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(71) Applicant (*for all designated States except US*): **SHELL INTERNATIONALE RESEARCH MAATSCHAPPIJ B.V.** [NL/NL]; Carel van Bylandtlaan 30, NL-2596 HR The Hague (NL).

(72) Inventor; and

(75) Inventor/Applicant (*for US only*): **MITSUI, Hideaki** [JP/JP]; 2-3-2 Daiba, Minato-ku, Tokyo, Tokyo 135-8074 (JP).

(74) Agent: **SHELL INTERNATIONAL B.V.**; Intellectual Property Services, PO Box 384, NL-2501 CJ The Hague (NL).

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(54) Title: LUBRICATING COMPOSITION

(57) Abstract: The present invention provides a lubricating composition comprising a base oil and a poly (meth)acrylate with terminal hydroxyl groups, an amine-based and/or phenolic anti-oxidant and an alkaline earth metal salicylate.



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LUBRICATING COMPOSITION

This invention relates to lubricating compositions and in particular relates to lubricating compositions for which shear stability, oxidative stability and thermal stability are required.

5 Lubricating oils, and gear oils in particular, are used under high load conditions, so that gear oils so used are required to have excellent shear stability. Furthermore, in recent years gear units have become more compact, with the aim of becoming more lightweight, and
10 so the rise in oil temperatures has become higher than ever and good lubricating oils also combining superior oxidative stability and thermal stability have been required.

 Hitherto, to meet these requirements, shear
15 stability has been increased by using, as additives, polymethacrylate viscosity controllers (see Japanese Patent No. 2732187). This alone is not enough for oxidative stability and thermal stability, and really satisfactory lubricating compositions have not been
20 obtained.

 By dint of various experiments and repeated investigations to improve gear oils, the inventors have realised that it is not possible, as mentioned above, to obtain good oxidative stability and thermal stability
25 simply by blending a viscosity controller with superior shear stability into a base oil, but that it is possible to obtain a lubricating composition which has a small amplitude of change in kinetic viscosity and viscosity index even at the times of high temperatures when

oxidation is prone to occur, and which is capable of being used in the same state at all times.

This invention has produced lubricating compositions by blending a poly(meth)acrylate with terminal hydroxyl groups and a phenolic anti-oxidant and/or an amine-based anti-oxidant and an alkaline earth metal salicylate and/or an alkaline earth metal phenate in a synthetic and/or mineral oil base oil.

The lubricating compositions of this invention are lubricating compositions with excellent shear stability and also noticeably good oxidative stability and thermal stability. In particular, because the amplitude of changes in kinetic viscosity and viscosity index is small even at times of high-temperature oxidation, and a good balance of various functions such as lubrication of, for example, gears and maintenance of high shear stability is provided, it is possible to use them for long periods in the same state at all times.

Also, these lubricating compositions can be used not only in gear oils but with broader effectiveness in industrial lubricating oils such as gearbox oils such as AT (Automatic Transmission) oils, MT (Manual Transmission) oil and CVT (Continuously Variable Transmission) oils and internal combustion engine lubricating oils for diesel engines, petrol engines, gas engines and so on.

The aforementioned base oil is not specially limited and it is possible to use, for example, mineral oils and synthetic oils, or mixtures of these. Those preferred are high-viscosity-index mineral oils with a viscosity index of 90 - 160 (ASTM D2270), hydrocarbon-based synthetic oils and ester-based synthetic oils. Also, the preferred cloud point of the base oil (JIS K2269) is -5°C or below,

and preferably from -15°C to -70°C . If the cloud point is within this range, there will be little separation of wax and the low-temperature viscosity will be good. In addition, the kinetic viscosity of the base oil is preferably from 1 to 14 mm^2/s at 100°C (ASTM D445).

The base oil used here, if a mineral oil, may be either a solvent refined oil or a hydrorefined oil, or a mixture thereof. As regards the aromatic component ($\%C_A$) based on ring analysis, it typically is not more than 5, but preferably not more than 3 and even more preferably not more than 2.

The aforementioned synthetic oils include - apart from Fischer-Tropsch derived base oils - lubricating base oils which have been treated by special processes including the de-waxing process which isomerises and removes specific wax fractions and the hydrofinishing process. These synthetic oils preferably have a viscosity index of not less than 130, a paraffin component ($\%C_P$) according to ring analysis of not less than 90%, and a CCS viscosity at -35°C of not more than 3,000 mPas. By selecting suitable lubricating-oil additives and incorporating them in these synthetic oils, it is possible to obtain a lubricating composition which has even higher shear stability and higher oxidative stability.

The aforementioned poly(meth)acrylate with terminal hydroxyl groups is preferably a copolymer, and is more preferably a polymer which takes as its essential constituent monomers an alkyl (meth)acrylate having alkyl groups of 1 - 20 carbons and a hydroxyl-containing vinyl monomer.

