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(71) Applicant: **Idemitsu Kosan Co., Ltd.**
Chiyoda-ku
Tokyo 100-8321 (JP)

(72) Inventors:
- **FUJINAMI, Yukitoshi**
  Ichihara-shi, Chiba 299-0107 (JP)
- **KAMIMURA, Hideto**
  Ichihara-shi, Chiba 299-0107 (JP)

(74) Representative: **HOFFMANN EITLE**
Patent- und Rechtsanwälte
Arabellastrasse 4
81925 München (DE)

(54) LUBRICANT COMPOSITION

(57) The present invention provides a lubricating composition, particularly a grease composition and a lubricating oil composition, containing an aralkylated diphenylamine and a phenol compound having a molecular weight of not less than 340 which are compounded into a base oil. The lubricating composition is hardly decomposed or volatilized even at high temperatures and has a long oxidation life so that the lubricating characteristics thereof can be maintained for a long period of time.

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Description

[Technical Field]

[0001] The present invention relates to a lubricating composition and, more particularly, to a high temperature grease composition used for the lubrication of various machines and apparatuses such as automobiles, electric appliances, construction machines and machine tools as well as bearings and to a lubricating oil composition used for a long period of time under high temperatures in oil hydraulic, compression and vacuum pumps, bearings, gears, etc.

[Background Art]

[0002] A lubricating composition is widely used in various machines such as automobiles, electric appliances, construction machines and machine tools. Such machines have been demanded year by year for meeting requirements of compact size, high output, light weight and simple maintenance. As a consequence, lubricating conditions of lubricating compositions become severe more and more. To make a machine compact in size and high in output is to reduce the dimension thereof when the output thereof is the same. When the dimension is reduced, the heat energy discharged from surfaces of the machine is reduced to cause an increase of the temperature of a lubrication section thereof. On the other hand, to attain lightness in weight, it is necessary to use a material that has low heat conductivity such as a non-metal. This results in a further increase of the temperature, Simple maintenance has the same meaning as extension of service life. To extend the oxidation life, the lubrication characteristics must be kept for a long time. In this circumstance, there is a demand for a lubricating composition having a long oxidation life so that the lubricating characteristics thereof can be maintained for a long period of time, particularly a high temperature grease composition having a high dropping point and a high temperature lubricating oil composition.

[0003] Hitherto, a variety of high temperature greases having a high dropping point have been proposed. For example, Patent Document 1 discloses a grease containing a metal deactivator for plastics and a lithium salt of a hydroxyfatty acid, a dilithium salt of an aliphatic dicarboxylic acid or a lithium salt of an aliphatic monocarboxylic acid. Patent Document 2 discloses a grease composition including a base oil of a synthetic lube oil, a thickening agent of a urea compound, (a) an aromatic amine compound and (b) a hindered ester compound and further containing (c) at least one compound selected from phthalimide compounds and phosphoric ester compounds having an aromatic ring.

Patent Document 3 discloses a grease composition containing a base oil, a thickening agent, an antioxidant and an aromatic dibasic acid or a metal salt of an aromatic dibasic acid (excluding lithium terephthalate).

Patent Document 4 discloses a grease composition obtained by compounding a thickening agent composed of a C_{12} to C_{24} fatty acid having at least one hydroxyl group and a lithium salt of a C_2 to C_{12} aliphatic dicarboxylic acid into a base oil which contains, as essential ingredients, a mineral oil having a kinematic viscosity at 40°C of 300 to 500 mm^2/s and a synthetic hydrocarbon oil having a kinematic viscosity at 40°C of 20 to 300 mm^2/s and which has a kinematic viscosity at 40°C of 60 to 200 mm^2/s.

Further, Patent Document 5 discloses a lubricating composition for rolling bearings which contains (a) a urethane prepolymer having an isocyanate group content of 6 to 10 % by weight, (b) a grease selected from a metal soap type grease and a non-metal soap type grease, and (c) an amine curing agent, and which has a hardness after curing of 60 to 85 in International Rubber Hardness Degree (IRHD).

The above-described inventions are contemplated to attain a long service life of lubricating compositions at high temperatures but are still unsatisfactory to meet the recent severe requirements.

