadecene, and 1-octadecene.
20

The acid or anhydride group of the comb polymer may be esterified by any suitable technique and although preferred it is not essential that the maleic anhydride or fumaric acid be at least 50% esterified. Examples of alcohols which may be used
25 include n-decan-1-ol, n-dodecan-1-ol, n-tetradecan-1-ol, n-hexadecan-1-ol, and n-octadecan-1-ol. The alcohols may also include up to one methyl branch per chain, for example, 1-methylpentadecan-1-ol or 2-methyltridecan-1-ol. The alcohol may be a mixture of normal and single methyl branched alcohols. It is preferred to use pure alcohols rather than the commercially available alcohol mixtures but if mixtures are

used the R_{12} refers to the average number of carbon atoms in the alkyl group; if alcohols that contain a branch at the 1 or 2 positions are used R_{12} refers to the straight chain backbone segment of the alcohol.

- 5 These comb polymers may especially be fumarate or itaconate polymers and copolymers such for example as those described in EP-A-153176, -153177 and -225688, and WO 91/16407.

Particularly preferred fumarate comb polymers are copolymers of alkyl fumarates
10 and vinyl acetate, in which the alkyl groups have from 12 to 20 carbon atoms, more especially polymers in which the alkyl groups have 14 carbon atoms or in which the alkyl groups are a mixture of C_{14} / C_{16} alkyl groups, made, for example, by solution copolymerizing an equimolar mixture of fumaric acid and vinyl acetate and reacting the resulting copolymer with the alcohol or mixture of alcohols, which are
15 preferably straight chain alcohols. When the mixture is used it is advantageously a 1:1 by weight mixture of normal C_{14} and C_{16} alcohols. Furthermore, mixtures of the C_{14} ester with the mixed C_{14} / C_{16} ester may advantageously be used. In such mixtures, the ratio of C_{14} to C_{14} / C_{16} is advantageously in the range of from 1:1 to 4:1, preferably 2:1 to 7:2, and most preferably about 3:1, by weight. The
20 particularly preferred comb polymers are those having a number average molecular weight, as measured by vapor phase osmometry, of 1,000 to 100,000, more especially 1,000 to 30,000.

Other suitable comb polymers are the polymers and copolymers of alpha-olefins
25 and esterified copolymers of styrene and maleic anhydride, and esterified copolymers of styrene and fumaric acid; mixtures of two or more comb polymers may be used in accordance with the invention and, as indicated above, such use may be advantageous. Other examples of comb polymers are hydrocarbon polymers, e.g., copolymers of ethylene and at least one alpha-olefin, the alpha-

olefin preferably having at most 20 carbon atoms, examples being n-decene-1 and n-dodecene-1. Preferably, the number average molecular weight of such a copolymer is at least 30,000 measured by GPC. The hydrocarbon copolymers may be prepared by methods known in the art, for example using a Ziegler type catalyst.

Polar nitrogen compounds. Such compounds are oil-soluble polar nitrogen compounds carrying one or more, preferably two or more, substituents of the formula $>NR_{13}$, where R_{13} represents a hydrocarbyl group containing 8 to 40 atoms, which substituent or one or more of which substituents may be in the form of a cation derived therefrom. The oil soluble polar nitrogen compound is generally one capable of acting as a wax crystal growth inhibitor in fuels, it comprises for example one or more of the following compounds:

An amine salt and/or amide formed by reacting at least one molar proportion of a hydrocarbyl-substituted amine with a molar proportion of a hydrocarbyl acid having from 1 to 4 carboxylic acid groups or its anhydride, the substituent(s) of formula $>NR_{13}$ being of the formula $--NR_{13}R_{14}$ where R_{13} is defined as above and R_{14} represents hydrogen or R_{13} , provided that R_{13} and R_{14} may be the same or different, said substituents constituting part of the amine salt and/or amide groups of the compound.

Ester/amides may be used, containing 30 to 300, preferably 50 to 150, total carbon atoms. These nitrogen compounds are described in U.S. Patent No. 4,211,534. Suitable amines are predominantly C_{12} to C_{40} primary, secondary, tertiary or quaternary amines or mixtures thereof but shorter chain amines may be used provided the resulting nitrogen compound is oil soluble, normally containing about 30 to 300 total carbon atoms. The nitrogen compound preferably contains at least one straight chain C_8 to C_{40} , preferably C_{14} to C_{24} , alkyl segment.

Suitable amines include primary, secondary, tertiary or quaternary, but are preferably secondary. Tertiary and quaternary amines only form amine salts. Examples of amines include tetradecylamine, cocoamine, and hydrogenated tallow amine. Examples of secondary amines include dioctadecyl amine and methylbehenyl amine. Amine mixtures are also suitable such as those derived from natural materials. A preferred amine is a secondary hydrogenated tallow amine, the alkyl groups of which are derived from hydrogenated tallow fat composed of approximately 4% C14, 31% C16, and 59% C18.