As specific examples of the aforementioned alkyl (meth)acrylate (a) having alkyl groups with 1 - 20 carbons, mention may be made of

(a1) Alkyl (meth)acrylates having alkyl groups with 1 - 4 carbons:
for example, methyl (meth)acrylate, ethyl (meth)acrylate, n- or iso-propyl (meth)acrylate and n-, iso- or sec-butyl (meth)acrylate

(a2) Alkyl (meth)acrylates having alkyl groups with 8 - 20 carbons:

for example, n-octyl (meth)acrylate, 2-ethylhexyl (meth)acrylate, n-decyl (meth)acrylate, n-isodecyl (meth)acrylate, n-undecyl (meth)acrylate, n-dodecyl (meth)acrylate, 2-methylundecyl (meth)acrylate, n-tridecyl (meth)acrylate, 2-methyldodecyl (meth)acrylate, n-tetradecyl (meth)acrylate, 2-methyltridecyl (meth)acrylate, n-pentadecyl (meth)acrylate, 2-methyltetradecyl (meth)acrylate, 2-hexadecyl (meth)acrylate, and n-octadecyl (meth)acrylate, n-eicosyl (meth)acrylate, n-docosyl (meth)acrylate, and methacrylates of Dobanol 23 [a mixture of 12-carbon and 13-carbon oxoalcohols made by Mitsubishi Kagaku Ltd] and Dobanol 45 [a mixture of 13-carbon and 14-carbon oxoalcohols made by Mitsubishi Kagaku Ltd]

(a3) Alkyl (meth)acrylates having alkyl groups with 5 - 7 carbons:
for example, n-pentyl (meth)acrylate and n-hexyl (meth)acrylate.

Of the aforementioned (a1) - (a3), those preferred are substances that belong to (a1) and (a2). Most preferred are the substances of (a2). Also, among those of the aforementioned (a1), those preferred, from the standpoint of viscosity index, are those with alkyl

groups with 1 - 2 carbons. Further, among those of the
aforementioned (a2), those preferred, from the standpoint
of solubility in the base oil and low-temperature
characteristics, are those with alkyl groups with 10 - 20
5 carbons, and more preferably those with 12 - 14 carbons.

The hydroxyl-containing vinyl monomer (b) which
forms the copolymer with the aforementioned alkyl
(meth)acrylate having alkyl groups of 1 - 20 carbons is a
vinyl monomer containing one or more (preferably one or
10 two) hydroxyl groups in each molecule. As specific
examples, mention may be made of

(b1) Hydroxyalkyl (2 - 6 carbons) (meth)acrylates):
for example, 2-hydroxyethyl (meth)acrylate, 2 or 3-
hydroxypropyl (meth)acrylate, 2-hydroxybutyl
15 (meth)acrylate and 1-methyl-2-hydroxyethyl (meth)acrylate

(b2) Mono- or di-hydroxyalkyl (1 - 4 carbons)
(meth)acrylamides:
for example, N,N-dihydroxymethyl (meth)acrylamide, N,N-
dihydroxypropyl (meth)acrylamide and N,N-di-2-
20 hydroxybutyl (meth)acrylamide

(b3) Vinyl alcohols (formed by hydrolysis of vinyl
acetate units)

(b4) Alkenols of 3 - 12 carbons:
for example, (meth)allyl alcohol, isocrotyl alcohol, 1-
25 octenol and 1-undecenol

(b5) Alkene diols of 4 - 12 carbons:
for example, 1-butene-3-ol, 2-butene-1-ol and 2-butene-
1,4-diol

(b6) Hydroxyalkyl (1 - 6 carbons) alkenyl (3 - 10
30 carbons) ethers:
for example, 2-hydroxyethylpropenyl ether

(b7) Hydroxyl-containing aromatic monomers:
for example, o-, m- or p-hydroxystyrene

(b8) Polyhydric (3 - 8 valence) alcohols:

for example, alkane polyols, intramolecular or intermolecular dehydrates thereof, alkenyl (3 - 10 carbons) ethers or (meth)acrylates of sugars (e.g. glycerine, pentaerythritol, sorbitol, sorbitan, diglycerol, sucrose) (e.g. sucrose (meth)acrylate)

(b9) Vinyl monomers containing polyoxyalkylene chains and hydroxyl groups:

for example mention may be made of mono(meth)acrylates or mono(meth)allyl ethers of polyoxyalkylene glycols (2 - 4 alkylene group carbons, degree of polymerisation 2 - 50) or polyoxyalkylene polyols {polyoxyalkylene ethers of the aforementioned 3 - 8 valence alcohols (alkylene group carbons 2 - 4, degree of polymerisation 2 - 100)} {for example, polyethylene glycol (degree of polymerisation 2 - 9) mono(meth)acrylate, polypropylene glycol (degree of polymerisation 2 - 12) mono(meth)acrylate or polyethylene glycol (degree of polymerisation 2 - 30) mono(meth)allyl ether}.

Of the aforementioned (b1) - (b9), those preferred, from the standpoint of viscosity index improvement effect, are (b1), especially 2-hydroxyethyl methacrylate.

The respective proportions of the monomers which constitute the aforementioned copolymer of the aforementioned hydroxyl-containing poly(meth)acrylate are, from the standpoint of the viscosity index, preferably as follows.

The lower limit of the aforementioned constituent (a) is preferably 50% by mass and more preferably 75% by mass. The upper limit is preferably 95% by mass and more preferably 90% by mass.

The lower limit of the aforementioned constituent (b) is preferably 5% by mass, more preferably 7% by mass

and even more preferably 11% by mass. The upper limit is preferably 50% by mass, more preferably 30% by mass and even more preferably 25% by mass.

For the aforementioned (a), it is possible to use as appropriate (a1), (a2) and (a3) together. In such cases, the lower limit of the aforementioned (a1) is preferably 0% by mass and more preferably 1% by mass. The upper limit is preferably 20% by mass and more preferably 10% by mass.

