A viscosity index improver, which comprises a polymer (A) having a solubility parameter of 8.6-9.4, a crystallizing initiation temperature of equal to or less than -15°C, and a steric hindrance factor (F) of 0-13, said factor F being defined by the following equation:

\[ F = 4X + Y \]

wherein X and Y represent the total numbers of atoms at the 6th position and the 7th position, respectively, in the side chains; said polymer (A) having a Mw of 5,000-2,000,000 and comprising units of at least one monomer selected from the group consisting of:

(a) a monomer represented by the general formula:

\[ CH_2=CH\left(R^{\prime}\right)=COO-(AO)_n-R \]

wherein \( R^{\prime} \) is hydrogen atom or methyl group, \( R \) is a \( C_1-C_6 \) alky group, \( n \) is 0 or an integer of 1-20 giving 0-10 on average, \( A \) is an alkylene group containing 2-4 carbon atoms, plural \( A \)'s in case of \( n \) being at least 2 are the same or different, and the polyoxyalkylene moiety (AO)\(_n\) in case of the plural \( A \)'s being different comprises random-wise or block-wise distributed oxyalkylene groups; (b) an alkyl alkenyl ether; (c) an alkenyl carboxylate; and (d) a nitrogen-containing unsaturated monomer.

The suitable monomers, 2-decyl-tetradecyl methacrylate and 2-decyl-tetradecyl acrylate compose the polymer (A), are also described.
VISCOSITY INDEX IMPROVER AND LUBE OIL CONTAINING THE SAME

BACKGROUND OF THE INVENTION

[0001] Field of the Invention

[0002] This invention relates to a viscosity index improver (hereinafter referred to as VI). More particularly, it relates to a VII for lube oils, such as engine oils, automatic transmission fluids (ATF), continuously variable transmission fluids (CVTF), gear oils and hydraulic fluids.

[0003] Description of the Prior Art

[0004] As VIIs to improve viscosity index (hereinafter referred to as VI) of lube oils, there have been known herebefore copolymers of C12-alkyl (meth) acrylates (f or instance, U.S. Pat. No. 5,622,924). The word, "(meth)acrylate" represents acrylate and/or methacrylate and also "C1, alkyl" represents alkyl group containing 1-18 carbon atoms; and similar expressions are used hereinafter.

SUMMARY OF THE INVENTION

[0005] It is an object of the present invention to provide a VII capable of imparting an improved VI to lube oil.

[0006] It is another object of this invention to provide a viscosity improver concentrate capable of imparting an improved VI to a lube oil.

[0007] It is still another object of the invention to provide a lube oil composition having an improved VI.

[0008] It is yet another object of the invention to provide a monomer consisting of 2-decyl-tetradecyl methacrylate or 2-decyl-tetradecyl acrylate.

[0009] Briefly, these and other objects of this invention as hereinafter will become more readily apparent have been attained broadly by a VII, comprising a polymer (A) or (A11) as follows. Polymer (A) has a solubility parameter (hereinafter referred to as SP) of 8.6-9.4, a crystallizing initiation temperature (hereinafter referred to as TC) of equal to or less than -15°C, and a steric hindrance factor F, defined by the following equation (1), of 0-13.

\[
F = 4X + Y
\]  

(1)

[0010] In the equation (1), X and Y represent the total numbers of atoms at the 6th position and the 7th position, respectively, in the side chains, counted from the backbone.

[0011] Polymer (A) comprises units of at least one monomer selected from the group consisting of an acrylic monomer (hereinafter referred to as (a)) represented by the following general formula (2), an alkyl alkenyl ether (hereinafter referred to as (b)), an alkyl carboxylate (hereinafter referred to as (c)) and a nitrogen-containing unsaturated monomer (hereinafter referred to as (d)).

\[
R^1\quad \text{CH}==\text{C}==\text{COOATG}--R
\]  

(2)

[0012] In the general formula (2), R1 is hydrogen atom or methyl group, R is a C3-4-alkyl group, n is 0 or an integer of 1-20 giving 0-10 on average, and A is an C2-4-alkylene group.

[0013] Polymer (A) is preferably a copolymer (A1), comprising units of at least one monomer (a) represented by the general formula (2) wherein R is a branched C16-40-alkyl group (hereinafter referred to as R1).

[0014] Copolymer (A11), in another aspect of this invention, comprises units of at least one monomer (a11) represented by the general formula (2) wherein R is a branched C20-40-alkyl group (hereinafter referred to as R11), and units of at least one other alkyl (meth)acrylate. Said (meth)acrylate (a11) is capable of providing a homopolymer having a TC of equal to or less than 5°C.

[0015] Polymers (A) and (A11) have a weight-average molecular weight (hereinafter referred to as Mw) of usually 5,000-200,000.

[0016] In the above, "polymer" represents copolymer and/or homopolymer; and such expression is used hereinafter.

BRIEF DESCRIPTION OF THE DRAWINGS

[0017] FIG.1, FIG.2 and FIG.3 show the 1H—NMR spectrum, the 13C—NMR spectrum, and the IR spectrum of 2-decyl-tetradecyl methacrylate, respectively.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS MONOMERS COMPOSING THE POLYMER (A)

[0018] The following monomers (a) to (m) compose the polymer (A).

[0019] (a) Acrylic monomers (hereinafter referred to as (a))

[0020] Monomers (a) are represented by the above-mentioned general formula (2). In the general formula (2), n is 0 or an integer of 1-20 (preferably 0-10) giving 0-10 (preferably 0-9) on average, particularly n is 0. Suitable C2-4 alkylene groups that is shown "A" in the formula (2), include ethylene, propylene, and 1,2-, 2,3-, 1,3- and 1,4-butylene groups, as well as combinations of two or more of these alkylene groups. Among alkylene groups, preferred are ethylene, propylene, 1,2-butylene and combinations of them.

[0021] In case of n is at least 2, the said A is represented as 1,3-alkylene. Plural A's may be the same or different, and the polyyoxyalkylene moiety (AOx) in case of the plural A's being different can comprise random-wise and/or block-wise distributed oxyalkylene groups.

[0022] R0 is hydrogen atom or methyl group, preferably methyl group.

[0023] Suitable C1-10 alkyl groups (R) include, for example,

[0024] (1) R1, namely branched C16-40 alkyl groups;

[0025] (2) C1-4 alkyl groups, such as methyl, ethyl, n- and i-propyl, and n-, i-, sec- and t-butyl groups;

[0026] (3) straight-chain and branched-chain C3-11 alkyl groups, such as n- and i-octyl, 2-ethylhexyl, n- and i-nonyl, n- and i-decyl, n- and i-dodecyl, 2-methylundecyl, n- and i-tridecyl, 2-methylundecyl, n- and i-tetradecyl, 2-methyltridecyl, n- and i-pentadecyl and 2-methylpentadecyl groups;
[0027] (4) straight-chain C_{16-30} alkyl groups, such as n-hexadecyl, n-octadecyl and n-nonadecyl groups;

[0028] (5) straight-chain C_{20-40} alkyl groups, such as n-eicosyl, n-docosyl, n-tetracosyl and n-octacosyl groups; and

[0029] (6) straight-chain and branched C_{4-alkyl} groups, such as n-, i-, sec- and neo-pentyl, n- and i-hexyl 2-methylpentyl and n- and i-heptyl groups.

[0030] Suitable branched C_{16-40} alkyl groups (R') have usually 1-12 branchings, preferably 1 branching. Branched C_{18-40} alkyl groups (R') are inclusive of branched C_{20-40} alkyl groups (R') and branched C_{16-19} alkyl groups (R'\text{)}

[0031] Illustrative of suitable groups R'\text{ are, for example,}

[0032] 1-alkyl groups (e.g., 1-ethyloctadecyl, 1-hexyltetradecyl, 1-octyldecyl, 1-butylhexacosyl, 1-hexadecyldecyl, 1-decyltetradecyl, 1-undecyl-tridecyl groups, etc.);

[0033] 2-alkyl groups (e.g., 2-hexyltetradecyl, 2-hexyldecyltetradecyl, 2-undecyl-tridecyl, 2-octylhexadecyl, 2-hexylhexacosyl, 2-dodecyl-hexadecyl, 2-tridecylpentadecyl, 2-decylcyclopentadecyl, 2-octylcyclopentadecyl, 2-tetradecylcyclohexadecyl, 2-tridecyltridecyl, 2-tetradecyl-tetradecyl, 2-hexadecyclooctadecyl, 2-tetradecyleicosyl and 2-hexadecycleicosyl groups, etc.);

[0034] 3-alkyl to 34-alkyl groups (e.g., 3-alkyl, 4-alkyl, 5-alkyl, 32-alkyl, 33-alkyl, 34-alkyl, etc.); and

[0035] alkyl groups containing one or more branchings (e.g., alkyl groups of oxoalcohols corresponding to propylene oligomers (from heptamer to undecamer), ethylene-propylene (molar ratio 16/1-11) oligomers, iso-butylen glycol oligomers (from pentamer to octamer), \alpha-olefins(C_{5-20}) oligomers from tetramer to octamer, etc.).