Patent Document 6 proposes the use of a styrenized diphenylamine, particularly 4,4'-bis(α-methylbenzyl)diphenylamine, as an antioxidant for a lubricating composition. Patent Document 6 does not at all consider the conjoint use thereof with other antioxidants.

Patent Document 7 proposes an antiwear bearing oil composition in which an alkylated diphenylamine or a hindered phenol compound is incorporated as an antioxidant into a base oil together with a nonionic surfactant and an anti-wear agent for the purpose of improving anti-wearing property and stability against oxidation. Patent Document 7 does not at all suggest the conjoint use of an amine-type antioxidant and a phenol compound for the purpose of improving the service life at high temperatures.

Thus, in the present circumstance, no sufficient studies have been made to develop an advantageous combination of an amine-type antioxidant with a phenol-type antioxidant in order to improve the effect of the prevention of deterioration by oxidation of the lubricating oil at high temperatures.

[0004]

[Patent Document 1] Japanese Unexamined Patent Application Publication No. H05-86392
[Patent Document 2] Japanese Unexamined Patent Application Publication No. H11-228985
[Patent Document 3] Japanese Unexamined Patent Application Publication No. H11-256184

[Patent Document 4] Japanese Unexamined Patent Application Publication No. 2000-26877
[Patent Document 5] Japanese Unexamined Patent Application Publication No. 2000-319681
[Patent Document 6] Japanese Unexamined Patent Application Publication No. H09-53087 [Patent Document 7] Japanese Unexamined Patent Application Publication No. 2005-29647

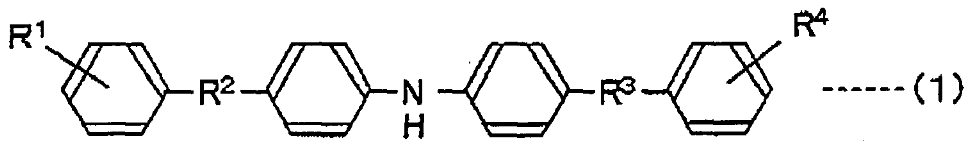
[Disclosure of the Invention]

[0005] The present invention has been made for solving the above-mentioned problems and has as its object the provision of a lubricating composition, particularly a grease composition and a lubricating oil composition, which are hardly decomposed or volatilized even at high temperatures and have a long oxidation life so that the lubricating characteristics thereof can be maintained for a long period of time.
The present inventors have made an earnest study with a view toward accomplishing the above objects and have found that the objects can be fulfilled by compounding an aralkylated diphenylamine and a specific phenol compound into a base oil, The present invention has been completed on the basis of such findings,
Thus, the present invention provides a lubricating composition containing a base oil, an aralkylated diphenylamine and a phenol compound having a molecular weight of not less than 340.

[Best Mode for Carrying Out the Invention]

[0006] A base oil used in the lubricating composition of the present invention is not specifically limited. Any customarily employed mineral oil or synthetic oil may be used. Examples of usable base oil include mineral oils such as paraffinic mineral oils, intermediate base mineral oils and naphthenic mineral oils; refined mineral oils obtained by processing the above mineral oils by solvent deasphalting, solvent extraction, hydrocracking, solvent dewaxing, hydrodewaxing or hydrorefining; mineral oils produced by isomerization of waxes; hydrocarbon synthetic oils such as poly-α-olefins; fats and oils; synthetic esters; and synthetic ethers. Among these base oils, the refined mineral oils and synthetic oils are preferred, To be more specific, base oils having a flash point of 180°C or higher, preferably 200°C or higher, are preferred. A base oil having a flash point of 180°C or higher can be suitably used for a high temperature grease composition. It is also preferred that the base oil have a % C_A of 1 or less, more preferably 0.5 or less. As used herein C_A represents an aromatic content as determined by the n-d-M ring analysis method (ASTM D 3238). The term "% C_A of a base oil" is intended to refer to C_A of the base oil in terms of % by mass. It is further preferred that the base oil have a sulfur content of 20 ppm or less, more preferably 10 ppm or less.
As the poly-α-olefin used as the base oil in the present invention, there may be used various kinds of α-olefin polymers. Generally used are polymers of a C_6 to C_{18} α-olefin having a lubrication viscosity. From the standpoint of thermal stability, sealing property and lubricity, polymers of 1-dodecene, 1-dacene or 1-octene are preferred. For reasons of thermal stability, hydrogen-treated poly-α-olefins are particularly suitably used. These poly-α-olefns may be used singly or as a mixture of two or more thereof.
The kinematic viscosity of the base oil is not specifically restricted. However, the kinematic viscosity of the base oil is generally suitably selected from a range of 2 mm^2/s to 600 mm^2/s at 40°C, more preferably 10 mm^2/s to 400 mm^2/s.
[0007] Next, as regards the aralkylated diphenylamine used in the lubricating composition of the present invention, compounds represented by the following chemical formula (1) are preferred:
[0008]