The lower limit of the aforementioned (a2) is preferably 50% by mass and more preferably 70% by mass. The upper limit is preferably 95% by mass and more preferably 90% by mass.

Also, the lower limit of the aforementioned (a3) is preferably 0% by mass and more preferably 1% by mass. The upper limit is preferably 20% by mass and more preferably 10% by mass.

The lower limit of the total of the aforementioned (a) + (b) is preferably 55% by mass and more preferably 82% by mass. The upper limit is preferably 100% by mass.

It is possible to copolymerise other monomers together with the aforementioned (a) and (b) in the aforementioned hydroxyl-containing poly(meth)acrylate copolymer. Such polymers include monomers (c) containing nitrogen atoms. Specific examples include:

(c1) Monomers containing nitro groups: for example, 4-nitrostyrene

(c2) Vinyl monomers containing primary - tertiary amino groups: for example,

(c2-1) Vinyl monomers containing primary amino groups: for example, alkenyl amines of 3 - 6 carbons [(meth)allyl amine, crotyl amine and so on], aminoalkyl

(2 - 6 carbons) (meth)acrylates [aminoethyl
(meth)acrylate and so on]

(c2-2) Vinyl monomers containing secondary amino
groups: for example, alkyl (1 - 6 carbons) aminoalkyl (2
5 - 6 carbons) (meth)acrylates [t-butylaminoethyl
methacrylate, methylaminoethyl (meth)acrylate, and so
on], diphenylamine (meth)acrylamides [4-diphenylamine
(meth)acrylamide, 2-diphenylamine (meth)acrylamide and so
on], 6 - 12-carbon dialkenylamines [di(meth)allylamine
10 and so on]

(c2-3) Vinyl monomers containing tertiary amino
groups: for example, dialkyl (1 - 4 carbons) aminoalkyl
(2 to 6 carbons) (meth)acrylates [dimethylaminoethyl
(meth)acrylate, diethylaminoethyl (meth)acrylate, and so
15 on], dialkyl (1 - 4 carbons) aminoalkyl (2 - 6 carbons)
(meth)acrylamides [dimethylaminoethyl (meth)acrylamide,
diethylaminoethyl (meth)acrylamide, dimethylaminopropyl
(meth)acrylamide and so on], aromatic vinyl monomers
containing tertiary amino groups [N,N-
20 dimethylaminostyrene and so on]

(c2-4) Vinyl based monomers containing nitrogen-
containing heterocycles: [morpholinoethyl (meth)acrylate,
4-vinylpyridine, 2-vinylpyridine, N-vinylpyrrol, N-
vinylpyrrolidone, N-vinylthiopyrrolidone and so on]

(c3) Amphoteric vinyl monomers:
for example, N-(meth)acryloyl oxy (or amino) alkyl (1 -
10 carbons) N,N-dialkyl (1 - 5 carbons) ammonium-N-alkyl
(1 - 5 carbons) carboxylates (or sulphates), for example
N-(meth)acryloyl oxyethyl N,N-dimethylammonium-N-methyl
30 carboxylate, N-(meth)acryloyl aminopropyl N,N-
dimethylammonium-N-methyl carboxylate, and N-
(meth)acryloyl oxyethyl N,N-dimethylammoniumpropyl
sulphate, and so on

(c4) Monomers containing nitrile groups; for example, (meth)acrylonitrile.

Such monomers also include aliphatic hydrocarbon based vinyl monomers (d). For example, they include
5 alkenes of 2 - 20 carbons [ethylene, propylene, butene, isobutylene, pentene, heptene, diisobutylene, octane, dodecene, octadecene and so on], and alkadienes of 4 - 12 carbons [butadiene, isoprene, 1,4-pentadiene, 1,6-heptadiene, 1,7-octadiene and so on].

10 Further, there are alicyclic hydrocarbon based vinyl monomers (e): for example, cyclohexene, (di)cyclopentadiene, pinene, limonene, indene, vinylcyclohexene, and ethylidene bicycloheptene.

Also, there are aromatic hydrocarbon based vinyl
15 monomers (f): for example, styrene, α -methylstyrene, vinyltoluene, 2,4-dimethylstyrene, 4-ethylstyrene, 4-isopropylstyrene, 4-butylstyrene, 4-phenylstyrene, 4-cyclohexylstyrene, 4-benzylstyrene, 4-crotylbenzene and 2-vinylnaphthalene.

20 And there are vinyl esters, vinyl ethers or vinyl ketones (g): for example, vinyl esters of 2 - 12-carbon saturated fatty acids [vinyl acetate, vinyl propionate, vinyl butyrate, vinyl octanate and so on], 1 - 12-carbon alkyl, aryl or alkoxyalkyl vinyl ethers [methylvinyl
25 ether, ethylvinyl ether, propylvinyl ether, butylvinyl ether, 2-ethylhexylvinyl ether, phenylvinyl ether, vinyl 2-methoxyethyl ether, vinyl 2-butoxyethyl ether and so on], and 1 - 8-carbon alkyl or aryl vinylketones [methylvinylketone, ethylvinylketone, phenylvinylketone
30 and so on].