[0036] Examples of suitable groups R^{12} include 2-alkyl groups (e.g., 2-hexyldecyl, 2-hexylundecyl, 2-ochlydecyl, 2-octyldecyl, 2-butyldodecyl, 2-butyltridecyl, 2-methyl-ll-tetradecyl, 2-methylhexyldecyl groups, etc.).

[0037] Among these groups R^{12} and R^{12}, preferred in regard to V1 and low viscosity even at low temperature are groups R^{12}, particularly those of C_{22-34}. More preferred are those of C_{22-28}, especially of C_{24}. Preferred types in this regard are 2-alkyl groups, represented by the general formula:

\[
\text{R}^{1} \quad \text{CH}_{2} \quad \text{CH} = \text{R}^{2}
\]

[0038] Wherein R' and R" are the same or different straight-chain C_{18-20} alkyl groups. The most preferred R'' is a dodecyl group. The most preferred R' is a dodecyl group.

[0039] The most preferred R in the formula (2) is a 2-decyltetradecyl group.

[0040] Suitable acrylic monomers (a) include, for example, monomers of the general formula (2) wherein R is a branched C_{16-40} alkyl group R'' (hereinafter referred to as (a1)), C_{14-alkyl}(meth)acrylates (hereinafter referred to as (a2)), C_{15-alkyl}(meth)acrylates (hereinafter referred to as (a3)), straight-chain C_{16-30}(meth)acrylates (hereinafter referred to as (a4)), straight-chain C_{20-40}(meth)acrylates (hereinafter referred to as (a5)) and C_{15-alkyl}(meth)acrylates (hereinafter referred to as (a6)).

[0041] Monomers (a1) include monomers (a11) of the general formula (2) wherein R is a branched C_{20-40} alkyl group R'' and monomers (a12) of the general formula (2) wherein R is a branched C_{16-19} alkyl group R'\text{. Among these, preferred are monomers (a1), particularly monomers (a11)}

[0042] Monomers (a1), having R''\text{, are capable of providing a homopolymer having a Tc of equal to or less than 5° C, preferably equal to or less than 0° C, more preferably equal to or less than -15° C. Tc is measured with respect to a homopolymer prepared by polymerizing a particular monomer under the following conditions.}

[0043] Into a reaction vessel equipped with a stirrer, a heating and cooling device, a thermometer, a dropping funnel and nitrogen gas inlet tube, 25 parts of toluene is charged. After the atmosphere in the vessel is replaced with nitrogen gas, a monomer solution comprising 100 parts of monomer, 0.3 parts of a dodecyl mercaptan (hereinafter referred to as DM) that is a chain transfer agent and 0.5 parts of a 2,2'-azo-bis-(2,4- dimethyl)valeronitrile (hereinafter referred to as ADVN) is added dropwise from the dropping funnel. This addition is made over a period of 4 hours, at 85° C, in the absence of air. The reaction mixture is held at 85° C for a period of 2 hours, so that the polymerization proceeds well. Thereafter, toluene is evaporated under reduced pressure, at 130° C, for 3 hours, and a resultant homopolymer is obtained.

[0044] Illustrative of suitable monomers (a1) are 2-decyltetradecyl methacrylate (Tc=-30° C), 2-tetradecylethacylate (Tc=3° C), 2-octadecylethacylate (meth)acrylate, diethylene glycol mono-2-decyltetradecylether (meth)acrylate, dipropylene glycol mono-2-decyltetradecylether (meth)acrylate, etc. Tc in the parentheses is Tc of the homopolymer comprises the monomer.

[0045] There may be used two or more of these monomers, for instance, combinations of (a1) and (a2) with or without (a3)-(a4), and combinations of (a11) and (a22) with or without at least one of (a3)-(a5), (a12), (a4) and (a5).

[0046] (b) Alkyl alkylol ethers (hereinafter referred to as (b))

[0047] Suitable monomers (b) include, for example one represented by the general formula R-O-D, wherein D is a C_{2-10} (preferably C_{2-4}, particularly C_{2-3}) alkyl group and R is a C_{1-10} (preferably C_{1-6} particularly C_{1-5}) alkyl group. Examples of the suitable alkyl group include vinyl, (meth)allyl and (iso)propenyl groups. Examples of the alkyl group R in the general formula include the same alkyl group R'' in the general formula (2) mentioned above in the said monomer (a).

[0048] Examples of suitable ethers (b) are alkyl vinyl ethers, and alkyl (meth)allyl ethers. Preferred are methyl vinyl ether, ethyl vinyl ether, methyl allyl ether and ethyl allyl ether.
(c) Alkenyl carboxylate (hereinafter referred to as (c))

Suitable monomers (c) include, for example, ones represented by the general formula R—COO—D, wherein R and D are the same as “R” and “D” in the above-mentioned general formula of the monomer (b). Illustrative of suitable carboxylates (c) are vinyl acetate, vinyl propionate, vinyl hexanoate, vinyl 2-ethylhexanoate and vinyl n-octanoate. Preferred are vinyl acetate and vinyl propionate.

(d) Nitrogen-containing unsaturated monomers (hereinafter referred to as (d))

Suitable monomers (d) are inclusive of amino-containing monomers (d1), amide-containing monomers (d2), and nitro-containing monomers (d3).

Suitable monomers (d1) include primary, secondary and tertiary amino-containing aliphatic monomers, for example,

mono-C₃₆₈ alkenyl amines (e.g., (d1) (meth) alkyl amines, crotyl amine, etc.), amino-containing acrylic monomers, for instance, amino-C₃₆₈ alkyl-(meth)acrylates (e.g., aminooethyl and aminopropyl (meth)acylate, etc.) mono-and di-C₃₆₈ alkyl-amino C₃₆₈ alkyl (meth)acrylates (e.g., (d1) methyl-aminoethyl, (d1)ethylaminooethyl, (d1)butylaminooethyl and (d1)methylaminopropyl (meth)acylate, etc.);

primary, secondary and tertiary amino-containing aromatic monomers, for example, aminostyrenes (e.g., (d1) (dimethyl)aminostyrene, phenylaminostyrene, etc.), (meth)acryl-amides (e.g., 4-and 2-phenylaminophenyl (meth)acrylamide, etc.);

amino-containing heterocyclic monomers, for example, morpholino C₃₆₈ alkyl (meth)acrylates, (e.g., morpholinoethyl (meth)acrylate, etc.), vinylpyridines, (e.g., 4-and 2-vinylpyridine, N-vinylpyrrole and N-vinylthio-pyrrolidone, etc.).

Suitable amide-containing monomers (d2) include

(meth)acrylamide; and

N-vinyl-carbonamides (e.g., N-vinyl-formamide, N-vinyl-2-acetamide, N-vinyl-n- and i-propionamide, N-vinylhydroxyacetamide, etc.).

Examples of nitro-containing monomers (d3) are nitrostyrenes, (e.g., 4-nitrostyrene, etc.).

Among monomers (d), preferred are monomers (d1). More preferred are tertiary amino-containing acrylic monomers, particularly dimethylaminooethyl, diethylaminooethyl and morpholinoethyl (meth)acrylates.

(e) Aliphatic hydrocarbon vinyl monomers (hereinafter referred to as (e))

Suitable monomers (e) include, for example, C₃₆₈ alkene (e.g., ethylene, propylene, butene, isobutylene, pentene, heptene, disobutylene, octene, dodecane, octadecene, etc.), and C₃₆₈ alkenes (e.g., butadiene, isoprene, 1, 4-pentadiene, 1, 6-heptadiene, 1, 7-octadiene, etc.).

(f) Allylic hydrocarbon vinyl monomers (hereinafter referred to as (f))

Suitable monomers (f) include, for example, cyclohexene, (di)cyclopentadiene, pinene, limonene, indene, vinylcyclohexene, ethylidenecycloheptene.

