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(54) Gear and transmission lubricant compositions of improved sludge-dispersibility, fluids comprising the same

(57) A gear or transmission lubricant composition, comprising a major portion of mineral base oil, containing added thereto (A) a phosphorus-containing metal-free organic compound, such as a phosphate ester or amine salt thereof, and (B) an oil-soluble copolymer of (a) an alkyl (meth)acrylate and (b) a N,N-dialkylaminoalkyl (meth)acrylate, shows improved sludge dispersibility, and is useful as automatic transmission fluid.

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BACKGROUND OF THE INVENTION

1. Field of the Invention:

This invention relates to gear and transmission lubricant compositions, having improved sludge-dispersibility, particularly, those useful for automotive gear and transmission fluids.

2. Description of the Prior Art:

Heretofore, in order to improve anti-wear or lubricating qualities and sludge-dispersibility, required for automotive gear and transmission fluids, there have been known those containing added thereto anti-wear or lubricating agents comprising phosphorus-containing organic compound, such as phosphate or phosphite esters or amine salts thereof, together with lower molecular weight dispersants, such as succinimides and benzyl amine. For example, US Patent 4,800,029 discloses an aotomatic transmission fluid (ATF) comprising a solvent-purified 150 neutral oil, containing added thereto an oleamide phosphate as anti-wear agent and polybutenyl succinimide as dispersant.

These fluids containing added thereto phosphorus-containing organic compounds together with lower molecular weight dispersants, however, have drawbacks, such that dispersabilities become insufficient under severe service conditions likely to form larger sludge, encounterd with friction or wear, accompanied with recent tendency of miniturization and output power up of automobiles; and it is desired to improve the dispersibility.

SUMMARY OF THE INVENTION

It is an object of the present invention to provide a gear or transmission lubricant composition having improved sludge-dispersibility.

It is another object of this invention to provide a gear or transmission lubricant composition capable of providing reduced sludge formation.

It is still another object of the invention to provide a gear or transmission lubricant composition capable of maintaining good sludge-dispersibility even at severe service conditions.

It is yet another object of the invention to provide a gear oil or a transmission fluid, particularly ATF, having improved sludge-dispersibility.

Briefly, these and other objects of the present In vention as hereinafter will become more readily apparent have been attained broadly by a gear or transmission lubricant composition, which comprises a major portion of mineral base oil, containing added thereto a minor proportion of (A) at least one phosphorus-containing metal-free organic compound and (B) at least one oil-soluble copolymer containing 92~99 % by weight of monomer unis of (a) alkyl (meth)acrylate and 1~8 % by weight of monomer unis of (b) N,N-dialkylaminoalkyl (meth)acrylate.

[In the above and hereinafter, (meth)acrylate represents acrylate and/or methacrylate; and similar expressions are used hereinafter].

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

Base Oil

Suitable base oils used in the present invention include mineral oils, having a viscosity of usually 1~50 cSt (centistokes), preferably 2~30 cSt at 100 °C. Base oils having a viscosity higher than 50 cSt give rise to energy loss because of too high viscosity resistance. Oils of less than 1 cSt are liable to result in evaporation during use at elevated temperature and to cause seizing on account of shortage of oil film exposed to extreme pressure at lubricationg parts. Viscosity index (hereinafter referred to as VI) of base oils is generally at least 60, preferably at least 70. Oils of VI less than 60 do not provide satisfactory viscosity-temperature properties. Illustrative of suitable base oils are 100 neutral oil, 150 neutral oil, 300 neutral oil, 500 neutral oil, 150 bright stoch and the like.

(A) Phosphorus-containing Organic Compound

Suitable phosphorus-containing metal-free organic compound (A) include phosphate esters, phosphite esters, phosphonate esters, and amine salts of these esters; as well as mixtures of two or more of these

compounds.

Examples of these compounds include ones represented by any of the following formulae (1), (2), (3) and (4).

$$O=P(OR)_p(OH)_{3-p} \quad (1)$$

$$O=P(OR)_q(OH)_{3-q} \cdot NH_rR'_{3-r} \quad (2)$$

$$P(OR)_p(OH)_{3-p} \quad (3)$$

$$P(OR)_q(OH)_{3-q} \cdot NH_rR'_{3-r} \quad (4)$$

In the formulae (1), (2), (3) and (4), p is an integer of 1, 2 or 3; q and r are independently integers of 1 or 2.