Further, there are unsaturated polycarboxylic acid esters (h): for example mention may be made of alkyl, cycloalkyl or aralkyl esters of unsaturated

polycarboxylic acids. These include 1 - 8-carbon alkyl diesters of unsaturated dicarboxylic acids such as maleic acid, fumaric acid, itaconic acid and so on [dimethyl maleate, dimethyl fumarate, diethyl maleate, dioctyl maleate and so on].

Also, there are vinyl monomers containing polyoxyalkylene chains (not containing hydroxyl groups) (i): for example, it is possible to use mono(meth)acrylates of monoalkyl (1 - 18 carbons) ethers of polyoxyalkylene glycols (2 - 4-carbon alkylene groups, degree of polymerisation 2 - 50) or polyoxyalkylene polyols [polyoxyalkylene ethers of the aforementioned 3 - 8 valence alcohols (2 - 4-carbon hydroxyl groups, degree of polymerisation 2 - 100)] [for example, methoxypolyethylene glycol (molecular weight 110 - 310) (meth)acrylate, lauryl alcohol ethylene oxide adduct (2 - 30 mol) (meth)acrylate, and so on].

And there are carboxyl-containing vinyl monomers (j): for example, vinyl monomers containing unsaturated monocarboxylic acids [(meth)acrylic acid, α -methy(meth)acrylic acid, crotonic acid, cinammic acid and so on], monoalkyl (1 - 8 carbons) esters of unsaturated dicarboxylic acids [maleic acid monoalkyl esters, fumaric acid monoalkyl esters, itaconic acid monoalkyl esters and so on] or two or more carboxyl groups; for example it is possible to use for copolymerisation monomers maleic acid, fumaric acid, itaconic acid, citraconic acid and so on.

Of the aforementioned additional monomers (c), (d), (e), (f), (g), (h), (i) and (j), those preferred are (c), and two or more kinds of (c) can be used together. Of the aforementioned (c), those preferred are (c2), with a

further preference for dimethylaminoethyl (meth)acrylate and diethylaminoethyl (meth)acrylate.

They are oil-soluble copolymers in which the lower limit of the weight-average molecular weight of these hydroxyl-containing poly(meth)acrylates is 3,000 but 5,000 is preferable, 8,000 is more preferable and 10,000 is especially preferable. The upper limit is 500,000, but 50,000 is preferable, 40,000 is more preferable, 35,000 is especially preferable and 30,000 is extremely preferable.

If the mass-average molecular weight is within the aforementioned range, it is possible to impart good shear stability. This mass-average molecular weight is according to gel permeation chromatography (GPC), and is obtained by conversion to polystyrene.

Also, the aforementioned mass-average molecular weight can be adjusted by means of temperature at time of polymerisation, monomer concentration (solvent concentration), amount of catalyst or amount of chain transfer agent.

The polydispersity (M_w/M_n) of this hydroxyl-containing poly(meth)acrylate is preferably 1 - 2.5, but 1.2 - 2 is preferable and 1.5 - 1.7 is especially preferable. If the polydispersity is small the shear stability is better. M_n is obtained in the same way as M_w , viz. by GPC.

In the case of the solubility parameter, the lower limit is preferably 8.6 but 9.2 is more preferable and 9.3 is especially preferable. The upper limit is preferably 11, but 10.5 is more preferable and 9.7 is especially preferable. If the solubility parameter is within the aforementioned range, there will be good solubility in the base oil. This solubility parameter

value is calculated according to the Fedors method
(Polym. Eng. Sci. 14 (2), 152, (1974)).

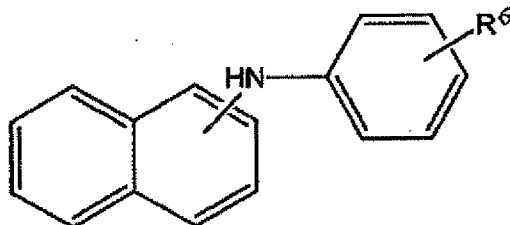
Further, the HLB (Hydrophilic-Lipophilic Balance) of
the hydroxyl-containing poly(meth)acrylate is preferably
5 0.5 - 7. If the HLB is within this range, the
demulsibility will be especially good. It is more
preferable if the HLB is 1 - 6.5, and especially
preferable if it is 1.5 - 6. This HLB number is
calculated on the basis of the HLB of Oda's method which
10 based on organic and inorganic principles ("New
Introduction to Surfactants", published by Sanyo Kasei
Kogyo Co. Ltd., page 128).

Also, the hydroxyl number of hydroxyl-containing
poly(meth)acrylates used as additives is 10 - 100,
15 preferably 20 - 50, and more preferably 25 - 35. The
measurement of the hydroxyl number is the value obtained
by measuring in accordance with JIS K3342 (1961). It
shows the amount of hydroxyl groups in the additive.

It is also possible to add the ordinary type of
20 poly(meth)acrylates of the prior art, which do not
contain hydroxyl groups, at the same time as the
poly(meth)acrylates containing hydroxyl groups. The
amount thereof is encompassed by the mass ratio
poly(meth)acrylates containing hydroxyl groups :
25 poly(meth)acrylates not containing hydroxyl groups being
100:0 - 40:60.

As examples of the aforementioned amine-based anti-
oxidants, mention may be made of aromatic amines such as
phenyl- α -naphthylamine-based compounds and
30 dialkyldiphenylamine-based compounds.

For these phenyl- α -naphthylamine-based compounds it
is preferable to use phenyl- α -naphthylamines as described
by the undermentioned General Formula (1).