(g) Aromatic hydrocarbon vinyl monomers (hereinafter referred to as (g))

Suitable monomers (g) include, for example, styrene, a-methylstyrene, vinyltoluene, 2,4-dimethylstyrene, 4-ethylstyrene, 4-isopropylstyrene, 4-butylstyrene, 4-phenylstyrene, 4-cyclohexylstyrene, 4-benzylstyrene, 4-crotylbenzene and 2-vinylnapthalene.

(h) Vinyl ketones (hereinafter referred to as (h))

Suitable monomers (h) include, for example, C₃₆₈,₈ ary1 vinylketones (e.g., methylvinylketone, ethylvinylketone, phenylvinylketone, etc.).

(i) Vinyl monomers having epoxy group (hereinafter referred to as (i))

Suitable monomers (i) include, for example, glycidyl(methyl)acrylate and glycidyl(methyl)allyl ether.

(j) Vinyl monomers having halogen (hereinafter referred to as (j))

Suitable monomers (j) include, for example, vinyl chloride, vinyl bromide, vinylidene chloride, (meth)allyl chloride, styrene halide (e.g. dichlorostyrene, etc.).

(k) Esters consisting of unsaturated polycarboxylic acid (hereinafter referred to as (k))

Suitable monomers (k) include, for example, alkyl, cycloalkyl or aralkyl esters of unsaturated polycarboxylic acid. Among these esters, preferred are C₃₆₈ alkyl diester consisting of unsaturated dicarboxylic acid such as maleic acid, fumaric acid, itaconic acid, (e.g., dimethylmaleate, dimethylfumarate, diethylmaleate, dioctylmaleate, etc.). (l) vinyl monomers having hydroxyl group (hereinafter referred to as (l))

Suitable monomers (l) include, for example,

aromatic vinyl monomer having hydroxyl group (e.g., p-hydroxy styrene, etc.), hydroxy-C₃₆₈ alkyl (meth)acrylate (e.g., 2-hydroxyethyl (meth)acrylate, 2- or 3-hydroxypropyl(methyl)acrylate, etc.);

mono- or di-hydroxy-C₃₆₈ alkyl substituted (meth)acrylamide (e.g., N,N-di hydroxymethyl (meth)acrylamide, N,N-di hydroxypropyl (meth)acrylamide, N,N-di-2-hydroxybutyl(methyl)acrylamide, etc.);

vinyl alcohol, that is obtained by hydrolysis of vinyl acetate;

C₃₆₈ alkene (e.g., (meth)allylalcohol, crotylalcohol, iso-crotylalcohol, 1-octenol, 1 undecenol, etc.);

C₄₋₁₂ alkenediol (e.g., 1-butene-3, ol, 2-buutene-1, 2, 2-buten-1, 4-diol, etc.);

hydroxy-C₃₋₁₀ alkyl-C₃₋₁₀ alknyl ether (e.g., 2-hydroxyethyl-propenyl ether, etc.);

polyvalent alcohol having 3-8 hydroxy groups;
(0084) alkane polyol;
(0085) its intra- or inter-molecular dehydration product; and
(0086) C₃-₁₀ alkyl ether and (meth) acrylate, of a saccharide, for example, glycerol, pentaerythritol, sorbitol, sorbitan, diglycerol, and sucrose (e.g., sucrose (meth)allyl ether, etc.).
(0087) (m) vinyl monomers having carboxylic acid group (hereinafter referred to as (m))
(0088) Suitable monomers (m) include,
(0089) vinyl monomers having monocarboxylic acid group, for instance, unsaturated monocarboxylic acid (e.g., (meth)acrylic acid, α-methyl(meth)acrylic acid, crotonic acid, cinnamic acid, etc.);
(0090) mono C₃-₈ alkyl ester of unsaturated dicarboxylic acid (e.g., mono-alkyl maleate, mono-alkyl fumarate, mono-alkyl itaconate, etc.); and
(0091) vinyl monomers having dicarboxylic acid group, (e.g., maleic acid, fumaric acid, itaconic acid, citraconic acid, etc.).

(0092) When VII is required property of a detergent, it is preferred that the polymer (A) comprises units of (d). When VII is not required property of a detergent, the monomer of (d) is not necessary to comprise the polymer (A).

POLYMER (A)

(0093) Several kinds of monomers that compose (A) include, preferably, at least (a), at least (b) or at least (a) and (b). The sum amount of (a) and (b), preferably at least 30%, more preferably 50-100%, particularly 80-100% against total amount of monomer(s) to be used for synthesis (A) (% stands for weight percentages hereafter, unless it is specifically mentioned otherwise). With regard to the ratio of (a) and (b), (a)/(b) is generally 30-100/0-70, preferably 50-100/ 0-50. If (c) and/or (d) is used together with (a) and/or (b), the amount of (c) preferably at most 45%, particularly at most 40%, and the amount of (d), preferably at most 12%, particularly at most 10%, against total amount of several monomers to be used for synthesis (A).

(0094) If (d) to (m) is employed by requirement, together with the monomers (a) to (c) for synthesis (A), the sum amount, if plural kinds of monomers (d) to (m) are employed, or the amount if single monomer selected from the group consisting of (d) to (m) is employed, is preferably 0-20%, particularly 0.1-10% against total weight of monomers ((a) to (m)) to be used for synthesis (A).

(0095) The polymer (A1) contains generally 5-90%, preferably 10-80%, particularly 10-60%, most particularly 10-45% of units of (a1), and contain generally 10-60%, preferably 20-50%, particular 20-45% of units of (a2). (A1) contains generally 0-85%, preferably 10-70%, particularly 10-60% of units of (a3) and/or (a4) (in particular, such monomers having 10-18 carbon atoms). (A1) contains preferably 0-20%, more preferably 0-10% of units of (a5) and/or (a6).

(0096) In addition to (A1), example of the polymer (A) contains 5-20% of units of (a2), 30-70% of units of (a3), and 5-20% of units of (a4) Other examples of the polymer (A) is homopolymers comprises the monomer (b), such as homopolymer of methyl vinyl ether, homopolymer of the monomer that has general formula (2) and R is branched-alkyl group having 4-8 carbon atoms, and homopolymer of ethylene glycol mono-2-ethylhexyl-methacrylate, and the like.

(0097) The polymer (A) has a weight average molecular weight (Mw) of generally 5,000 to 2,000,000, preferably 8,000 to 500,000, preferably more than 10,000 to 250,000. If Mw is 5,000 or more, (A) has adequate capability of increasing viscosity so that usually oil dose not need excess amount of (A). If Mw is 2,000,000 or less, (A) has adequate shear stability. Mw is measured by gel permeation chromatography using calibration curve of polystyrene.

(0098) The polymer (A) has a SP value of generally 8.6-9.4, preferably 9.0-9.35, particularly 9.1-9.3. If SP is between the above range, (A) has an adequate solubility to base oil and also adequate ability of improving VI. The SP value in the present invention is one measured by the Fедor's method [Polym.Eng.Sci.14 (2) 152, (1974)].

(0099) (A) has a Tc of generally equal to or less than −15°C, preferably equal to or less than −17.5°C, particularly −20 to −70°C, more particularly −35 to −70°C. If Tc is equal to or less than −15°C, (A) does not crystallize at low temperature, so that (A) has an excellent low temperature behavior. Tc value is measured using differential scanning calorimeter “UNIX DSC-7” (PERKIN-ELMER Corp.) applying 5 mg of polymer as a specimen, measuring the crystallizing initiation temperature (Tc) under cooling from 100 °C to −45°C at a rate of −10°C/min.

(0100) Further, (A) has a steric hindrance factor, F of generally 0-13, preferably 0-12.5, more preferably 0-10, particularly 0-8, more particularly 0-7. The F is defined the above-mentioned equation (1). Namely, considering a monomeric unit constituting polymer (A), X represents the total numbers of atoms at the sixth position in a side chain from the backbone. Y represents the total numbers of atoms at the seventh position atom in a side chain. If monomeric unit has plural side chains, X and Y are counted respective side chain and added to the total number, F is the sum of four times X², and Y². The position is counted from the backbone (as shown in the following example) that a particular side chain bonded with, is assigned the number 0, and goes sequentially to the direction to outside of the particular side chain. The total number X and also Y are the sum of the atoms, that is, the kind of atom does not affect the total number. When the polymer (A) is copolymer, F is the average of F of each monomer unit calculated based on the molar fractions of each monomer unit in the copolymer. The F briefly expresses degree of steric hindrance of side chain in the polymer. The greater F means the more degree of steric hindrance.