10

Examples of suitable carboxylic acids and their anhydrides for preparing the nitrogen compounds include ethylenediamine tetraacetic acid, and carboxylic acids based on cyclic skeletons, e.g., cyclohexane-1,2-dicarboxylic acid, cyclohexene-1,2-dicarboxylic acid, cyclopentane-1,2-dicarboxylic acid and naphthalene dicarboxylic acid, and 1,4-dicarboxylic acids including dialkyl spirobis lactones. Generally, these acids have about 5 to 13 carbon atoms in the cyclic moiety. Preferred acids useful in the present invention are benzene dicarboxylic acids e.g., phthalic acid, isophthalic acid, and terephthalic acid. Phthalic acid and its anhydride are particularly preferred. The particularly preferred compound is the amide-amine salt formed by reacting 1 molar portion of phthalic anhydride with 2 molar portions of dihydrogenated tallow amine. Another preferred compound is the diamide formed by dehydrating this amide-amine salt.

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Other examples are long chain alkyl or alkylene substituted dicarboxylic acid derivatives such as amine salts of monoamides of substituted succinic acids, examples of which are known in the art and described in U.S. Patent No. 4,147,520, for example, which is incorporated herein by reference. Suitable amines may be those described above.

25

Other examples are condensates, for example, those described in EP-A-327427.

Compounds containing a cyclic ring system- carrying at least two substituents of the general formula below on the ring system

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where A is a linear or branched chain aliphatic hydrocarbylene group optionally interrupted by one or more hetero atoms, and R_{15} and R_{16} are the same or different and each is independently a hydrocarbyl group containing 9 to 40 atoms optionally interrupted by one or more hetero atoms, the substituents being the same or different and the compound optionally being in the form of a salt thereof. Advantageously, A has from 1 to 20 carbon atoms and is preferably a methylene or polymethylene group. Such compounds are described in WO 93/04148.

15 Hydrocarbon polymer. Examples of suitable hydrocarbon polymers are those of the general formula



wherein $T=H$ or UR_{21} wherein $R_{21}=C_1$ to C_{40} hydrocarbyl, and $U=H$, T, or aryl and v and w represent mole fractions, v being within the range of from 1.0 to 0.0, w being in the range of from 0.0 to 1.0.

The hydrocarbon polymers may be made directly from monoethylenically unsaturated monomers or indirectly by hydrogenating polymers from polyunsaturated monomers, e.g., isoprene and butadiene. Examples of hydrocarbon polymers are disclosed in WO 91/11488.

Preferred copolymers are ethylene alpha-olefin copolymers, having a number average molecular weight of at least 30,000. Preferably the alpha-olefin has at most 28 carbon atoms. Examples of such olefins are propylene, n-butene,

isobutene, n-octene-1, isooctene-1, n-decene-1, and n-dodecene-1. The copolymer may also comprise small amounts, e.g., up to 10% by weight, of other copolymerizable monomers, for example olefins other than alpha-olefins, and non-conjugated dienes. The preferred copolymer is an ethylene-propylene copolymer.

5

The number average molecular weight of the ethylene alphaolefin copolymer is, as indicated above, preferably at least 30,000, as measured by gel permeation chromatography (GPC) relative to polystyrene standards, advantageously at least 60,000 and preferably at least 80,000. Functionally no upper limit arises but
10 difficulties of mixing result from increased viscosity at molecular weights above about 150,000, and preferred molecular weight ranges are from 60,000 and 80,000 to 120,000.

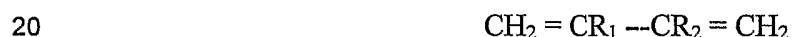
Advantageously, the copolymer has a molar ethylene content between 50 and 85
15 per cent. More advantageously, the ethylene content is within the range of from 57 to 80%, and preferably it is in the range from 58 to 73%; more preferably from 62 to 71%, and most preferably 65 to 70%.

Preferred ethylene alpha-olefin copolymers are ethylene-propylene copolymers
20 with a molar ethylene content of from 62 to 71% and a number average molecular weight in the range 60,000 to 120,000; especially preferred copolymers are ethylene-propylene copolymers with an ethylene content of from 62 to 71% and a molecular weight from 80,000 to 100,000.

25 The copolymers may be prepared by any of the methods known in the art, for example using a Ziegler type catalyst. The polymers should be substantially amorphous, since highly crystalline polymers are relatively insoluble in fuel oil at low temperatures.

- Other suitable hydrocarbon polymers include a low molecular weight ethylene-alpha-olefin copolymer, advantageously with a number average molecular weight of at most 7,500, advantageously from 1,000 to 6,000, and preferably from 2,000 to 5,000, as measured by vapor phase osmometry. Appropriate alpha-olefins are as given above, or styrene, with propylene again being preferred. Advantageously the ethylene content is from 60 to 77 molar per cent, although for ethylene-propylene copolymers up to 86 molar per cent by weight ethylene may be employed with advantage.
- 10 The hydrocarbon polymer may most preferably be an oil-soluble hydrogenated block diene polymer, comprising at least one crystallizable block, obtainable by end-to-end polymerization of a linear diene, and at least one non-crystallizable block, the non-crystallizable block being obtainable by 1,2-configuration polymerization of a linear diene, by polymerization of a branched diene, or by a mixture of such polymerizations.