R and R' are independently selected from the group consisting of saturated or unsaturated alkyl groups containing at least 4 carbon atoms, aryl groups and alkyl-subsituted aryl groups. Examples of R and R' include straight-chain or branched, saturated or unsaturated alkyl groups (aliphatic hydrocarbyl groups) containing 4~30 or more, preferably 4~20 carbon atoms, such as n-, iso-, sec- and t-butyl, hexyl, octyl, 2-ethylhexyl, decyl, dodecyl, tridecyl, tetradecyl, hexadecyl, octadecyl, eicocyl, and oleyl groups; aryl groups, such as phenyl and naphthyl groups; and aryl groups subsituted substituted with one or more alkyl groups containing 1~20, preferably 1~10 carbon atoms in the alkyl group, such as tolyl group. These alkyl, aryl and alkyl-subsituted aryl groups may be ether group-containing ones, such as lauroxyethyl, lauroxypropyl, oleoxyethyl groups.

Illustrative examples of these compounds of the following formulae (1), (2), (3) and (4) are as follows:

(1) mono-, di- and tri-alkyl and/or aryl phospates, such as mono-oleyl phosphate, tricrezyl phosphate, and dibutyl lauroxypropyl phosphate;

(2) salts of mono- or di-alkyl and/or aryl phospates as above, with mono- or di-alkyl amine, such as di-2-ethylhexyl amine;

(3) mono-, di- and tri-alkyl and/or aryl phospites, such as di-n-butyl phospite, tributyl phospite,

(4) salts of mono- or di-alkyl and/or aryl phospites as above, with mono- or di-alkyl amine, such as di-2-ethylhexyl amine.

Phosphorus-containing compounds, as written in C.J.Boner "Gear and Transmission Lubricants" (1964 Reinhold Publishing Corp.), page 94, Table 3.8, may also be used.

Among these phosphorus-containing metal-free organic compound (A), preferred are those of the formula (1), particularly alkyl phosphate containing 4~18 carbon atoms in the alkyl group. The most preferred is mono-oleyl phosphate.

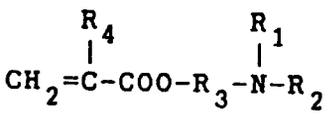
The amount of the phosphorus-containing metal-free organic compound (A), usually 0.01~5 %, preferably 0.1~3 %, based on the weight of the lubricant composition.

(B) Oil-soluble Copolymer

Suitable alkyl (meth)acrylates (a), constituting said oil-soluble copolymer (B), are ones contains 1~24 carbon atoms in the alkyl group; and include, for example: (a_1) C8~20 alkyl (meth)acrylates, such as octyl, decyl, dodecyl, tridecyl, tetradecyl, hexadecyl, octadecyl and eicocyl (meth)acrylates; (a_2) C1~4 alkyl (meth)acrylates, such as methyl, ethyl, propyl and butyl (meth)acrylates; (a_3) C5~7 alkyl (meth)acrylates, such as pentyl, hexyl and heptyl (meth)acrylates; (a_4) C21~24 alkyl (meth)acrylates, such as Nafol 20+ and Nafol 22+ (produced by Kondea-Chemie; and combinations of two or more of them.

Among these, preferred are (a_1) (particularly decyl methacrylate and dodecyl methacrylate), and combinations thereof with (a_2) (particularly methyl methacrylate).

Suitable N,N-dialkylaminoalkyl (meth)acrylate (b), constituting said oil-soluble copolymer (B), include one by the following formula (5):



(5)

wherein R_1 and R_2 are the same or different alkyl groups containing not more than 10 carbon atoms, R_3 is an alkylene group containing 2~10 carbon atoms, and R_4 is hydrogen atom or methyl group.

Illustrative of (b) are N,N-dimethylaminoethyl (meth)acrylates, N,N-diethylaminoethyl (meth)acrylates, N,N-diethylaminohexyl (meth)acrylates, N,N-dimethylaminopropyl (meth)acrylates, N,N-dibutylaminooctyl (meth)acrylates, and mixtures of two or more of them. Among these, preferred are N,N-dimethylaminoethyl methacrylate and N,N-diethylaminoethyl methacrylate.

Said oil-soluble copolymer (B) may contain monomer unis of (c) one or more of N-vinyl-pyrrolidone and morpholinoalkyl (meth)acrylates, to improve sludge dispersibility. Suitable morpholinoalkyl (meth)acrylates include ones containing 2~4 or more carbon atoms in the alkylene, such as morpholinoethyl and morpholinopropyl (meth)acrylates. Among these, preferred is N-vinylpyrrolidone.