Formula 1

[In Formula (1), R⁶ denotes a hydrogen atom, or a linear or branched alkyl group of 1 - 16 carbons.]

If R⁶ in General Formula (1) is an alkyl group, said alkyl group is, as mentioned above, a linear or branched group of 1 - 16 carbons. As specific examples of such alkyl groups, mention may be made of methyl groups, ethyl groups, propyl groups, butyl groups, pentyl groups, hexyl groups, heptyl groups, octyl groups, nonyl groups, decyl groups, undecyl groups, dodecyl groups, tridecyl groups, tetradecyl groups, pentadecyl groups and hexadecyl groups (these alkyl groups may be linear or branched). If the number of carbons in R⁶ exceeds 16, the proportion of the functional groups in the molecules will be small, and the anti-oxidant performance may decrease.

When R⁶ in the aforementioned General Formula (1) is an alkyl group, it is preferable, from the standpoint of excellence of solubility, if it is a branched alkyl group of 8 - 16 carbons, and a branched alkyl group of 8 - 16 carbons derived from oligomers of 3- or 4-carbon olefins is more preferable. As specific examples of 3- or 4-carbon olefins, mention may be made of propylene, 1-butene, 2-butene and isobutylene, but from the standpoint of solubility propylene or isobutylene is preferred.

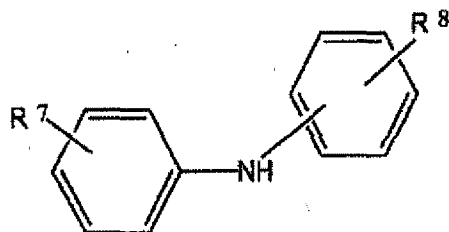
In order to obtain even better solubility, it is preferable if R⁶ is a branched octyl group derived from an isobutylene dimer, a branched nonyl group derived from a propylene trimer, a branched dodecyl group derived from

an isobutylene trimer, a branched dodecyl group derived from a propylene tetramer or a branched pentadecyl group derived from a propylene pentamer. Also, it is especially preferable if it is a branched octyl group derived from an isobutylene dimer, a branched dodecyl group derived from an isobutylene trimer or a branched dodecyl group derived from a propylene tetramer.

Also, if R^6 is an alkyl group, it can be attached at any position to the phenyl group, but it is preferable if it is the p-position relative to the amino group. Further, the amino group can be attached at any position to the naphthyl group, but it is preferable if it is the α -position.

For the phenyl- α -naphthylamines denoted by General Formula (1), commercial products may be used and synthetic compounds may also be used. In the case of synthetic compounds, these may be synthesised easily, using a Friedel-Crafts catalyst, by effecting a reaction with a phenyl- α -naphthylamine and an alkyl halide compound of 1 - 16 carbons or a reaction with a phenyl- α -naphthylamine and a 2- to 16-carbon olefin or a 2- - 16-carbon olefin oligomer. As specific examples of the Friedel-Crafts catalyst it is possible to use metal halides such as aluminium chloride, zinc chloride and iron chloride, and acidic catalysts such as sulphuric acid, phosphoric acid, phosphorus pentoxide, boron fluoride, acid clay and activated clay.

For these dialkyldiphenylamines it is preferable to use dialkyldiphenylamines as described by the undermentioned General Formula (2).

Formula 2

[In Formula (2), R⁷ and R⁸ may be the same or different and each denotes an alkyl group of 1 - 16 carbons.]

As specific examples of the alkyl groups denoted by R⁷ and R⁸, mention may be made of methyl groups, ethyl groups, propyl groups, butyl groups, pentyl groups, hexyl groups, heptyl groups, octyl groups, nonyl groups, decyl groups, undecyl groups, dodecyl groups, tridecyl groups, tetradecyl groups, pentadecyl groups and hexadecyl groups (these alkyl groups may be linear or branched).

Also, in order that even better solubility may be obtained, it is more preferable if each of R⁷ and R⁸ is a isopropyl group derived from propylene, a tert-butyl group derived from isobutylene, a branched hexyl group derived from a propylene dimer, a branched octyl group derived from an isobutylene dimer, a branched nonyl group derived from a propylene trimer, a branched dodecyl group derived from an isobutylene trimer, a branched dodecyl group derived from a propylene tetramer or a branched pentadecyl group derived from a propylene pentamer.

Furthermore, it is most preferable if it is a tert-butyl group derived from isobutylene, a branched hexyl group derived from a propylene dimer, a branched octyl group derived from an isobutylene dimer, a branched nonyl group derived from a propylene trimer, a branched dodecyl group derived from an isobutylene trimer or a branched dodecyl group derived from a propylene tetramer.

If a compound is used in which one or both of R^7 and R^8 is a hydrogen atom, there is a risk that sludge will occur owing to oxidation of said compound itself. Also, if the number of carbons in the alkyl group exceeds 16, the proportion of the functional groups in the molecules will be small, and the anti-oxidant characteristics at high temperatures may decrease.

The alkyl groups denoted by R^7 or R^8 may be attached to any position of the respective phenyl groups, but it is preferable if it is the p-position relative to the amino group, in other words it is preferable if the dialkyldiphenylamine denoted by General Formula (2) is a p,p'-dialkyldiphenylamine.