Advantageously, the block copolymer before hydrogenation comprises units derived from butadiene only, or from butadiene and at least one comonomer of the formula



- wherein R_1 represents a C_1 to C_8 alkyl group and R_2 represents hydrogen or a C_1 to C_8 alkyl group. Advantageously the total number of carbon atoms in the comonomer is 5 to 8, and the comonomer is advantageously isoprene.
- 25 Advantageously, the copolymer contains at least 10% by weight of units derived from butadiene.

In general, the crystallizable block or blocks will be the hydrogenation product of the unit resulting from predominantly 1,4- or end-to-end polymerization of

butadiene, while the non-crystallizable block or blocks will be the hydrogenation product of the unit resulting from 1,2-polymerization of butadiene or from 1,4-polymerization of an alkyl-substituted butadiene.

- 5 A polyoxyalkylene compound. Examples are polyoxyalkylene esters, ethers, ester/ethers and mixtures thereof, particularly those containing at least one, preferably at least two, C10 to C30 linear alkyl groups and a polyoxyalkylene glycol group of molecular weight up to 5,000, preferably 200 to 5,000, the alkyl group in
 10 said polyoxyalkylene glycol containing from 1 to 4 carbon atoms. These materials form the subject of EP-A-0 061 895. Other such additives are described in U.S. Pat. No. 4,491,455.

The preferred esters, ethers or ester/ethers are those of the general formula



where R_{31} and R_{32} may be the same or different and represent

- (a) n-alkyl--
 20 (b) n-alkyl-CO--
 (c) n-alkyl-O--CO(CH₂)_x -- or
 25 (d) n-alkyl-O--CO(CH₂)_x --CO--

x being, for example, 1 to 30, the alkyl group being linear and containing from 10 to 30 carbon atoms, and D representing the polyalkylene segment of the glycol in which the alkylene group has 1 to 4 carbon atoms, such as a polyoxymethylene,

polyoxyethylene or polyoxytrimethylene moiety which is substantially linear; some degree of branching with lower alkyl side chains (such as in polyoxypropylene glycol) may be present but it is preferred that the glycol is substantially linear. D may also contain nitrogen.

5

Examples of suitable glycols are substantially linear polyethylene glycols (PEG) and polypropylene glycols (PPG) having a molecular weight of from 100 to 5,000, preferably from 200 to 2,000. Esters are preferred and fatty acids containing from 10-30 carbon atoms are useful for reacting with the glycols to form the ester additives, it being preferred to use a C18 -C24 fatty acid, especially behenic acid. The esters may also be prepared by esterifying polyethoxylated fatty acids or polyethoxylated alcohols.

10

Polyoxyalkylene diesters, diethers, ether/esters and mixtures thereof are suitable as additives, diesters being preferred for use in narrow boiling distillates, when minor amounts of monoethers and monoesters (which are often formed in the manufacturing process) may also be present. It is preferred that a major amount of the dialkyl compound be present. In particular, stearic or behenic diesters of polyethylene glycol, polypropylene glycol or polyethylene/polypropylene glycol mixtures are preferred.

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Other examples of polyoxyalkylene compounds are those described in Japanese Patent Publication Nos. 2-51477 and 3-34790, and the esterified alkoxylated amines described in EP-A-117,108 and EP-A-326,356.

25

It is within the scope of the invention to use two or more additional flow improvers advantageously selected from one or more of the different classes outlined above.

If an additional flow improver is employed, it is advantageously employed in a proportion within the range of from 0.01% to 1%, advantageously 0.05% to 0.5%, and preferably from 0.075 to 0.25%, by weight, based on the weight of fuel.

- 5 The pour point depressant additive of the invention may also be used in combination with one or more other co-additives such as known in the art, for example the following: detergents, particulate emission reducers, storage stabilizers, antioxidants, corrosion inhibitors, dehazers, demulsifiers, antifoaming agents, cetane improvers, cosolvents, package compatibilizers, and lubricity
10 additives.

Additive concentrates according to the invention advantageously contain between 3 and 75%, preferably between 10 and 65%, of the pour point depressant additive in an oil or a solvent miscible with oil.

15

- The concentrate comprising the additive in admixture with a suitable solvent are convenient as a means for incorporating the additive into bulk oil such as distillate fuel, which incorporation may be done by methods known in the art. The concentrates may also contain the other additives as required and preferably
20 contain from 3 to 75 wt %, more preferably 3 to 60 wt %, most preferably 10 to 50 wt % of the additives preferably soluble in oil. Examples of solvent are organic solvents including hydrocarbon solvents, for example petroleum fractions such as naphtha, kerosene, diesel and heater oil; aromatic hydrocarbons such as aromatic fractions, e.g. those sold under the `SOLVESSO` tradename; alcohols and/or
25 esters; and paraffinic hydrocarbons such as hexane and pentane and isoparaffins. The solvent must, of course, be selected having regard to its compatibility with the additive and with the oil.

The oil, preferably crude oil or fuel oil, composition of the invention advantageously contains the pour point depressant polymer of the invention in a proportion of 0.0005% to 1%, advantageously 0.001 to 0.1%, and preferably 0.01 to 0.06% by weight, based on the weight of oil.