(0101) Following is an example of calculating F. A number of the right shoulder of atoms shows the position of atoms counted from backbone.
Example Copolymer

2-Decyl-tetradecyl Methacrylate/Methyl Methacrylate=40/60 (molar ratio)

[0102] The left-hand side-chain: 2-decyl-tetradecyl methacrylate residue. The total number of atoms at the sixth position =6 (i.e., total number of atoms suffixed 6 at their right shoulder) The total number of atoms at the seventh position =6

$F_{5}^{a=6}=6x4+6=30$

[0103] The right-hand side-chain: methyl methacrylate residue. The total number of atoms at the sixth position =0. The total number of atoms at the seventh position =0

$F_{5}^{a=0}=6x4+6=12$

[0104] Molar ratio=40:60

$F=30x0.4+6x0.6=12$

[0105] If the F is 0-13, steric hindrance around backbone is small. Consequently, the polymer is easy to come to shrink at low temperature, and viscosity index becomes larger and viscosity at low temperature becomes low.

[0106] Means to adjust Mw and also the above-mentioned physical properties of polymer (A) in the present invention, is as follows. The Mw can be adjusted, for example, by changing temperature, monomer concentration (solvent concentration), quantity of catalyst and quantity of chain transfer agent, at polymerization. The SP value can be adjusted by selecting adequate kind of monomers and choosing their molar ratio by calculating SP value of the intended polymer using SP value of each constituting unit (such SP value is calculated by the Fedors method). For example, SP value of polymer can be adjusted by selecting monomer(s) having appropriate length of alkyl group(s). The longer such alkyl length is, the smaller SP of polymer becomes. Adversely, the shorter such alkyl length is, the larger SP of polymer becomes. The Tc can be adjusted by selecting appropriate length of a methylene-chain existing in backbone and/or side-chain of polymer. For example, Tc becomes higher if the monomer having longer methylene-chain at an alkyl group in its side chain, is employed. Adversely, Tc becomes lower if the monomer having shorter methylene-chain at an alkyl group in its side chain, is employed. The F can be adjusted by selecting kinds of monomer and their molar ratio. For example, the F becomes smaller when employed more quantity of monomer(s) having less number of atoms at the sixth or the seventh position.

[0107] The polymer has HLB value of preferably 0.5-6, more preferably 1.5-5, particularly 1.5-5. If HLB is in this range, in particular, anti-emulsification is preferable. The above HLB value is calculated using HLB definition of Oda method based on a general concept of organic and inorganic nature of organic compound ("New Introduction to Surface Active Agents" T. FUJIMOTO, SANYO CHEMICAL INDUSTRIES, LTD.P 197-201).

CO POLYMER (A11)

[0108] Another component of the present invention is the copolymer (A11). The copolymer (A11) contains generally 5-90%, preferably 10-80%, more preferably 10-70%, particularly 10-60%, more particularly 10-45% of units of (a11). The copolymer (A11) contains generally 5-95%, preferably 20-90%, more preferably 30-90%, particularly 40-90%, more particularly 55-90% of units of alkyl (methyl)acrylates that are other than (a11). The expression “alkyl (meth)acrylates that are other than (a11)” means such acrylates are without the definition of the monomer group (a11); and similar expression is used hereinafter.

[0109] The monomers that are other than (a11), include the above-mentioned monomer (a2), (a3), (a12), (a4) and (a5). The copolymer (A11) includes generally 10-60%, preferably 20-50%, particularly 25-45% of units of (a2). The copolymer (A11) includes generally 0-85%, preferably 10-70%, particularly 10-60% of total units of (a3), (a12), (a4) and (a5).

[0110] In one most preferable embodiment, the copolymer (A11) is prepared by polymerizing 10-40% 2-decyl-tetradecyl methacrylate, 20-45% methyl methacrylate and 10-60% alkyl (meth) acrylates that are within the groups of (a3) and (a4) and also have C_{10-18} straight-chain alkyl group.

[0111] If VII is required the property of a detergent as well as VII, in one preferable embodiment, the copolymer (A11) also include the 0.1-10% (d) based on the total weight of monomers consisting (A11), especially, one or several monomer(s) selecting from the group consisting of dimethylaminoethyl (meth)acrylate, diethylaminooethyl (meth)acrylate and morpholinooethyl (meth)acrylate; the said three compounds are within the monomer (d).

[0112] The preferable Mw, SP, Tc and the F of the copolymer (A11), are the same range of ones of the polymer (A) as described above.

[0113] As the VII of the present invention, (A11) can be used by itself or (A11) can be used together with (A) that is other than (A11). A ratio of such combined usage is preferably (A11)/(A) other than (A11)=100/0-20/80, more preferably 100/0-70/30.
PREPARATION OF THE POLYMERS (A) AND (A11)

[0115] The polymers (A) and (A11) of the present invention can be prepared by conventional methods well known to those of skill in the art. For instance, the polymer is prepared by radical polymerization of above-mentioned monomer(s) with solvent and polymerization catalyst.

[0116] The solvent includes, for example, aromatic compounds such as aromatic solvents having 7-15 carbon atoms (e.g., toluene, xylene, ethylbenzene, alkylbenzene having 9-10 carbon atoms, mixtures of trimethyl benzene, ethyl-toluene, etc.); ketone solvents (e.g., butanone, etc.); and mineral oils such as solvent refining oils, paraffin oils, isoparaffin containing and/or hydrogenolysis high viscosity index oils, hydrocarbon synthetic lubricants (e.g., poly alpha-olefinic synthetic lubricant), ester synthetic lubricants, naphthenic oils, and the like.

[0117] The polymerization catalyst includes, for example, azo catalyst (e.g., 2,2'-azo-bis(isobutyronitrile), 2,2'-azo-bis-(2-methyl) butyronitrile, ADVN, dimethyl 2,2'-azo-bis-isobutylate, etc.); and peroxide catalyst (e.g., t-butyl-peroxypivalate, t-ethyl-peroxypivalate, t-buty1-peroxynitroctanoate, t-butyl-peroxynitrodecanoate, t-butyl-peroxo-2-ethylhexanoate, t-butyl-peroxysobutylate, t-amyl-peroxo-2-ethylhexanoate, 1,1,3,3-tetramethylbutyl-peroxy-2-ethylhexanoate, dibuty1-peroxytrimethyl adipate, benzoyl peroxide, cumyl peroxide, lauryl peroxide, etc.).

[0118] Further, if necessary, chain transfer agent (e.g., alkyl mercaptan having 2-20 carbon atoms, mercaptocetic acid, mercaptopropionic acid, triethylene glycol dimercaptan, etc.) can be used in the synthesis.

[0119] The concentration of monomer(s) is preferably 40-95%, more preferably 60-90% based on weight of all chemicals including solvent in synthesis. The concentration of polymerization catalyst is preferably 0.1-5%, more preferably 0.15-0.5% based on weight of all monomer(s) in synthesis. The concentration of chain transfer agent is preferably 0.5%, more preferably 0.3% based on weight of all monomer(s) in synthesis.

[0120] The polymerization temperature is preferably 50-140°C, more preferably 70-120°C.

[0121] In addition, polymerization reaction can be bulk polymerization, emulsion polymerization or suspension polymerization in addition to the above-mentioned solution polymerization. Copolymerization can be by random copolymerization or alternating copolymerization, preferably random copolymerization. And also graft copolymerization or block copolymerization can be employed.

THE VISCOSITY INDEX IMPROVER

[0122] The viscosity index improver (VII) of the present invention, can be a solvent-free polymer (A1) or (A11), or can be a solution of the polymer (A) or (A11). The solution of the polymer prepared by solution polymerization, can be used as VII concentrates. In other embodiment, a diluent can also be added to a substantially solvent-free polymer, usually by dissolving the substantially solvent-free polymer in an appropriate diluent, making VII concentrates. The solution of the polymer, namely VII concentrate is preferable. Because, the polymer dissolves easily in base oil, if the polymer is diluted with diluent beforehand.

[0123] Examples of the diluents (hereinafter referred as (C)) are C<sub>12-18</sub> aliphatic hydrocarbons (e.g., hexane, heptane, cyclohexane, octane, decalin, kerosene, etc.), the above-mentioned aromatic compound and/or inorganic oils. A preferable diluent among these examples is mineral oil. The VII concentrates of the present invention, contains VII of preferably 10-90%, more preferably 30-80% and also contains diluent of preferably 10-90%, more preferably 20-70%.