For the dialkyldiphenylamines denoted by General Formula (2), commercial products may be used and synthetic compounds may also be used. In the case of synthetic compounds, these may be synthesised easily, using a Friedel-Crafts catalyst, by effecting a reaction with a diphenylamine and an alkyl halide compound of 1 - 16 carbons or a reaction with a diphenylamine and a 2- to 16-carbon olefin or an oligomer of these. For the Friedel-Crafts catalyst it is best to use the metal halides or acidic catalysts illustrated in the explanation of the aforementioned phenyl- α -naphthylamine based compounds.

It is possible to use only one kind of the aforementioned aromatic amines denoted by General Formulas (1) and (2), and it is possible to use mixtures of two or more kinds with different structures, but in order to maintain the anti-oxidant characteristics at high temperatures over long periods, it is preferable to use a phenyl- α -naphthylamine as denoted by General Formula (1) and dialkyldiphenylamine as denoted by

General Formula (2) together. The mixing ratio in this case is arbitrary, but is preferably within the range of a mass ratio of 1/10 - 10/1.

The amount of these amine-based anti-oxidants is preferably 0.01% by mass - 5% by mass, but is more preferably 0.05% by mass - 2% by mass. If it is less than 0.01% by mass, the effect is not obtained, and if more than 5% by mass is included, no extra effect is obtained.

As preferred examples of the aforementioned phenolic anti-oxidants which are blended in the lubricating composition, mention may be made of 4,4'-methylenebis(2,6-di-tert-butylphenol), 4,4'-bis(2,6-di-tert-butylphenol), 4,4'-bis(2-methyl-6-tert-butylphenol), 2,2'-methylenebis(4-ethyl-6-tert-butylphenol), 2,2'-methylenebis(4-methyl-6-tert-butylphenol), 4,4'-butylidenebis(3-methyl-6-tert-butylphenol), 4,4'-isopropylidenebis(2,6-di-tert-butylphenol), 2,2'-methylenebis(4-methyl-6-nonylphenol), 2,2'-isobutylidenebis(4,6-dimethylphenol), 2,2'-methylenebis(4-methyl-6-cyclohexylphenol), 2,6-di-tert-butyl-4-methylphenol, 2,6-di-tert-butyl-4-ethylphenol, 2,4-dimethyl-6-tert-butylphenol, 2,6-di-tert- α -dimethylamino-p-cresol, 2,6-di-tert-butyl-4(N,N'-dimethylaminomethylphenol), 4,4'-thiobis(2-methyl-6-tert-butylphenol), 4,4'-thiobis(3-methyl-6-tert-butylphenol), 2,2'-thiobis(4-methyl-6-tert-butylphenol), bis(3-methyl-4-hydroxy-5-tert-butylbenzyl) sulphide, bis(3,5-di-tert-butyl-4-hydroxybenzyl) sulphide, 2,2'-thio-diethylenebis[3-(3,5-di-tert-butyl-4-hydroxyphenyl) propionate], tridecyl-3-(3,5-di-tert-butyl-4-hydroxyphenyl) propionate, pentaerythrityl-tetrakis[3-(3,5-di-tert-butyl-4-hydroxyphenyl) propionate], octyl-3-(3,5-di-tert-butyl-4-hydroxyphenyl) propionate,

octadecyl-3-(3,5-di-tert-butyl-4-hydroxyphenyl) propionate, and octyl-3-(3-methyl-5-tert-butyl-4-hydroxyphenyl) propionate. These may also be used in mixtures of two or more kinds.

5 The amount of these phenolic anti-oxidants is preferably 0.01 - 5% by mass, and more preferably 0.05 - 2% by mass. If it is less than 0.01% by mass, there is no effect, and if more than 5% by mass is included no extra effect can be discerned.

10 Also included in these lubricating compositions are alkaline earth metal sulphonates, alkaline earth metal phenates, alkaline earth metal salicylates and alkaline earth metal naphthenates. For these alkaline earth metals, mention may be made of calcium, and magnesium.
15 These may be used alone or in combinations of two or more kinds. These substances are normally known as metallic detergents.

 Normally, it is preferable to use sulphonates, phenates or salicylates of calcium or magnesium. It is
20 possible to select the base number and amount thereof arbitrarily depending on the kind and purpose of the lubricating oil to which they are applied, but normally it is preferable if the base number is 0 - 500 mgKOH/g by the perchlorate method (ASTM D2986), and the amount is
25 preferably be 0.1 - 10% by mass and more preferably 0.5 - 3% by mass.

 It has been evident that compatibility can be seen between the combinations of anti-oxidants and metallic detergents which are incorporated in the
30 poly(meth)acrylates which have terminal hydroxyl groups and the aforementioned synthetic and/or mineral base oil. Blended combinations of base oil and poly(meth)acrylates with terminal hydroxyl groups and amine-based anti-

oxidants and/or phenolic anti-oxidants and alkaline earth metal salicylates are good. Also, blended combinations of base oil and poly(meth)acrylates with terminal hydroxyl groups and phenolic anti-oxidants and alkaline earth metal salicylates and/or alkaline earth metal phenates are good.

Examples

In order to prepare the Examples and the Comparative Examples shown in Table 1, the following materials were used.