5

In one embodiment, the oil-containing composition of the invention comprises crude oil, i.e. oil obtained directly from drilling and before refining.

The oil may be a lubricating oil, which may be an animal, vegetable or mineral oil, such, for example, as petroleum oil fractions ranging from naphthas or spindle oil to SAE 30, 40 or 50 lubricating oil grades, castor oil, fish oils, oxidized mineral oil, or biodiesels. Such oils may contain additives depending on its intended use; examples are viscosity index improvers such as ethylene-propylene copolymers, succinic acid based dispersants, metal containing dispersant additives and zinc dialkyldithiophosphate antiwear additives. The pour point depressant of this invention may be suitable for use in lubricating oils as a flow improver, ***pour point depressant*** or dewaxing aid.

In another embodiment the oil is a fuel oil, e.g., a petroleum-based fuel oil, especially a middle distillate fuel oil. Such distillate fuel oils generally boil within the range of from 110°C. to 500°C., e.g. 150°C. to 400°C. The fuel oil may comprise atmospheric distillate or vacuum distillate, cracked gas oil, or a blend in any proportion of straight run and thermally and/or catalytically cracked distillates. The most common petroleum distillate fuels are kerosene, jet fuels, diesel fuels, heating oils and heavy fuel oils. The heating oil may be a straight atmospheric distillate, or it may contain minor amounts, e.g. up to 35wt %, of vacuum gas oil or cracked gas oil or of both. The above-mentioned low temperature flow problem is most usually encountered with diesel fuels and with heating oils. The invention is also applicable to vegetable-based fuel oils, for example rapeseed oil, used alone or in admixture

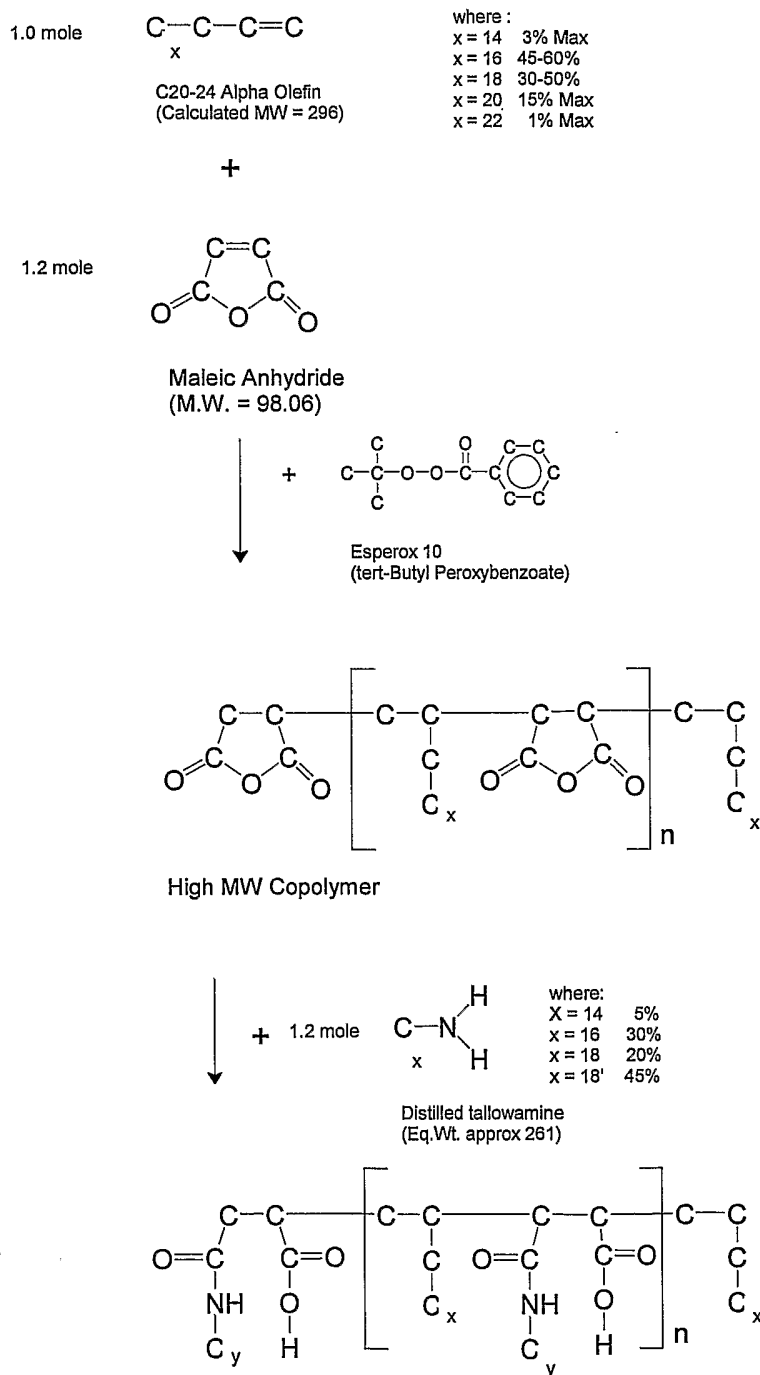
with a petroleum distillate oil.