THE LUBE OIL COMPOSITION

[0124] Base oil in which VII of the present invention is added, is not particularly limited. Preferably, such base oil has a kinematic viscosity at 100°C of, typically 1-15 mm²/s, more often 2-5 mm²/s. Preferably, such base oil has a VI value of typically at least 80, more often at least 100. The finished lube oil composition that is added the VII of the present invention into base oil, is improved to have larger VI and shows improved fuel efficiency.

[0125] In addition, such base oil has a cloud point (defined in JIS K2269) of, preferably equal to or less than −5°C, more preferably equal to or less than −10°C, particularly equal to or less than −15°C. If a cloud point of base oil is the range mentioned above, quantities of deposition of wax is so small at low temperature, that viscosity behavior at low temperature is excellent. Such base oil includes, for example, mineral oils that is mentioned above. Preferable mineral oils are high viscosity index oils contained isoparaffin and/or manufactured by hydrocracking. Normally, the lube oil composition of present invention include 0.5-30% of the polymer (A) or (A11).

[0126] In one embodiment, the finished lube oil composition is intended as engine oil, preferably, 0.5-15% of the (A) or (A11), are added to base oil having a 3-10 mm²/s kinematic viscosity at 100°C. In another embodiment, the finished lube oil composition is intended as gear oil, preferably, 3-30% of the (A) or (A11), are added to base oil having 3-10 mm²/s a kinematic viscosity at 100°C. In yet another embodiment, the finished lube oil composition is intended as automatic-transmission fluid (e.g., ATF, CTVF etc.), preferably, 2-25% of the (A) or (A11), is added to base oil having 2-6 mm²/s a kinematic viscosity at 100°C. In further embodiment, the finished lube oil composition is intended as traction oil, preferably, 0.5-15% of the (A) or (A11), are added to base oil having 1-5 mm²/s a kinematic viscosity at 100°C. In yet further embodiment, the finished lube oil composition is intended as hydraulic oil, preferably, 0.5-25% of the (A) or (A11), is added to base oil having 1-10 mm²/s a kinematic viscosity at 100°C.

[0127] The lube oil compositions of this invention containing VII of (A) or (A11), may further contain, optionally, another kind of additives. The examples of such another kind of additives are copolymers of alkyl (meth)acrylate (other than such copolymer classified (A)); such copolymers are hereinafter referred to as (B) Examples of (B) are copolymers comprise units derived from (a), and such copolymers have at least one of SP, TC, F or Mw of without the aforesaid range that preferable (A) are encompassed. Preferable monomers comprise (B), are the monomers within a group selecting from the group consisting of (a2), (a3), (a4), (a5), and (a6), that are included the above-
mentioned monomer group (a), and are the monomers from any group of (a2) to (a6). In one preferred embodiment, the copolymer (herein after referred to as (B1)) is composed of (a2) and (a3), or composed of (a2) and (a4), or composed of (a2), (a3) and (a4). In another preferred embodiment, the copolymer (hereinafter referred to as (B2)) is composed of two or more kind of monomers selecting from (a3) and/or (a4). In the (B1), the monomer ratio of (a2)/(a3)+(a4) is preferably (0-40)/(60-100), more preferably (5-35)/(65-95). In one particular embodiment of (B2), at least one kind of monomer composing (B2) has one having 12 to 18 carbon atoms, and average carbon atoms of all the monomers (B2) is 12 to 16, and the content of a branched-alkyl group is 0-30 mole %.

0128 In one particular embodiment, the copolymer (B1) comprises (a2), (a3) and (a4), for example, copolymers of methyl methacrylate/dodecyl methacrylate/tetradecyl methacrylate/hexadecyl methacrylate (0-20%/20-45%/20-45%/0-20%). In one particular embodiment, the copolymer (B2) comprises (a3) and (a4), for example, copolymers of dodecyl methacrylate/hexadecyl methacrylate (10-50%/50-90%), that have an average carbon atoms of 12.5-13.8, and have branched-alkyl group contents of 0 mol %;

0129 copolymers of dodecyl methacrylate/hexadecyl methacrylate (10-50%/50-90%), that have an average carbon atoms of 12.5-13.8, and have branched-alkyl group contents of 0 mol %; and

0130 copolymers comprises two kinds of monomers of (a3), for example, copolymers of dodecyl methacrylate/tetradecyl methacrylate (90-70%/10-30%), that have an average carbon atoms of 12.2-12.6, and have branched-alkyl group contents of 0 mol %; and

0131 copolymers of dodecyl acrylate/dodecyl methacrylate (10-40%/90-60%), that have an average carbon atoms of 12, and have branched-alkyl group contents of 0 mol %.

0132 As the additional VII, (B) may use alone, or may use more than two kinds together. Mw of (B) is preferably 5,000-1,000,000, more preferably 10,000-250,000.

0133 The lube oil composition of the present invention may contain further alkyl (meth)acrylate ester copolymers (B 11) other than the copolymer (A11). In one embodiment, (B11) include alkyl (meth)acrylate ester copolymers that comprise (a11) of less than 5% or of greater than 90%. In another embodiment, (B11) include copolymers within the definition of (B) and comprise the units of the monomers (a11) of less than 5% or of greater than 90%. Preferable monomers compose (B11), are the same monomers as the ones that (B) are composed of, which are described above. Preferable (B11) has the same Mw range as the (B) has, which are also described above.

0135 (B11) can be prepared by the same method as one for (A) preparation, mentioned above.

0136 The (B) or (B11) can be mixed to (A) or (A11) in advance, then add to a base oil. And also, (B) or (B11), and (A) or (A11) can be separately added to a base oil.

0137 The total amount of the (B) and (A), or (B) and (A11), to be added to a base oil is the same preferable range as the one of (A) or (A11), above-mentioned.

0138 The lube oil composition of this invention may further contain one or more additives usually used in a lube oil. Such additives include, for example, detergents, also referred to as an overbased or neutral metal salt (e.g., overbased alkali or alkaline earth metal salts of a sulfonate, phenate, naphthalene, salicylate, carbonate, or mixtures thereof, etc.), dispersants (e.g., succinimide type; bis type, mono type and borate type, Mannich dispersants, etc.), antioxidants (e.g., hindered phenolic antioxidants, secondary aromatic amine antioxidants, etc.), friction modifier (e.g., long chain fatty acids; oleic acid, long chain fatty acid esters; oleate, long chain amines; oleylamine, long chain amide; olefamidete, etc.), antiwear agents (e.g., molybdenum dithio phosphite, molybdenum dithio carbamate, zinc dialkyl dithiophosphate, etc.), extreme-pressure agents (e.g., sulfur phosphate compounds, sulfur compounds, phosphide compounds, chloro compounds, etc.), antifoam agents (e.g., silicone oil, metallic soap, fatty acid ester, phosphate compounds, etc.), demulsifying agents (e.g., teta ammonium salt compounds, sulfated oil, phosphate compounds, etc.) and corrosion inhibitors (e.g., nitrogen compound; benztriazole, 1,3,4-thiodiazoyl-2,5-bis dialkyl dithiocarbamate, etc.).

0139 These additives can be used in such amounts: 0-20%, preferably 0.1-10% of the detergent; 0-20%, preferably 2-10% of the dispersant; 0-5%, preferably 0.1-3% of the antioxidants; 0-5%, preferably 0.1-1% of the friction modifier; 0-5%, preferably 0.1-3% of the antiwear agent; 0-20%, preferably 1-10% of the extreme-pressure agent; 2-1000 ppm, preferably 10-700 ppm of the antifoam agent; 0-3%, preferably 0-1% of the demulsifying agent; and 0-3%, preferably 0-2% of the corrosion inhibitor.

0140 Lube oil compositions of this invention are useful as engine oils (such as an engine for means of transportation and engine for machine tools), gear oil, transmission lube oil (particularly, ATF and fluid for CVT), traction oil, shock-absorber oil, power steering oil, and the like.

2-DECYL-TETRADECYL (METH)ACRYLATE, AND ITS POLYMER

0141 Another component of the present invention is a monomer of 2-decyl-tetradecyl (meth)acrylate (hereinafter referred as DTDA), a homopolymer of the DTDA and the copolymers comprising of the units of DTDA.

0142 The 2-decyl-tetradecyl (meth)acrylate is presented by the general formula (4):

![Formula](4)

0143 In the formula (4), R⁴ is methyl group (i.e., 2-decyl-tetradecyl methacrylate) or R⁴ is hydrogen atom (i.e., 2-decyl-tetradecyl acrylate).