1. Base Oil A: a paraffinic hydrofinished mineral oil in which the kinetic viscosity at 100°C (ASTM D445) was 4.2 mm²/s and the viscosity index was 120 (ASTM D2270) (results of ring analysis according to ASTM-D3238: %C_p = 78, %C_N = 22, %C_A = 0)
2. Base Oil B: a Fischer-Tropsch synthetic GTL (gas-to-liquid)/XHVI-5.2 classed as Group III according to the API base oil classification in which the kinetic viscosity at 100°C was 5.10 mm²/s and the viscosity index was 149
3. Polymethacrylate 1 with terminal hydroxyl groups (OH-PMA 1): such that the hydroxyl number is 49 mgKOH/g, the mass-average molecular weight is approximately 30000 and (a) is 83% by mass and (b) 17% by mass. (The additives used here are diluted in mineral oil, so that the content as polymer is approximately 50%.)
4. Polymethacrylate 2 with terminal hydroxyl groups (OH-PMA 2): such that the hydroxyl number is 47 mgKOH/g, the weight-average molecular weight is approximately 16000 and (a) is 83.5% by mass and (b) 16.5% by mass. (The additives used here are diluted in mineral oil, so that the content as polymer is approximately 50%.)

5. Amine-based anti-oxidant (A1): a dialkyldiphenylamine, the alkyl groups being an octyl group and a butyl group

6. Amine-based anti-oxidant (A2): a phenyl-naphthylamine, the alkyl group being an octyl group

7. Phenolic anti-oxidant (P): octyl-3-(3,5-di-tert-butyl-4-hydroxyphenyl) propionate

8. Calcium (Ca) sulphonate: base number approximately 400 mgKOH/g

9. Calcium (Ca) salicylate: base number approximately 160 mgKOH/g

10. Calcium (Ca) phenate: base number approximately 250 mgKOH/g

Example 1

On the basis of the blend shown in Table 1, 30.00 parts (parts by mass, and likewise hereafter) of polymethacrylate with phosphate ester added at the terminals (OH-PMA 2), 1.25 parts of amine-based anti-oxidant (A2) and 1.25 parts of Ca salicylate were added to 217.50 parts of Base Oil A, and after thorough agitation and mixing a lubricating composition was obtained.

Examples 2 to 5

Each of the lubricating compositions was obtained as per Example 1 on the basis of the blends shown in Table 1.

Comparative Examples 1 to 3

Each of the lubricating compositions was obtained as per Example 1 on the basis of the blends shown in Table 2.

Oxidation Performance Tests

Oxidation performance tests were carried out on the lubricating compositions of the prepared Examples and Comparative Examples.

The oxidation performance tests were heating tests for 60 hours at 165.5°C using the test method as per the oxidative stability tests for internal combustion engine lubricating oil (ISOT) stipulated in JIS K2514. Measurements were made for the following items in respect of each "oil before test" and "oil after test" before and after the tests.

1. 100°C kinetic viscosity (ASTM D445)
2. 40°C kinetic viscosity (ASTM D445)
3. Viscosity index (VI) (ASTM D2270)
4. Acid number (AN) (Units: mgKOH/g) (ASTM D2986)
5. Base number (BN) (Units: mgKOH/g) (ASTM D2986)

Also, assessments were made after further obtaining values for the following items in respect of each "oil after test".

6. Percentage increase in 100°C kinetic viscosity (%)
(ASTM D445)
7. Assessment of percentage increase in 100°C kinetic
viscosity (ASTM D445)

[Assessment criteria] Less than 5.0% "0" (good)

5% or more "X" (bad)

8. Amount of increase in acid number (AN) (ASTM D2986)
9. Assessment of amount of increase in acid number (AN)
(ASTM D2986)

[Assessment criteria] Less than 1.0 "0" (good)

1.0 or more "X" (bad)

Results

The results of the aforementioned tests are shown in Tables 3 and 4.

Discussion

As shown in Table 3, the compositions of Examples 1 - 5 had little variation in 100°C kinetic viscosity before and after the tests, and the percentage increase in 100°C kinetic viscosity was low at -0.5 - 2.3%, so that an assessment of "O" (good) was obtained. Also, the rise in 40°C kinetic viscosity was small, of the order of 2 - 4%, and the viscosity index (VI) decreased by about 6% in Example 5 whereas in the other cases there was virtually no change. The acid number (AN) decreased slightly in Examples 1 and 4 and rose a little in Examples 3 and 5, but the amount of increase in acid number was not so large, and assessment of the amount of increase in each case was satisfactory. Furthermore, the base number (BN) exhibited values of the order of 0.67 - 0.83 before the tests, and the rate of decrease thereof after the tests was smallest in Example of Embodiment 1, at 40%, next highest were Examples 2, 3 and 4, and Example 5 was highest at 85%, but all cases were lower than the 95% of Comparative Example 3. Satisfactory thermal oxidative stability was thus obtained for each of the Examples, and overall the results were good.

On the other hand, in the cases of Comparative Examples 1 and 2, precipitation was already discernible in the fresh oil before the tests on the lubricating compositions, and it was obvious that they could not be used as lubricating oils. Therefore, no further oxidation performance tests were carried out on these. In the case of Comparative Example 3, the percentage increase in 100°C kinetic viscosity was large, at 9.7%, and the assessment was "X" (bad). The 40°C kinetic viscosity also increased 21%. Further, the amount of increase in acid number was large at 3.98 and the assessment there was

"X". The base number (BN) was 0.64 before the test, but after the test it had decreased by about 95%. Therefore, none of the examples in Comparative Examples 1 - 3 gave satisfactory results.