Said copolymer (B) may further contain monomer unis of (d) one or more additional monomers. Exemplery of additional monomers (d) are aromatic vinyl compounds, such as styrene and vinyltoluene; esters (such as alkyl esters containing not more than 20 carbon atoms in the alkyl group) of unsaturated dicarboxylic acid (such as maleic, fumaric and itaconic acids), for example, dibutyl, dioctyl and dilauryl maleates, and dihexyl, dihexadecyl and dioctadecyl fumarates; and vinyl esters (ones containing not more than 5 carbon atoms in the alkyl group), such as vinyl acetate and vinyl propionate; and so on. Among these, preferred is styrene, in view of VI and bodying effects.

The contents of these monomers unis of (a), (b), (c) and (d) in said oil-solubult copolymer (B) are as follows:

	Usually	preferably
(a)	92~99 %	94~98 %
(a_1)	52~99 %	64~93 %
(a_2)	0~40 %	5~30 %
(b)	1~8 %	2~6 %
(c)	0~10 %	~ %
(d)	0~30 %	0~20 %

In the above and hereinafter, % represents % by weight.

Copolymer (B) can be produced by usual polymerization thechniques, for instance, by radical polymerization of (a) and (b) with or without (c) and/or (d), within a solvent, such as mineral oil. There may be used any polymerization catalysts, for example, azo compounds, such as azobis-isobutyrenitrile (hereinafter referred to as AIBN) and azobisvaleronitrile, and peroxides, such as benzoyl peroxide, cumyl peroxide and lauryl peroxide, with or without chain transfer agents, such as mercaptans (lauryl mercaptan and the like).

Said copolymer (B) is oil-soluble and is effective as a VI improver in addition to dispersant. To attain these effects, (B) has a weight-average molecular weight (hereinafter referred to as $\overline{Mw}$), as measured by GPC (gel permeation chromatography) using calibration curve of polystyrene, of generally 20,000~200,000, preferably 30,000~150,000. Polymer of too high molecualr weight causes degradation to form shorter chain polymer when subjected to shearing and cannot maintain necessary viscosity and VI for a long period of time. Polymer of too low molecular weight is to be used in a larger amount in order to attain sufficient viscosity.

The gear or transmission lubricant composition of the present invention, usually contains, as a practical use level of the lubricant, 0.01~5 %, preferably 0.05~3 %, more preferably 0.1~2 % of said phosphorus-containing organic compound (A) and 1~30 %, preferably 2~25 %, more preferably 3~20 % of said oil-soluble copolymer (B).

Concentrate containing (A) and/or (B) in higher concentration than the above range may be prepared, and this is diluted to lebel of practical use.

The composition of this invention may further contains one or more additives, usually used in gear and transmission lubricants. Such additives include, for example, detergents, such as sulfonates, salicylates, phenates and naphthenates; dispersants, such as alkenylsuccinimides and Mannich condensates; anti-oxidants, such as thiophosphates, amines and hindered phenols; oiliness additives, such as fatty acids and esters thereof; antiwear agent, other than (A), such as molybdenum dithiophosphate and molybdenum carbamate; and extreme pressure agents, such as sulfur-containing compounds, phosphorus-containing compounds and chlorine-containing compounds. These additives can be used in such amounts : 0~10 % of the detergent, 0~10 % of the dispersant, 0~5 % of the anti-oxidant, 0~3 % of the oiliness additive, 0~10 % of the antiwear agent, and 0~10 % of the extreme pressure agent.

Compositions of the invention, containing said phosphorus-containing organic compound (A) and said oil-soluble copolymer (B), are useful as gear and transmission lubricants, particularly automotive gear lubricants. Excellent effects can be attained especially when used as automatic transmission fluid for torque converters.

Having generally described the invention, a more complete understanding can be obtained by reference to certain specific examples, which are included for purposes of illustration only and are not intended to be limiting unless otherwise specified.

In the following examples, parts represents parts by weight.

Preparation of Copolymers

Into a reaction vessel equipped with a stirrer, a thermometer and a condensor, 150 parts of a mineral oil (100 neutral oil) were charged and heated to 70 °C under an atmosphere of nitrogen. Then, thereto were added dropwise the monomers (parts) written in Table 1 together with 1.7 parts of AIBN and 2.0 parts of lauryl mercaptan over 2 hours at the temperature, followed by heating to 100 °C for 3 hours to complete the polymerization to obtain a solution of copolymer having $\overline{Mw}$ as written in Table 1.