The invention will now be illustrated by the following nonlimiting example.

Example 1

- 5 Aromatic 150 (about 25% by weight of the product), C-20-24 Alpha Olefin (1.0 mole), and Maleic Anhydride (1.15 moles) are stirred in a flask equipped with an inert nitrogen subsurface sparge to eliminate air from the product and overhead and set for total reflux. The mixture is heated to 130°C and then tert-butyl peroxybenzoate (0.02 moles) is slowly added continuously over a two to three hour
- 10 period while maintaining the temperature at 130°C and then allowed to react in for an additional hour. The flask is then set to collect distillate and the premelted tallowamine (1.15 moles) is then added to the mixture allowing the exotherm along with external heating to hold the product at 150°C for 2 hours. The resulting product was tested as a potential wax crystalline modifier against our current
- 15 product (PC-105) used for this application. The pour point test results (attached) show that the experimental product (labeled RLC-2) was better at 200 ppm treating levels than our current PC-105 (labeled RLC-1) at 600 ppm treating levels. When the experimental product was used at the 600 ppm treating levels, it was even more effective (i.e. reduced the pour point of the crude all the way to 20°F) at
- 20 reducing the pour point of the crude that would normally not flow at 70°F without treatment.

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The pour point test results are compiled in Table 1, below.

Table 1

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Sample Analysis						(D5853-95, Procedure 9.1.5)	
Test	Akzonobel Pour Point						
Description:	Depressant Evaluation						
Sample ID	GoM Crude	GoM Crude	GoM Crude	GoM Crude	GoM Crude	GoM Crude	GoM Crude
Sample Description:	No Additive	200ppm RLC-1	600ppm RLC-1	200ppm RLC-2	200ppm RLC-2	600ppm RLC-2	600ppm RLC-2
Start Time	9:17	9:17	9:17	9:17	9:17	9:17	9:17
Start Temp.	120F	120F	120F	120F	120F	120F	120F

Bath 2 (70°F)	Time: 13:00					
	Flowing	Flowing	Flowing	Flowing	Flowing	Flowing
115°F	✓	✓	✓	✓	✓	✓
110°F	✓	✓	✓	✓	✓	✓
105°F	✓	✓	✓	✓	✓	✓
100°F	✓	✓	✓	✓	✓	✓
95°F	✓	✓	✓	✓	✓	✓
90°F	✓	✓	✓	✓	✓	✓
85°F	✓	✓	✓	✓	✓	✓

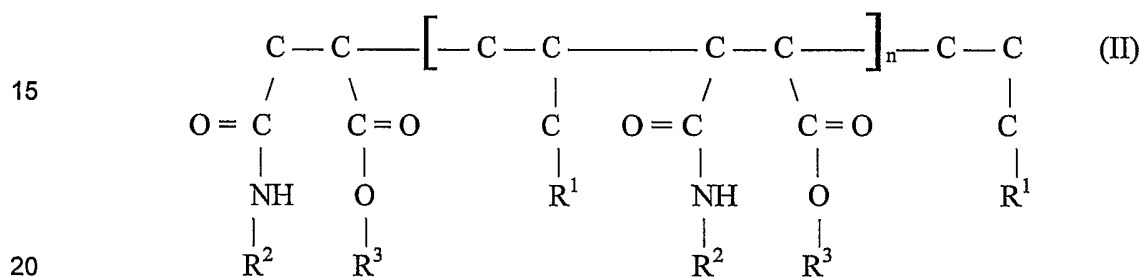
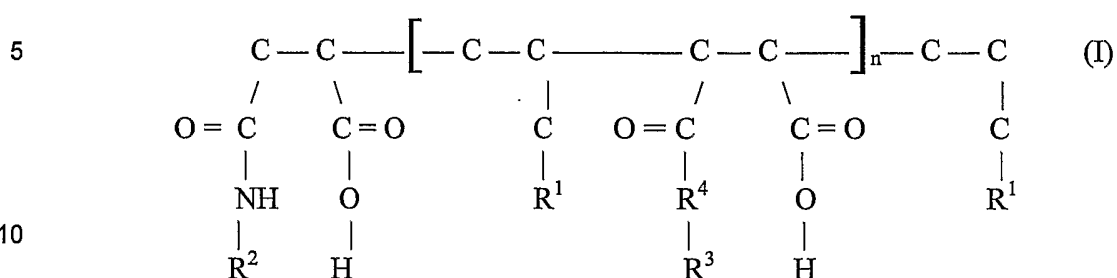
Bath 3 (32°F)		Time: 13:50				
80°F	✓	✓	✓	✓	✓	✓
75°F	✓	✓	✓	✓	✓	✓
70°F	No Flow	No Flow	✓	✓	✓	✓
65°F	□	□	□	✓	✓	✓
60°F	□	□	□	No Flow	✓	✓
55°F	□	□	□	□	✓	✓
50°F	□	□	□	□	✓	✓