[Chemical Formula 1]



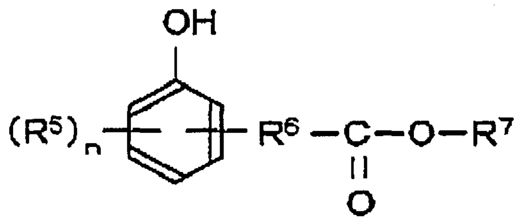
[0009] In the above chemical formula (1), R^1 and R^4 each independently preferably represent a C_0 to C_{24} alkyl group, and R^2 and R^3 each independently preferably represent a C_1 to C_5 alkylene group, more preferably a C_1 to C_3 alkylene group. As used herein "C_0" means that the corresponding substituent R^1 or R^4 is not present.
Specific examples of the aralkylated diphenylamine include 4,4'-bis(α,α-dimethylbenzyl)diphenylamine, 4,4'-bisbenzyldiphenylamine, 4,4'-diphenethyldiphenylamine and 4,4'-bis(α-methylbenzyl)diphenylamine. From the standpoint of extended oxidation life, 4,4'-bis(α,α-dimethylbenzyl)diphenylamine is preferred.
The aralkylated diphenylamine is preferably used in an amount of 0.01 to 10 % by mass, more preferably 0.1 to 5 % by

mass, particularly preferably 0.1 to 2 % by mass, based on the lubricating composition. When the amount is 0.01 % by mass or greater, deterioration by oxidation can be effectively prevented. An amount of 10 % by mass or less is economically advantageous.

[0010] One preferred example of the phenol compound having a molecular weight of not less than 340, preferably not less than 350, used in the present invention is a compound represented by the following chemical formula (2).

[0011]

[Chemical Formula 2]



-------(2)

[0012] In the above chemical formula (2), R^5 is preferably a C_1 to C_{18} alkyl group, R^6 is preferably a C_1 to C_5 alkylene group, particularly preferably C_1 to C3 alkylene group, R^7 is preferably a C_1 to C_{24} alkyl group, and n is 1 or 2.

As a specific example of the compound represented by the above chemical formula (2), there may be mentioned octadecyl-3-(3,5-di-tert-butyl-4-hydroxyphenyl)propionate (molecular weight: 520.89).

[0013] As another preferred example of the phenol compound having a molecular weight of not less than 340 used in the present invention, there may be mentioned a bisphenol compound. Examples of the bisphenol compound include 2,2'-methylenebis(4-methyl-6-tert-butylphenol) (molecular weight: 340.51). 2,2'-methylenebis(4-ethyl-6-tert-butylphenol) (molecular weight: 368.54), 4,4'-thiobis(3-methyl-6-tert-butylphenol) (molecular weight: 358.55), 4,4'-butylidenebis (3-mathyl-6-tert-butylphenol) (molecular weight: 382.59), 4,4'-methylenebis(2,6-di-tert-butyl phenol) (molecular weight: 424.68), and 3,9-bis[1,1-dimethyl-2-[β-(3-tert-butyl-4-hydroxy-5-methylphenyl)propionyloxy]ethyl]-2,4,8,10-tetraoxaspiro[5,5]undecane (molecular weight: 740.98).