Table 1

Copolymer	B1	B2	B3	B4	B5	b1	b2	b3
Lauryl methacrylate	250	150	150	246	250	250	261	226
Hexadecyl methacrylate	—	—	85	—	—	—	—	—
Octadecyl methacrylate	23	23	—	23	23	23	27	23
Decyl acrylate	—	96	—	—	—	—	—	—
Methyl methacrylate	70	—	70	70	55	70	70	70
Butyl methacrylate	—	70	—	—	—	—	—	—
Dimethylaminoethyl methacrylate	18	—	—	—	15	—	3	42
Diethylaminoethyl acrylate	—	22	—	—	—	—	—	—
Dibutylaminoethyl methacrylate	—	—	18	—	—	—	—	—
Dimethylaminopropyl methacrylate	—	—	—	15	—	—	—	—
Morpholinoethyl methacrylate	—	—	—	7	—	18	—	—
N-vinyl-pyrrolidone	—	—	—	—	18		—	—
Styrene	—	—	30	—	—	—	—	—
$\overline{Mw}$, $\times 10^3$	40	61	100	90	88	73	100	98

Examples 1 to 10, and Comparative Examples 1 to 6

According to the following Formulation I or II (%), mineral oil compositions were prepared.

Formulation	I	II
Each copolymer solution	10	18
Oleyl amine salt of dilauryl phosphate	1	-
Octyl amine salt of dioleyl phosphate	-	1
Polybutenylsuccinimide (Hitec E638*)	3	-
Polyolefin sulfide (TLA369, produced by Texaco)	-	5
Perbasic calcium sulfonate (Hitec E611*)	1	1
Dialkylzinc dithiophosphate (Amoco 194)	0.3	-
Dialkylzinc dithiophosphate (Amoco 198)	-	0.5
2,6-di-tert-butyl-p-crezole (Lubrizol 817)	0.2	-
A mineral oil (100 neutral)	84.5	74.5

(Notes) *:produced by Ethyl Cooper.

Resistance to oxidation of each composition was evaluated in accordance with JIS K2514, measuring the amounts of sludge (pentane-insuluble matter, %) of Methods A and B. Method A represents the amount of sludge obtained by centrifuging the oil after the test, and Method B represents the amount of sludge obtained by centrifuging the oil to which a flocculant was added after the test. The amounts of Methds A and B show resistance to oxidation, and the difference between the amounts of Methds A and B means sludge dispersability.

The results were as shown in Table 2.

Table 2

Example		Example					Comparative Example		
No.		1	2	3	4	5	1	2	3
Copolymer		B1	B2	B3	B4	B5	b1	b2	b3
Formulation		I	I	I	I	I	I	I	I
Resistance to Oxidation	Method A	0.02	0.02	0.05	0.03	0.05	0.91	1.08	2.96
	Method B	0.33	0.32	0.49	0.35	0.38	0.95	1.13	3.01
	Difference	0.31	0.30	0.44	0.32	0.30	0.04	0.05	0.05
Example		Example					Comparative Example		
No.		6	7	8	9	10	4	5	6
Copolymer		B1	B2	B3	B4	B5	b1	b2	b3
Formulation		II	II	II	II	II	II	II	II
Resistance to Oxidation	Method A	0.05	0.03	0.06	0.03	0.05	0.90	1.23	2.99
	Method B	0.35	0.32	0.36	0.39	0.35	0.94	1.28	3.05
	Difference	0.30	0.29	0.30	0.36	0.30	0.04	0.05	0.06

As apparent from Tables 1 and 2, compositions of the present invention provided extremely small amount of sludge and showed excellent sludge dispersibility and resistance to oxidation.

Compositions of this invention, when used as gear and transmission lubricants, particularly automatic transmission fluid for torque converters, can attain excellent sludge dispersibility with remarkably reducing sludge formation.

Claims

1. A gear or transmission lubricant composition, which comprises
a major portion of mineral base oil, having a viscosity of 1~50 cSt. at 100 °C and having a viscosity index of at least 60; containing, based on the weight of the composition,
0.01~5 % of (A) at least one phosphorus-containing metal-free organic compound, selected from the group consisting of phosphate esters, phosphite esters, phosphonate esters, and amine salts of these esters;
and 1~30 % of (B) at least one oil-soluble copolymer containing 92~99 %, preferably 94~98 % by weight of monomer unis of (a) alkyl acrylate or methacrylate preferavly containing 1~24 carbon atoms in the alkyl group, and 1~8 %, preferably 2~6 % by weight of monomer unis of (b) N,N-dlalkylaminoalkyl acrylate or methacrylate.

2. A composition according to Claim 1, wherein (A) is selected from the group consisting of compounds represented by any of the following formulae (1), (2), (3) and (4):

$O = P(OR)_p(OH)_{3-p}$ (1)

$O = P(OR)_q(OH)_{3-q} \cdot NH_rR'_{3-r}$ (2)

$P(OR)_p(OH)_{3-p}$ (3)

$P(OR)_q(OH)_{3-q} \cdot NH_rR'_{3-r}$ (4)

wherein p is an integer of 1~3; q and r are independently integers of 1 or 2; R and R' are independently selected from the group consisting of saturated or unsaturated alkyl groups containing at least 4 carbon atoms, aryl groups and alkyl-subsituted aryl groups.