Bath 4 (0°F)	Time: 14:44					
45°F	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>
40°F	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	No Flow	<input checked="" type="checkbox"/>
35°F	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input checked="" type="checkbox"/>
30°F	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input checked="" type="checkbox"/>
25°F	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input checked="" type="checkbox"/>
20°F	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input checked="" type="checkbox"/>
15°F	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	No Flow	No Flow

[illegible]

What is claimed is:

1. An oil composition having improved low temperature properties comprising an oil and an effective amount of a pour point depressant additive composition that comprises at least one pour point depressant additive of the formulae (I) - (II):



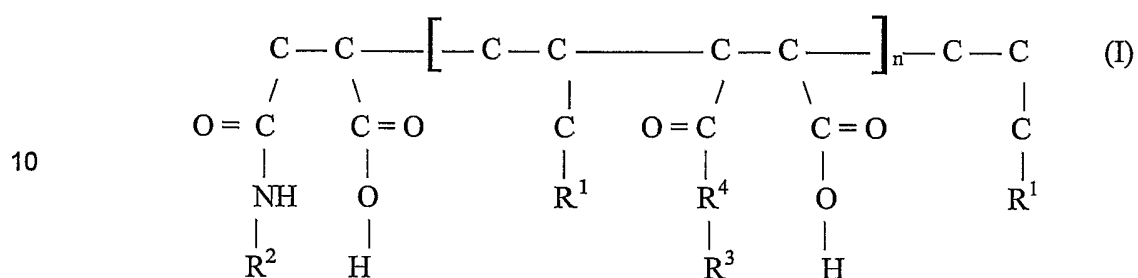
wherein R¹, R² and R³ are independently selected from hydrocarbyl groups containing up to 50 carbon atoms, R⁴ is selected from NH or O and n is an integer of from 0 to 50.

2. The composition of claim 1 wherein R¹, R² and R³ are each independently selected from C₆-C₃₀ saturated or unsaturated substituted, or unsubstituted alkylene groups; and n is an integer of from 1-30.

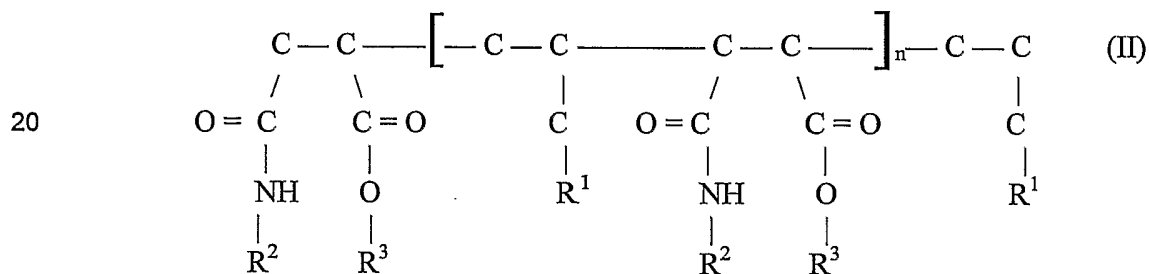
3. The composition of claim 1 wherein R^1 , R^2 and R^3 are each independently selected from C_8 - C_{24} saturated or unsaturated, substituted or unsubstituted alkylene groups; and n is an integer of from 1-20.
- 5 4. The composition of claim 1 wherein said oil is selected from the group consisting of an animal, vegetable or mineral based lubricating oil, crude oil, fuel oil, castor oil, fish oils, oxidized mineral oil, biodiesel and mixtures thereof.
- 10 5. The composition of claim 1 wherein said oil composition having improved low temperature properties comprises 0.0001% to 1% by weight of the pour point depressant additive composition of the invention, based on the weight of oil.
- 15 6. The composition of claim 1 wherein said oil composition having improved low temperature properties comprises 0.0001 to 1.0% by weight of the pour point depressant additive composition of the invention, based on the weight of oil.
- 20 7. The composition of claim 1 wherein said oil composition having improved low temperature properties comprises 0.0001 to 1.0% by weight of the pour point depressant additive composition of the invention, based on the weight of oil.
8. The composition of claim 1 wherein said oil is crude oil or fuel oil.
9. The composition of claim 1 wherein the oil has a wax content of 0.1 to 20% by weight, measured at 10 degrees below wax appearance temperature.
- 25 10. The composition of claim 1 one or more other co-additives such as known in the art, for example the following: detergents, particulate emission reducers, storage stabilizers, antioxidants, corrosion inhibitors, dehazers, demulsifiers,

antifoaming agents, cetane improvers, cosolvents, package compatibilizers, and lubricity additives.

11. A pour point depressant additive concentrate that comprises at least one pour point depressant additive of the formulae (I)- (II):



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wherein R^1 , R^2 and R^3 are independently selected from hydrocarbyl groups containing up to 50 carbon atoms, R^4 is selected from NH or O and n is an integer of from 0 to 50, and an acceptable solvent.

12. The concentrate of claim 11 wherein R^1 , R^2 and R^3 are each independently selected from C_6 - C_{30} saturated or unsaturated, substituted or unsubstituted alkylene groups; and n is an integer of from 1-30.