[0014] As a further preferred example of the phenol compound having a molecular weight of not less than 340 used in the present invention, there may be mentioned a polyphenol compound other than the bisphenol compound. Examples of the polyphenol compound include 1,1,3-tris(2-methyl-4-hydroxy-5-tert-butylphenyl)butane (molecular weight: 544.83), 1,3,5-trimethyl-2,4,6-tris(3,5-di-tert-butyl-4-hydroxybenzyl)benzene (molecular weight: 775.21), tetrakis-[methylene-3-(3',5'-di-tert-butyl-4'-hydroxyphenyl)propionate]methene (molecular weight: 1177.66), bis[3,3'-bis-(4'-hydroxy-3'-tert-butylphenyl)butyric acid] glycol ester (molecular weight: 794.42), 1,3,5-tris(3',5'-di-tert-butyl-4'-hydroxybenzyl)-S-triazin-2,4,6-(1H,3H,5H)trion (molecular weight: 784.09).

As a further preferred example of the phenol compound having a molecular weight of not less than 340 used in the present invention, there may be mentioned a tocophenol (molecular weight 430.71) and its derivatives.

When the molecular weight of the above-described phenol compounds is not less than 340, the effect of the prevention of deterioration by oxidation is significant Such an effect is further improved when the molecular weight is not less than 350. When the molecular weight is not greater than 1,500, there is no fear of causing dissolution failure in the base oil.

Among the above-exemplified phenol compounds having a molecular weight of not less than 340, octadecyl-3-(3,5-di-tert-butyl-4-hydroxyphenyl)propionate (molecular weight: 520.89) and 2,2'-methylenebis(4-ethyl-6-tert-butylphenol) (molecular weight: 368.54) are particularly preferred from the view point of improving the effect of the prevention of deterioration by oxidation.

[0015] The phenol compound having a molecular weight of not less than 340 is preferably used in an amount of 0.01 to 10 % by mass, more preferably 0.1 to 5 % by mass, particularly preferably 0.1 to 3 % by mass, based on the lubricating composition, When the amount is 0.01 % by mass or more, the effect of the prevention of deterioration by oxidation is obtainable. An amount of 10 % by mass or less is advantageous from the standpoint of economy.

[0016] The thickening agent used in the present invention is not specifically restricted. A soap thickening agent or a non-soap thickening agent may be used. Preferably used is a thickening agent which can provide a grease composition having a dropping point of 230°C or higher. When the grease composition has a dropping point of 230°C or higher, a possibility of causing problems in relation to lubrication such as softening at high temperatures and resulting leakage or baking can be suppressed.

As the soap thickening agent, there may be mentioned a metal soap obtained by saponifying a carboxylic acid or its ester with a metal hydroxide such as an alkali metal hydroxide or an alkaline earth metal hydroxide. Examples of the metal include sodium, calcium, lithium and aluminum. Examples of the carboxylic acid include fats and oils, crude fatty acids obtained by hydrolyzing fats and oils and removing glycerin therefrom, monocarboxylic acids such as stearic acid, monohydroxycarboxylic acids such as 12-hydroxystearic acid, dibasic carboxylic acids such as azelaic acid, and aromatic carboxylic acids such as terephthalic acid, salicylic acid and benzoic acid. These soap thickening agents may be used singly or in combination. A preferred example of the soap thickening agent is a lithium soap using 12-hydroxystearic acid. When compounding a soap thickening agent into a base oil, it is possible to add a carboxylic acid and the above-mentioned metal hydroxide into the base oil to perform saponification thereof in the base oil.

[0017] As another type of the soap thickening agent, there may be mentioned various complex soaps.