0144 A DTDA can be prepared by an esterification using 2-decyl-tetradecyl alcohol and (meth) acrylic acid, or can be prepared by a transesterification using 2-decyl-tetradecyl alcohol and (meth)acrylic acid derivatives. The 2-decyl-tetradecyl alcohol is commercially available, for example, under the trade name of "ISOFOIL24" from CONDEA Chemie GmbH. The (meth)acrylic acid derivatives include...
an (meth)acrylic acid halide (e.g., (meth)acrylic acid chloride, (meth)acrylic acid bromide, etc.), an (meth)acrylate acid anhydride, and a short-chain alkyl (carbon number 1-4, such as methyl, ethyl, etc.) (meth)acrylate, preferably methyl (meth)acrylate. The esterification or transesterification is carried out with or without solvent.

[0145] For example, the esterification or transesterification with or without solvent is carried out as follows: Alcohol, polymerization inhibitor, (solvent), a catalyst and (meth)acrylic acid or its derivative described above, are charged in a reactor and are reacted under normal or reduced pressure at 70-140°C, preferably 100-120°C. The solvent is, for example, the above-mentioned aromatic solvent, mineral oil, and the like. Preferred solvents are benzene, toluene, xylene and the like, because using such solvent, it is easy to separate and remove by-products of water or lower alcohol. The polymerization inhibitor is, for example, a phenol compound (e.g., hydroquinone, hydroquinone monomethyl ether, p-benzoquinone, t-butyl cresol, catechol, etc.), phenothiazine, oxygen and air. These are used alone or together. The catalyst is for example, an acid catalyst (e.g., sulfuric acid, hydrochloric acid, p-toluenesulfonic acid, methanesulfonic acid, benzenesulfonic acid, xylene sulfonic acid, etc.) or base catalyst (e.g., sodium hydroxide, potassium hydroxide, sodium carbonate, etc.). The reaction liquid that the reaction was completed, is washed with water or aqueous alkali solution, if necessary, and refined removing the catalyst, the polymerization inhibitor or unreacted (meth)acrylic acid.

[0146] The homopolymer of the DTDA is prepared by the same process as the process of the (A1) homopolymer, mentioned above. The copolymer having the DTDA is prepared by the same process as the process of the copolymer (A) or (A1), mentioned above.

EXAMPLE

[0147] Having generally described the invention, a more complete understanding can be obtained with reference to certain specific examples, which are included for purposes of illustration only and are not intended to limit the scope of the present invention.

[0148] In the following examples, parts represents parts by weight.

DTDA SYNTHESIS

[0149] Into a 2 litter reaction vessel equipped with a thermometer, a stirrer, a dehydrator, a condenser, an air inlet tube, a nitrogen gas inlet tube, and a dropping funnel, 1000 parts of an “ISOFOL 24,” 1.1 parts of a hydroquinone and 4 parts of a concentrated sulfuric acid were charged. 315.8 parts of methacrylic acid were added dropwise into the reaction mixture, over two hours, at the temperature 90°C, with bubbling air at gas flow for 25 mL/min. Simultaneously, the vessel was warming, so that the reaction mixture reached 120°C when the addition was completed. The mixture was maintained at 120°C for two hours to complete the esterification. Reducing the pressure to 4 kPa from atmospheric pressures, at 125°C, the unreacted methacrylic acid was removed. Then, 32 parts of 10% sodium hydroxide water solutions were added with stirring under less than 30°C, to neutralize the solution. Then, the upper layer was separated from the lower layer. In the upper layer including crude 2-decyl-tetradecyl methacrylate, five parts of an adsorbent “KYOWAAD-500SH” (Kyowa chemical industry Co., Ltd.) were added and stirred for 60 min., at 60°C, then containing water was removed by evaporation. The product was separated from the solid impurities by filtration. The 1,100 parts of 2-decyl tetradecyl methacrylate was obtained. The solidifying point was –33° C. to –35° C.

[0150] FIG. 1 shows a 1H—NMR spectrum of the product, FIG. 2 shows a 13C—NMR spectrum of the product, and FIG. 3 shows an IR absorption spectrum of the product.

[0151] Referring to the FIG. 1, the spectrum shows following resonance peaks, shapes, coupling constants and the number of hydrogen atoms: 1H—NMR (CDCl3,300 MHz): δ 6.08 (s, 1H), 5.52 (s,1H), 4.04(d, J=6 Hz, 2H), 1.93 (s, 3H), 1.6-1.7 (m, 1H), 1.1-1.4 (m, 40H), 0.87 (t, J=6 Hz, 6H). Referring the FIG. 2, the spectrum shows following resonance peaks: 13C—NMR (CDCl3,300 MHz): 167.6, 136.7, 125.0, 67.3, 37.2, 31.8, 31.3, 29.8, 29.6, 29.5, 29.3, 26.6, 22.5, 18.1, 13.9. Referring the FIG. 3, the spectrum shows following absorption frequency: IR (NaCl): 2924, 2855, 1720, 1639, 1466, 1319, 1296, 1165, 1013,937, 814, 721cm⁻¹.

[0152] The 2-decyl tetradecyl acrylate is prepared by a similar process.

THE METHODS

[0153] [The method of measuring a Mw for the copolymers]

[0154] Molecular weight distribution was measured by gel-permeation chromatography (GPC). The conditions for the measurement were as follows:


[0156] Column: TSkgel-GMH16, (Toyoda Soda Co., Ltd.) connecting two columns in series

[0157] Column Temperature: 40°C

[0158] Specimen (Sample solution): 0.5 weight % tetrahydrofurian (THF) solution

[0159] Injection amount of specimen: 200 micro L

[0160] Detector: a refractive index detector

[0161] In addition, the calibration curve of molecular weight was prepared to use polystyrene as a reference standard.

[0162] [The method of measuring a low-temperature viscosity]

[0163] The low-temperature viscosity was measured following JPI-SS-26-85 at –40°C.

[0164] [The method of measuring a VI]

[0165] The viscosity index was measured following JIS-K-2283.
[0166] The method of measuring a shear stability

[0167] The shear stability was measured according to JASO M347-95, the period of test time was 12 hours. In addition, the liquid level is adjusted every three hours.

HOMOPOLYMER

[0168] The monomers listed in the Table 1 were polymerized following the above-mentioned method of the homopolymerization, and obtained the homopolymers. The crystallizing initiation temperature of the homopolymers is shown in table 1.

<table>
<thead>
<tr>
<th>Table 1 Monomer</th>
<th>Tc (° C.) of homopolymer</th>
</tr>
</thead>
<tbody>
<tr>
<td>a1-1 2-decyl-tetradecyl methacrylate</td>
<td>-30</td>
</tr>
<tr>
<td>a1-2 2-dodecyl-hexadecyl methacrylate</td>
<td>-14</td>
</tr>
<tr>
<td>a1-3 2-decyl-tetradecyloxyethyl methacrylate</td>
<td>-25</td>
</tr>
<tr>
<td>a3-1 2-ethylhexyl methacrylate</td>
<td>-40 (*)</td>
</tr>
<tr>
<td>a5-1 n-docoyl methacrylate</td>
<td>45</td>
</tr>
</tbody>
</table>

(*1) less than -40° C.

[0169] Except for the homopolymer consisting the units of (a5-1), the other homopolymers have Tc of less than 5° C.

COPOYMER PREPARATION

Example 1-9, Example 51, and Comparative Example 1-3

[0170] Into a reaction vessel equipped with a stirrer, a heating and cooling device, a thermometer, a dropping funnel and a nitrogen gas inlet tube, 25 parts of a toluene was charged. After the atmosphere in the vessel is replaced with nitrogen gas, the solution consisting of the listed amount (parts) of the listed monomer, DM and ADVN, in the table 2, was added dropwise from the dropping funnel. This addition was made over a period of 4 hours, at 85° C., in the absence of air. Further the reaction mixture was stirred at 85° C. for 2 hours, so that the polymerization proceeds well. Thereafter, toluene was evaporated under reduced pressure at 130° C., for 3 hours. The copolymers, (A-1) to (A-9), (B-1) and (X-1) to (X-3), were obtained. The physical property of the copolymers are shown in table 3.