13. The concentrate of claim 11 wherein R^1 , R^2 and R^3 are each independently selected from C_8 - C_{24} saturated or unsaturated, substituted or unsubstituted alkylene groups; and n is an integer of from 1-20.

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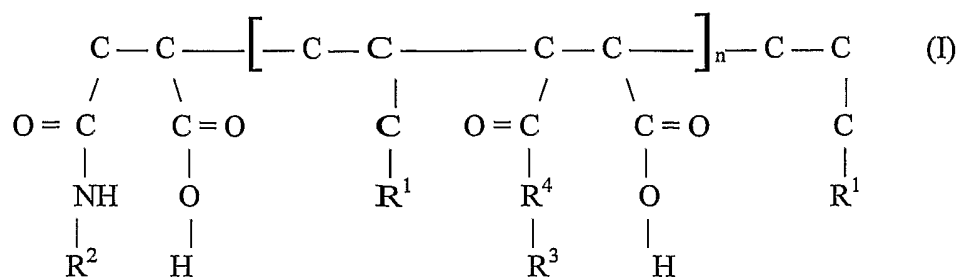
14. The concentrate of claim 11 wherein said solvent an organic solvent.

15. The concentrate of claim 11 wherein said organic solvent is selected from the group consisting of naphtha, kerosene, diesel, heater oil; aromatic hydrocarbon
10 fraction, alcohols, esters, hexane, pentane, isoparaffins and mixtures thereof.

16. The concentrate of claim 11 that contains between 3 and 75% of said pour point depressant additive.

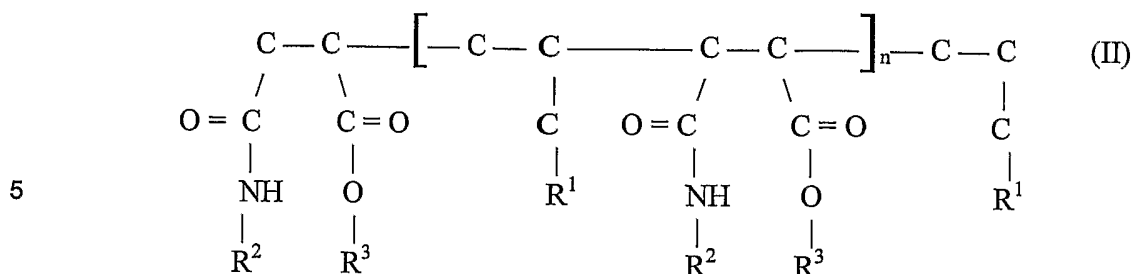
15 17. The concentrate of claim 16 that contains between 10 and 65%, of the pour point depressant additive.

18. A method of improving the low temperature flow properties of oil which comprises adding to said oil an effective amount of a pour point depressant
20 additive composition that comprises at least one pour point depressant additive of the formula (I):



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wherein R^1 , R^2 and R^3 are independently selected from hydrocarbyl groups containing up to 50 carbon atoms, R^4 is selected from NH or O and n is an integer of from 0 to 50, and an acceptable solvent.

19. The method of claim 18 wherein R^1 , R^2 and R^3 are each independently selected from C_6 - C_{30} saturated or unsaturated, substituted or unsubstituted alkylene groups; and n is an integer of from 1-30.

20. The method of claim 19 wherein R^1 , R^2 and R^3 are each independently selected from C_8 - C_{24} saturated or unsaturated, substituted or unsubstituted alkylene groups; and n is an integer of from 1-20.

21. The method of claim 18 wherein said oil is selected from the group consisting of an animal, vegetable or mineral based lubricating oil, crude oil, fuel oil, castor oil, fish oils, oxidized mineral oil, biodiesel and mixtures thereof.

22. The method of claim 18 wherein 0.0005% to 1% by weight of the pour point depressant additive composition, based on the weight of oil, is added.

23. The method of claim 1 wherein said oil is crude oil or fuel oil.

INTERNATIONAL SEARCH REPORT

International Application No
PCT/EP2005/003638

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 C10L1/22 C10M149/06 C10M133/16

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C10L C10M

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EP0-Internal

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
E	EP 1 526 167 A (CLARIANT GMBH) 27 April 2005 (2005-04-27) page 10, line 33 - line 42; claims 1,2,7-19; table 4 paragraphs '0035! - '0038!, '0040!, '0042!, '0047!, '0059! -----	1-23
E	EP 1 541 662 A (CLARIANT GMBH) 15 June 2005 (2005-06-15) page 12, line 36 - line 44; claims 1,2,7-20; table 5 paragraphs '0033!, '0034! ----- -/--	1-23

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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Date of the actual completion of the international search