Examples of the complex soap include a lithium complex soap, an aluminum complex soap and a calcium complex soap. Among these, the lithium complex soap may be obtained by reacting a fatty acid, such as stearic acid, oleic acid or palmitic acid, and/or a C_{12} to C_{24} hydroxyfatty acid having at least one hydroxyl group with a lithium compound, such as lithium hydroxide, together with an aromatic carboxylic acid and/or C_2 to C_{12} (more preferably C_4 to C_9) aliphatic dicarboxylic acid. Such a lithium complex soap is a more preferable thickening agent because of its superior heat resistance as compared with a lithium soap. As the C_{12} to C_{24} hydroxyfatty acid, 12-hydroxystearic acid is most preferred, though any other hydroxyfatty acid may be used. Such other hydroxyfatty acids may be, for example, 12-hydroxylauric acid and 16-hydroxypalmitic acid. As the aromatic carboxylic acid, there may be mentioned benzoic acid, o-phthalic acid, m-phthalic acid, terephthalic acid, trimellitic acid, pyromellitic acid, salicylic acid and p-hydroxybenzoic acid. As the C_2 to C_{12} aliphatic dicarboxylic acid, azelaic acid is most preferred, though any other aliphatic dicarboxylic acid may be used. Such other aliphatic dicarboxylic acid may be, for example, sebacic acid, oxalic acid, malonic acid, succinic acid, adipic acid, pimelic acid, suberic acid, undecanedicarboxylic acid and dodecanedicarboxylic acid. It is preferred that the aromatic carboxylic acid and/or C_2 to C_{12} aliphatic dicarboxylic acid be present in an amount of 20 to 90 % by mass based on a total mass of the fatty acid and/or C_{12} to C_{24} hydroxyfatty acid having at least one hydroxyl group and the aromatic carboxylic acid and/or C_2 to C_{12} aliphatic dicarboxylic acid. This is because a thickening agent having good thermal stability may be obtained and a grease composition having a long service life at high temperatures may be advantageously obtainable when the amount is within the range of 20 to 90 % by mass.

[0018] As a non-soap thickening agent, a urea compound or bentonite treated with an organic compound may be used. As the urea compound used as the thickening agent, there may be mentioned a diurea compound, a triurea compound, a tetraurea compound and a urea-urethane compound. Because the urea compound has excellent heat resistance and water resistance and is particularly excellent in stability at high temperatures, it is suitably used in a high temperature environment.

[0019] As the diurea compound, there may be mentioned, for example, a compound represented by the formula $R^8NHCONHR^9NHCONHR^8$ (wherein R^8 represents a straight chained or branched, saturated or unsaturated C_6 to C_{24} alkyl group and R^9 represents a divalent C_6 to C_{15} aromatic hydrocarbon group). The typical diurea compound may be obtained by reaction of a diisocyanate with a monoamine. The diisocyanate may be, for example, diphenylmethane diiocyanate, phenylene diisocyanate, diphenyl diisocyanate, phenyl diisocyanate or tolylene diisocyanate. The monoamine may be, for example, octylamine, dodecylamine, hexadecylamine, cyclohexylamine, aniline, toluidine, octadecylamine or oleylamine. Conventionally known urea thickening agents may also be suitably used.

[0020] Among the above-described various thickening agents, various complex soaps and urea compounds are preferred. The complex soaps and urea compounds may be used singly or in combination of two or more thereof.

The compounding amount of the thickening agent in the grease composition is not specifically restricted as long as the intended grease characteristics may be obtained but is preferably 10 to 30 % by mass, more preferably 10 to 20 % by mass, based on the grease composition.

The thickening agent used in the grease composition of the present invention serves to impart a desired consistency thereto. When the amount of the thickening agent is excessively small, a desired consistency is not obtainable. When the compounding amount is excessively large, the lubricity of the grease is reduced.

It is preferred that the grease composition of the present invention contain a base oil having a flash point of 180°C or higher, an aralkylated diphenylamine, a phenol compound having a molecular weight of not less than 340 and, additionally, a thickening agent for reasons of maintaining the lubricating characteristics at high temperatures for a long period of time.

[0021] In addition to the above-described chemicals, the grease composition and lubricating oil composition according to the present invention may optionally contain an additive or additives such as an anti-corrosive agent, an extreme pressure agent, a metal deactivator, a metallic detergent, a non-metallic detergent, an antifoaming agent, a viscosity increasing agent, a colorant and a water repellent agent.

As the anti-corrosive agent, there may be mentioned a metallic sulfonate and a succinic acid ester, As the metallic detergent, there may be mentioned a metal sulfonate, a metal salicylate and a metal phenate. As the non-metallic detergent, there may be mentioned succinimide. As the metal deactivator, there may be mentioned benzotriazol and thiadiazol. As the antifoaming agent, there may be mentioned methyl silicone, dimethyl silicone, fluorosilicone and polyacrylate.