3. A composition according to Claim 1 or 2, wherein the monomer (a) comprises (a_1) alkyl acrylate or methacrylate containing 8~20 carbon atoms in the alkyl group, and optionally (a_2) alkyl acrylate or methacrylate containing 1~4 carbon atoms in the alkyl group.

4. A composition according to Claim 3, wherein said copolymer contains 52~99 %, preferably 64~93 % by weight of monomer unis of (a_1), and 0~40 %, preferably 5~30 % by weight of mononer unis of (a_2).

5. A composition according to any one of Claims 1 to 4, wherein said copolymer further contains upto 10 % by weight of monomer unis of (c) at least one monomer selected from the group consisting of N-vinyl-pyrrolidone, morpholinoalkyl acrylate and morpholinoalkyl methacrylate; and/or upto 30 % by weight of monomer unis of (d) at least one monomer selected from the group consisting of aromatic vinyl compound, alkyl esters of unsaturated dicarboxylic acid containing not more than 20 carbon atoms in the alkyl group, and vinyl esters.

6. A composition according to any one of Claims 1 to 5, wherein said copolymer has a weight-average molecular weight of 20,000~200,000.

7. A composition according to any one of Claims 1 to 6, which further contains one or more additives as follows:

1) detergent preferably selected from sulfonates, salicylates, phenates and naphthenates;
2) dispersant preferably selected from alkenylsuccinimides and Mannich condensates;
3) anti-oxidant preferably selected from thiophosphates, amines and hindered phenols;
4) oiliness additive preferably selected from fatty acids and esters thereof;
5) antiwear agent preferably selected from molybdenum dithiophosphate and molybdenum carbamate; and
6) extreme pressure agent preferably selected from sulfur-containing compounds, phosphorus-containing compounds and chlorine-containing compounds.

8. A composition according to Claim 7, which contains said additive in such amounts as follows:

1) 0~10 % by weight of said detergent,
2) 0~10 % by weight of said dispersant,
3) 0~5 % by weight of said anti-oxidant,
4) 0~3 % by weight of said oiliness additive,
5) 0~10 % by weight of said antiwear agent, and
6) 0~10 % by weight of said extreme pressure agent.

9. A gear oil, particularly an automatic transmission fluid, comprising the composition according to any one of Claims 1 to 8.

10. A torque converter, contained therein the automatic transmission fluid according to Claim 9.

European Patent Office

EUROPEAN SEARCH REPORT

Application Number
EP 94 30 4031

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.6)
X	US-A-3 702 824 (R.C.SCHLICHT) * column 4, line 56 * * column 6, line 37 - line 38 * * column 6, line 40 - line 58 *	1,3,4, 6-10	C10M161/00 C10M167/00 //(C10M161/00, 137:02,137:04, 137:08,137:12, 149:04, 149:10), C10N20:04, C10N30:04, C10N30:10, C10N40:04
X	US-A-3 640 872 (M.A. WILLEY) * column 4, line 51 - line 52 * * column 5, line 7 - line 8 * * column 5, line 54 - line 56 * * column 5, line 71 - line 72 *	1-4,6-10	
A	GB-A-1 413 677 (SUN OIL COMPANY) * page 3, line 31 - line 64; example 1 *	1,2,5, 7-9	
A	US-A-3 309 317 (E. WITTNER) * column 1, line 47 - line 65 * * column 4, line 16 - line 22 * * column 4, line 71 - line 72 *	1,5,7,8	
A	US-A-2 892 784 (O.L.HARLE) * claim 1 *	1	TECHNICAL FIELDS SEARCHED (Int.Cl.6) C10M
D,A	US-A-4 800 029 (M. DASAI) * column 3, line 37 - line 40 * * column 3, line 48 - line 68 *	2	
A	US-A-4 036 768 (W.C. CRAWFORD) * column 5, line 10 * * column 6, line 10 - line 14 * * column 6, line 61 - line 63 *	1-4,6-10	

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	8 November 1994	Hilgenga, K

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
Y : particularly relevant if combined with another document of the same category
A : technological background
O : non-written disclosure
P : intermediate document

T : theory or principle underlying the invention
E : earlier patent document, but published on, or after the filing date
D : document cited in the application
L : document cited for other reasons

& : member of the same patent family, corresponding document

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