5 From this, it is evident that, given compositions in which a polymethacrylate with terminal hydroxyl groups and an amine-based and/or phenolic anti-oxidant and an alkaline earth metal salicylate are blended with a base oil or in which a polymethacrylate with terminal hydroxyl
10 groups and a phenolic anti-oxidant and a phenolic anti-oxidant and an alkaline earth metal salicylate and/or alkaline earth metal phenate are blended with a base oil, as in the cases of Examples 1 - 5, each combination is satisfactory.

15 On the other hand, it is evident that combinations as in the cases of Comparative Examples 1 and 2 of a polymethacrylate with terminal hydroxyl groups and an amine-based and/or phenolic anti-oxidant and an alkaline earth metal sulphonate in a base oil, or a combination as
20 in the case of Comparative Example 3 of a polymethacrylate with terminal hydroxyl groups and an amine-based anti-oxidant and an alkaline earth metal phenate in a base oil, are not desirable.

Table 1

	Example 1	Example 2	Example 3	Example 4	Example 5
Base oil A	217.50		225.00	225.00	225.45
Base oil B		217.50			
OH-PMA 1			22.50	22.50	22.50
OH-PMA 2	30.00	30.00			
Anti-oxidant A1		1.25	1.25		
Anti-oxidant A2	1.25				
Anti-oxidant P				1.25	1.25
Ca sulphonate					
Ca salicylate	1.25	1.25	1.25	1.25	
Ca phenate					0.80

Table 2

	Comparative Example 1	Comparative Example 2	Comparative Example 3
Base oil A	225.75	225.75	225.45
Base oil B			
OH-PMA 1	22.50	22.50	22.50
OH-PMA 2			
Anti-oxidant A1	1.25		1.25
Anti-oxidant A2			
Anti-oxidant P		1.25	
Ca sulphonate	0.50	0.50	
Ca salicylate			
Ca phenate			0.80

Table 3

	Example 1	Example 2	Example 3	Example 4	Example 5
(Fresh oil before test)					
100°C kinetic viscosity	5.395	6.203	5.229	5.227	5.225
40°C kinetic viscosity	24.68	28.85	23.57	23.52	23.53
Viscosity index (VI)	162	173	162	163	162
Acid number (AN)	0.29	0.29	0.29	0.28	0.11
Base number (BN)	0.81	0.83	0.83	0.80	0.67
(Oil after test)					
100°C kinetic viscosity	5.521	6.318	5.324	5.282	5.199
Ditto % increase	2.3	1.9	1.8	1.1	-0.5
Assessment of ditto % increase	0	0	0	0	0
40°C kinetic viscosity	25.45	29.88	24.38	23.97	24.23
Viscosity index (VI)	163	170	160	162	152
Acid number (AN)	0.28	0.39	0.70	0.26	0.80
Ditto amount of increase	-0.01	0.10	0.41	-0.02	0.69
Assessment of ditto amount of increase	0	0	0	0	0
Base number (BN)	0.49	0.34	0.30	0.40	0.10

Table 4

	Comparative Example 1	Comparative Example 2	Comparative Example 3
(Fresh oil before test)	Precipitate	Precipitate	
100°C kinetic viscosity			5.221
40°C kinetic viscosity			23.52
Viscosity index (VI)			162
Acid number (AN)			0.10
Base number (BN)			0.64
(Oil after test)			
100°C kinetic viscosity			5.73
Ditto % increase			9.7
Assessment of ditto % increase			X
40°C kinetic viscosity			28.46
Viscosity index (VI)			148
Acid number (AN)			4.08
Ditto amount of increase			3.98
Assessment of ditto amount of increase			X
Base number (BN)			0.03

C L A I M S

1. A lubricating composition comprising a base oil and a poly(meth)acrylate with terminal hydroxyl groups, an amine-based and/or phenolic anti-oxidant and an alkaline earth metal salicylate.

5 2. A lubricating composition comprising a base oil and a poly(meth)acrylate with terminal hydroxyl groups, a phenolic anti-oxidant and an alkaline earth metal salicylate and/or alkaline earth metal phenate.

10 3. Lubricating composition according to Claim 1 or 2 wherein said poly(meth)acrylate with terminal hydroxyl groups is a copolymer which contains an alkyl (meth)acrylate having an alkyl group of from 1 to 20 carbons and a hydroxyl-containing vinyl monomer which has one or more hydroxyl groups in each molecule.

15 4. Lubricating composition according to Claim 3 wherein said copolymer comprises from 50 to 95% by mass of the alkyl (meth)acrylate having an alkyl group of from 1 to 20 carbons and from 5 to 50% by mass of the hydroxyl-containing vinyl monomer which has one or more hydroxyl groups in each molecule.

20 5. Lubricating composition according to any of Claims 1 to 4 wherein the weight average molecular weight of said poly(meth)acrylate with terminal hydroxyl groups is from 3,000 to 500,000.

25 6. Lubricating composition according to any of Claims 1 to 5 wherein the polydispersity (Mw/Mn) of the aforementioned poly(meth)acrylate with terminal hydroxyl groups is from 1 to 2.5, the solubility parameter is from 8.6 to 11, the HLB value is from 0.5 to 7 and the hydroxyl number is from 10 to 100.

30

7. Use of the lubricating composition according to any of the preceding Claims for improving one or more of shear stability, thermal stability and oxidative stability.