2 September 2005

Date of mailing of the international search report

12/09/2005

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INTERNATIONAL SEARCH REPORT

International Application No
PCT/EP2005/003638

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 01/48122 A (ELF ANTAR FRANCE; EYDOUX, FRANCK; FLORES, PHILIPPE; VICHARD, DOMINIQUE) 5 July 2001 (2001-07-05) page 5, line 30 - page 6, line 8; claims 1-4,8-12; examples 1-3 page 9, line 11 - page 10, line 2 -----	1-23
X	US 4 339 246 A (YAMAMURA ET AL) 13 July 1982 (1982-07-13) column 4; claims 1-4 -----	1-8
X	GB 1 463 291 A (TEXACO DEV CORP) 2 February 1977 (1977-02-02) page 2, line 10 - line 28; claims 1,3,4,6-13 page 3, line 4 - line 43 -----	1,4-7, 10,11, 14-17
X	US 3 905 781 A (DORN ET AL) 16 September 1975 (1975-09-16) column 3, line 3 - line 15; claims 1-5,7-14 column 4, line 24 - line 30 column 5, line 28 - line 44 -----	1,4-10
X	US 4 356 002 A (KNEPPER ET AL) 26 October 1982 (1982-10-26) column 6; claims 1-16 column 8, line 46 - line 60 -----	1-10
X	US 3 003 858 A (JR. HARRY J. ANDRESS, ET AL) 10 October 1961 (1961-10-10) column 3, line 12 - column 4, line 12; claims 1-4,6,7 -----	1-10
A	DATABASE WPI Section Ch, Week 198409 Derwent Publications Ltd., London, GB; Class A17, AN 1984-051543 XP002343279 & JP 59 008790 A (KAO CORP) 18 January 1984 (1984-01-18) abstract -----	1-23
A	DATABASE WPI Section Ch, Week 198706 Derwent Publications Ltd., London, GB; Class A14, AN 1987-040191 XP002343177 & JP 61 296090 A (KAO CORP) 26 December 1986 (1986-12-26) abstract -----	1-23
	----- -/--	

INTERNATIONAL SEARCH REPORT

International Application No
PCT/EP2005/003638

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 2 542 542 A (LIPPINCOTT SAMUEL B ET AL) 20 February 1951 (1951-02-20) column 8, line 38 - line 43; claim 1 -----	1-23
A	US 2 615 845 A (LIPPINCOTT SAMUEL B ET AL) 28 October 1952 (1952-10-28) column 2; claims 1-4 column 3, line 69 - column 4, line 66 -----	1-23
A	EP 0 154 177 A (BAYER AG) 11 September 1985 (1985-09-11) claims 1-9 -----	1-23
A	US 4 163 645 A (CHENG, WILLIAM J ET AL) 7 August 1979 (1979-08-07) column 2, line 57 - column 3, line 10; claims 1-10 column 3, line 41 - column 4, line 62 -----	1-17

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/EP2005/003638

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
EP 1526167	A	27-04-2005	DE 10349851 A1 CA 2486035 A1 EP 1526167 A2 JP 2005126720 A US 2005113266 A1	16-06-2005 25-04-2005 27-04-2005 19-05-2005 26-05-2005
EP 1541662	A	15-06-2005	DE 10357880 A1 CA 2490049 A1 EP 1541662 A1 JP 2005171256 A US 2005126072 A1	28-07-2005 11-06-2005 15-06-2005 30-06-2005 16-06-2005
WO 0148122	A	05-07-2001	FR 2802940 A1 AT 284938 T AU 5787801 A DE 60016804 D1 DK 1252269 T3 EP 1252269 A1 ES 2234710 T3 WO 0148122 A1 HU 0204536 A2 JP 2003518549 T PL 356098 A1 PT 1252269 T US 2003163951 A1	29-06-2001 15-01-2005 09-07-2001 20-01-2005 11-04-2005 30-10-2002 01-07-2005 05-07-2001 28-05-2003 10-06-2003 14-06-2004 29-04-2005 04-09-2003
US 4339246	A	13-07-1982	JP 57018790 A AU 540029 B2 AU 7262881 A CA 1137315 A1 FR 2486537 A1 GB 2079784 A , B	30-01-1982 25-10-1984 20-10-1983 14-12-1982 15-01-1982 27-01-1982
GB 1463291	A	02-02-1977	US 3879306 A	22-04-1975
US 3905781	A	16-09-1975	NONE	
US 4356002	A	26-10-1982	US 4515603 A	07-05-1985
US 3003858	A	10-10-1961	NONE	
JP 59008790	A	18-01-1984	JP 1481329 C JP 63032120 B	10-02-1989 28-06-1988
JP 61296090	A	26-12-1986	NONE	
US 2542542	A	20-02-1951	FR 59908 E FR 989998 A GB 686381 A GB 686384 A	21-09-1954 17-09-1951 21-01-1953 21-01-1953
US 2615845	A	28-10-1952	NONE	
EP 0154177	A	11-09-1985	DE 3405843 A1 AT 47866 T CA 1244596 A1 DE 3574147 D1 DK 73985 A	29-08-1985 15-11-1989 08-11-1988 14-12-1989 18-08-1985

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/EP2005/003638

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP 0154177 A		EP 0154177 A2	11-09-1985
		IN 163624 A1	22-10-1988
		NO 850422 A ,B,	19-08-1985
		US 4670516 A	02-06-1987
US 4163645 A	07-08-1979	US 4121026 A	17-10-1978