<table>
<thead>
<tr>
<th>Table 2 Copolymer</th>
<th>Monomer</th>
<th>D</th>
<th>AD</th>
</tr>
</thead>
<tbody>
<tr>
<td>name</td>
<td>a1-1</td>
<td>a1-2</td>
<td>a1-3</td>
</tr>
<tr>
<td>Example 1</td>
<td>A-1</td>
<td>32</td>
<td>36</td>
</tr>
<tr>
<td>2</td>
<td>A-2</td>
<td>20</td>
<td>36</td>
</tr>
<tr>
<td>3</td>
<td>A-3</td>
<td>20</td>
<td>32</td>
</tr>
<tr>
<td>4</td>
<td>A-4</td>
<td>30</td>
<td>38</td>
</tr>
<tr>
<td>5</td>
<td>A-5</td>
<td>20</td>
<td>38</td>
</tr>
<tr>
<td>6</td>
<td>A-6</td>
<td>20</td>
<td>30</td>
</tr>
<tr>
<td>7</td>
<td>A-7</td>
<td>30</td>
<td>35</td>
</tr>
<tr>
<td>8</td>
<td>A-8</td>
<td>30</td>
<td>35</td>
</tr>
<tr>
<td>9</td>
<td>A-9</td>
<td>20</td>
<td>10</td>
</tr>
<tr>
<td>51</td>
<td>B-1</td>
<td>20</td>
<td>80</td>
</tr>
<tr>
<td>C. Example 1</td>
<td>X-1</td>
<td>48</td>
<td>50</td>
</tr>
<tr>
<td>2</td>
<td>X-2</td>
<td>55</td>
<td>45</td>
</tr>
<tr>
<td>3</td>
<td>X-3</td>
<td>40</td>
<td>30</td>
</tr>
</tbody>
</table>

a1-1: methyl methacrylate
a1-2: n-hexadecyl methacrylate
a3-1: n-octadecyl methacrylate
a5-1: n-docoyl methacrylate
d-1: N,N-dimethyl aminoethyl methacrylate
d-2: N,N-diethyl aminoethyl methacrylate
TABLE 3

<table>
<thead>
<tr>
<th>Copolymer name</th>
<th>Mw (x 10^4)</th>
<th>Tc (°C)</th>
<th>HLB</th>
<th>SP (°C)</th>
<th>F</th>
</tr>
</thead>
<tbody>
<tr>
<td>Example 1</td>
<td>2</td>
<td>9.2</td>
<td>40</td>
<td>7.2</td>
<td>3.1</td>
</tr>
<tr>
<td>Example 2</td>
<td>3</td>
<td>9.2</td>
<td>40</td>
<td>8.6</td>
<td>3.2</td>
</tr>
<tr>
<td>Example 3</td>
<td>4</td>
<td>9.2</td>
<td>40</td>
<td>5.6</td>
<td>3.2</td>
</tr>
<tr>
<td>Example 4</td>
<td>5</td>
<td>9.3</td>
<td>40</td>
<td>6.2</td>
<td>3.3</td>
</tr>
<tr>
<td>Example 5</td>
<td>6</td>
<td>9.2</td>
<td>40</td>
<td>8.1</td>
<td>3.0</td>
</tr>
<tr>
<td>Example 6</td>
<td>7</td>
<td>9.2</td>
<td>40</td>
<td>7.6</td>
<td>3.1</td>
</tr>
<tr>
<td>Example 7</td>
<td>8</td>
<td>9.2</td>
<td>40</td>
<td>7.5</td>
<td>3.1</td>
</tr>
<tr>
<td>Example 8</td>
<td>9</td>
<td>9.2</td>
<td>40</td>
<td>9.1</td>
<td>2.7</td>
</tr>
<tr>
<td>Example 9</td>
<td>10</td>
<td>9.0</td>
<td>-17</td>
<td>15.0</td>
<td>1.9</td>
</tr>
<tr>
<td>C. Example 1</td>
<td>2</td>
<td>9.0</td>
<td>-80</td>
<td>22.0</td>
<td>2.5</td>
</tr>
<tr>
<td>C. Example 2</td>
<td>3</td>
<td>9.5</td>
<td>-40</td>
<td>3.7</td>
<td>4.5</td>
</tr>
<tr>
<td>C. Example 3</td>
<td>3</td>
<td>9.2</td>
<td>19</td>
<td>6.0</td>
<td>2.7</td>
</tr>
</tbody>
</table>

(*1) less than 40°C.

[0172] The copolymer (B-1) of the above Example 51 was another copolymer that adding together with the VII of the present invention [(A-1) to (A-9)] into base oil.

VII CONCENTRATES

[0173] 65 parts of each of the copolymers (A-1) to (A-9) and (X-1) to (X-3) was dissolved in 35 parts of the mineral oil (solvent refining oil: kinematic viscosity at 100° C. 2.4 mm²/s). The VII concentrates were obtained.

[0174] 65 parts of the copolymer (B-1) was dissolved in 35 parts of the same mineral oil as the above. The copolymer concentrate was obtained.

LUBE OIL COMPOSITION

Example 10-18, Comparative Example 4-6

[0175] Into a container made by the stainless steel equipped with a stirrer, 0.5 parts of the base oil (B-1) were charged. Each of the concentrates of (A-1) to (A-9) and (X-1) to (X-3) and base oil (kinematic viscosity at 100° C. 3.0 mm²/s, a viscosity index, 117) was added respectively, so as to becoming the final lube oil composition has a kinematic viscosity at 100° C. of 6.0+0.1 mm²/s, and also becoming the final lube oil composition of 100 parts. The lube oil compositions (10-18) of the present invention and the composition of the comparative example (4-6) were obtained. The VI, low temperature viscosity at -40° C. and shear stability of the resultant compositions are given in table 4.

TABLE 4

<table>
<thead>
<tr>
<th>Amount of VII concentrate (part)</th>
<th>Copolymer name</th>
<th>Low Temp. Viscosity (mPa·s)</th>
<th>Shear Stability (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Example 10</td>
<td>17</td>
<td>A-1</td>
<td>229</td>
</tr>
<tr>
<td>11</td>
<td>17</td>
<td>A-2</td>
<td>232</td>
</tr>
<tr>
<td>12</td>
<td>17</td>
<td>A-3</td>
<td>234</td>
</tr>
<tr>
<td>13</td>
<td>17</td>
<td>A-4</td>
<td>232</td>
</tr>
<tr>
<td>14</td>
<td>17</td>
<td>A-5</td>
<td>232</td>
</tr>
<tr>
<td>15</td>
<td>17</td>
<td>A-6</td>
<td>229</td>
</tr>
<tr>
<td>16</td>
<td>17</td>
<td>A-7</td>
<td>228</td>
</tr>
<tr>
<td>17</td>
<td>13</td>
<td>A-8</td>
<td>263</td>
</tr>
<tr>
<td>18</td>
<td>17</td>
<td>A-9</td>
<td>218</td>
</tr>
<tr>
<td>C. Example 4</td>
<td>17</td>
<td>X-1</td>
<td>208</td>
</tr>
<tr>
<td>5</td>
<td>Not dissolved</td>
<td>X-2</td>
<td>—</td>
</tr>
<tr>
<td>6</td>
<td>17</td>
<td>X-3</td>
<td>231</td>
</tr>
</tbody>
</table>

(*1) more than 400,000 mPa·s

[0176] The compositions 10 to 18 are inventive examples and the compositions 4-6 are comparative examples. The compositions 10 to 18 have higher VI and lower low-temperature viscosity. The composition 4 shows lower VI. The X-2 in the composition 5 did not dissolve into the base oil. The composition 6 shows higher VI, however extremely high low-temperature viscosity.

LUBE OIL COMPOSITION

Example 19-27, Comparative Example 7-9

[0177] The procedure same as the Example 10 was repeated with the exception that the final lube oil composition has a kinematic viscosity at 100° C. of 5.0+0.1 mm²/s. The lube oil compositions (19-27) of the present invention
and the composition of the comparative example (7-9) were obtained. The VI, low-temperature viscosity at \(-40^\circ C\), and shear stability of the resultant composition are given in table 5.

<table>
<thead>
<tr>
<th>Example</th>
<th>VII concentrate (part)</th>
<th>Copolymer name</th>
<th>VI</th>
<th>Low Temp Viscosity (mPa.s)</th>
<th>Shear Stability (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>19</td>
<td>13</td>
<td>A-1</td>
<td>216</td>
<td>5700</td>
<td>9</td>
</tr>
<tr>
<td>20</td>
<td>13</td>
<td>A-2</td>
<td>218</td>
<td>600</td>
<td>9</td>
</tr>
<tr>
<td>21</td>
<td>13</td>
<td>A-3</td>
<td>217</td>
<td>600</td>
<td>9</td>
</tr>
<tr>
<td>22</td>
<td>13</td>
<td>A-4</td>
<td>218</td>
<td>550</td>
<td>9</td>
</tr>
<tr>
<td>23</td>
<td>13</td>
<td>A-5</td>
<td>218</td>
<td>580</td>
<td>9</td>
</tr>
<tr>
<td>24</td>
<td>13</td>
<td>A-6</td>
<td>216</td>
<td>520</td>
<td>9</td>
</tr>
<tr>
<td>25</td>
<td>13</td>
<td>A-7</td>
<td>215</td>
<td>570</td>
<td>9</td>
</tr>
<tr>
<td>26</td>
<td>10</td>
<td>A-8</td>
<td>241</td>
<td>400</td>
<td>20</td>
</tr>
<tr>
<td>27</td>
<td>13</td>
<td>A-9</td>
<td>204</td>
<td>400</td>
<td>10</td>
</tr>
<tr>
<td>7</td>
<td>13</td>
<td>X-1</td>
<td>195</td>
<td>660</td>
<td>12</td>
</tr>
<tr>
<td>8</td>
<td>Not dissolved</td>
<td>X-2</td>
<td>---</td>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td>9</td>
<td>13</td>
<td>X-3</td>
<td>217</td>
<td>&gt;400,000</td>
<td>9</td>
</tr>
</tbody>
</table>

(*1) more than 400,000 mPa.s

[0178] Similar result as the series of the experiments of table 4 was obtained.

What is claimed as new and desired to be secured by letters patent is:
1. A viscosity index improver, which comprises a polymer (A) having a solubility parameter of 8.6-9.4, a crystallizing initiation temperature of equal to or less than \(-15^\circ C\), and a steric hindrance factor (F) of 0-13, said factor F being determined by the following equation:

$$F = 4X + Y$$  \hspace{1cm} (1)

wherein X and Y represent the total numbers of atoms at the 6th position and the 7th position, respectively, in the side chains, counted from the backbone; said polymer (A) having a weight-average molecular weight of 5,000-2,000,000 and comprising units of at least one monomer selected from the group consisting of:
(a) a monomer represented by the general formula:

$$\text{CH}_3\text{C}=-\text{COO}-\text{(AO)}_n\text{R}$$  \hspace{1cm} (2)

wherein \(\text{R}^0\) is hydrogen atom or methyl group, \(\text{R}\) is a \(C_{1-20}\) alkyl group, \(n\) is 0 or an integer of 1-20 giving 0-10 on average, \(\text{A}\) is an alkylene group containing 2-4 carbon atoms, plural \(\text{A}\)'s in case of \(n\) being at least 2 are the same or different, and the polyoxyalkylene moiety (\(\text{AO}\)), in case of the plural \(\text{A}\)'s being different comprises random-wise or block-wise distributed oxyalkylene groups;
(b) an alkyl alkene ether;
(c) an alkene carbonylate; and
(d) a nitrogen-containing unsaturated monomer.

2. The improver of claim 1, wherein said polymer (A) contains units of said monomer (a), said monomer (b) or said monomers (a) and (b) in an amount of at least 30% by weight, with or without 0-45% by weight of units of said monomer (c), 0-12% by weight of units of said monomer (d) and 0-20% by weight of units of another monomer.

3. The improver of claim 1, wherein said polymer (A) is a copolymer (A1), comprising units of at least one monomer (a1) represented by the general formula (2) wherein \(\text{R}\) is a branched alkyl group containing 16-40 carbon atoms.

4. The improver of claim 3, wherein said copolymer (A1) comprises 5-90% by weight of units of said monomer (a1) and 10-60% by weight of units of an alkyl acrylate or methacrylate (a2) containing 1-4 carbon atoms in the alkyl group, with or without 0-85% by weight of units of at least one selected from the group consisting of an alkyl acrylate or methacrylate (a3) containing 8-15 carbon atoms in the alkyl group and a straight-chain alkyl acrylate or methacrylate (a4) containing 16-18 carbon atoms in the alkyl group.

5. The improver of claim 4, wherein said copolymer (A1) further comprises 0.1-10% by weight of units of said monomer (d).

6. The improver of claim 5, wherein said monomer (d) is at least one selected from the group consisting of dimethylaminoethyl acrylate, diethylaminoethyl acrylate, morpholinoethyl acrylate, and corresponding methacrylates.

7. A viscosity index improver, which comprises a copolymer (A11) having a weight-average molecular weight of 5,000-2,000,000, comprising 5-90% by weight of units of at least one monomer (a11) and 5-95% by weight of units of at least one alkyl acrylate or methacrylate other than said monomer (a11): said monomer (a11) being capable of providing a homopolymer having a crystallizing initiation temperature of equal to or less than 5°C and represented by the following general formula:

$$\text{CH}_3\text{C}=-\text{COO}-\text{(AO)}_n\text{R}$$  \hspace{1cm} (2)
wherein R² is hydrogen atom or methyl group, R is a branched alkyl group containing 20-40 carbon atoms, n is 0 or an integer of 1-20 giving 0-10 on average, A is an alkylene group containing 2-4 carbon atoms, plural A's in case of n being at least 2 are the same or different, and the polyoxalkylene moiety (AO)ₙ in case of the plural A's being different comprises random-wise or block-wise distributed oxyalkylene groups.

8. The improver of claim 7, wherein R is represented by the general formula:

$$\text{R}^2 \quad \text{CH} \_ \text{CH} \_ \text{R}^1$$

wherein R¹ and R² are the same or different straight-chain alkyl groups containing 8-18 carbon atoms.

9. The improver of claim 7, wherein said copolymer (A11) has a solubility parameter of 8.6-9.4, a crystallizing initiation temperature of equal to or less than -15°C, and a steric hindrance factor F of 0-10, said factor being defined by the following equation:

$$F = X + Y$$

wherein X and Y represent the total numbers of atoms at the 6th position and the 7th position, respectively, in the side chains, counted from the backbone.

10. The improver of claim 9, wherein said copolymer (A11) has a steric hindrance factor F of 0-10.

11. The improver of claim 7, wherein said copolymer (A11) comprises 5-90% by weight of units of said monomer (a11), and 10-60% by weight of units of an alkyl acrylate or methacrylate (a2) containing 1-4 carbon atoms in the alkyl group, with or without 0-85% by weight of units of at least one selected from the group consisting of an alkyl acrylate or methacrylate (a3) containing 8-15 carbon atoms in the alkyl group, a branched alkyl acrylate or methacrylate (a12) containing 16-19 carbon atoms in the alkyl group, a straight-chain alkyl acrylate or methacrylate (a4) containing 16-18 carbon atoms in the alkyl group and a straight-chain alkyl acrylate or methacrylate (a5) containing 20-40 carbon atoms in the alkyl group.

12. The improver of claim 7, wherein said copolymer (A11) comprises 10-45% by weight of units of 2-decyl-tetradecyl methacrylate, 20-45% by weight of units of methyl methacrylate, and 10-60% by weight of units of a straight-chain alkyl acrylate or methacrylate containing 10-18 carbon atoms in the alkyl group.

13. The improver of claim 7, wherein said copolymer (A11) further comprises 0.1-10% by weight of units of a nitrogen-containing unsaturated monomer (d).

14. The improver of claim 13, wherein said monomer (d) is at least one selected from the group consisting of N,N-dimethylaminoethyl acrylate, N,N-dimethylaminoethyl acrylate, dimethyloctyl amine acetate, and corresponding methacrylates.

15. A viscosity improver concentrate, which comprises 10-90% by weight of said improver of claim 1 and 10-90% by weight of a diluent.

16. A viscosity improver concentrate, which comprises 10-90% by weight of said improver of claim 7, and 10-90% by weight of a diluent.

17. A lube oil composition, which comprises a major amount of a base oil and 0.5-30% by weight of said improver of claim 7.

18. The composition of claim 17, wherein the base oil has a kinematic viscosity of 1-15 mm²/s at 100°C and a viscosity index of at least 80.

19. A lube oil composition, which comprises a major amount of a base oil and 0.5-30% by weight of said improver of claim 7.

20. The composition of claim 19, wherein the base oil has a kinematic viscosity of 1-15 mm²/s at 100°C and a viscosity index of at least 80.


22. A compound of 2-decyl-tetradecyl acrylate.

23. A homopolymer having a weight-average molecular weight of 5,000-2,000,000, comprises units of a compound selecting from the group consisting of the compound of claim 21 and the compound of claim 22.

24. A copolymer, having a weight-average molecular weight of 5,000-2,000,000, comprises 5-95% by weight of units of at least one monomer selecting from the group consisting of: an alkyl methacrylate or an alkyl acrylate other than the compound of claim 21 or claim 22; an alkyl alkenyl ether; an alkenyl carboxylate; and a nitrogen-containing unsaturated monomer.