[0022] According to the present invention, there can be provided a lubricating composition, particularly a grease composition and a lubricating oil composition, which are hardly decomposed or volatilized even at high temperatures and which have a long oxidation life so that the lubricating characteristics thereof can be maintained for a long period of time.

[Examples]

[0023] The present invention will be next described in more detail by way of examples but is not limited to the examples in any way
In the following Examples and Comparative Examples, various characteristics were tested in accordance with the methods described below.

(1) Flash point:

Flash point was measured in accordance with JIS K2265 (Cleveland open cup method).

(2) Dropping point:

Dropping point was measured in accordance with JIS K2220.

(3) Oxidation life:

Grease was applied on a cleaned SPCC steel plate in a thickness of 0.5 mm. The plate was then allowed to quiescently stand in a thermostat chamber and thereafter taken out from the chamber. The resulting specimen was measured by IR to determine the deterioration by oxidation. The oxidation life is a time period taken for the ratio $(I_{720})/(I_{1710})$ of the transmittance at 720 cm^{-1} to the transmittance at 1710cm^{-1} to be 1.2 or more.

(4) Oil separation;

Oil separation was measured in accordance with JIS K2220, but using a measuring temperature of 180°C.

(5) Bearing life:

A tester (ASTM D3336) was continuously operated at 10,000 rpm and at 180°C. The bearing life is a time period (in hours) for the tester to become no longer operable due to "burning".

(6) Stability test at high temperature (oil remaining percent):

A vessel and a thermostat air bath, specified in the lubricating oil thermal stability test (JIS K2540), were employed. A sample (1 g) was allowed to stand in the vessel at 170°C for 48 hours. The amount of the oil remaining in the vessel was then measured, from which an oil remaining percent was calculated. During the measurement, air was continuously fed to the vessel at a flow rate of 10 Uhr. The greater the oil remaining percent, the less likely the thermal decomposition is to occur, i.e. the better is the stability at high temperatures.

(7) Fluidity:

After the end of the above-described stability test at the high temperature, the lubricating oil was allowed to stand and cool at room temperature. The vessel was then slanted to determine the fluidity with naked eyes.

Examples 1 and 2 and Comparative Examples 1 to 7

[0024]

(1) In a grease preparation vessel, a half amount of a base oil, 10.2 % by mass of 12-hydroxystearic acid and 1.0 % by mass of calcium sulfonate were charged and heated with stirring for dissolution.
(2) In water was dissolved lithium hydroxide (monohydrate) in an amount of 2.7 % by mass, in which 2.1 % by mass of terephthalic acid was further dissolved. The thus obtained aqueous solution was added to the grease composition obtained in (1) above. The mixture was heated and mixed. When the temperature of 205°C was reached, the grease composition was further maintained at that temperature for 5 minutes.
(3) Next, the above grease composition was added with the remaining half of the base oil and cooled to 80°C at a rate of 50°C per hour. Then, as shown in Table 1, an aralkylated diphenylamine, an amine compound 1 or amine

compound 2, and a phenol compound 1, phenol compound 2 or phenol compound 3 were added to and mixed with the cooled composition.

(4) The resulting mixture was allowed to spontaneously cool to room temperature and finished using a three-roll blending machine. In like manner, nine kinds of grease compositions were obtained.

(5) Each of the nine grease compositions was subjected to the above tests (2) to (4). The results are summarized in Table 1.

Example 3

[0025]

(1) In two-third amount of a base oil, 1 mole of diphenylmethane-4,4'-diisocyanate (MDI) was dissolved with heating to obtain a raw material 1.

(2) In the remaining one-third amount of the base oil was dissolved 2 moles of octylamine with stirring to obtain a raw material 2.

(3) Next, while vigorously stirring the raw material 1 at 50 to 60°C in a grease preparation vessel, the raw material 2 was gradually added thereto. The mixture was heated with stirring. When the temperature of 165°C was reached, the grease composition was further maintained at that temperature for 1 hour.

(4) Then, an aralkylated diphenylamine and a phenol compound 1 were added to and mixed with the composition. The resulting mixture was allowed to spontaneously cool to room temperature and finished using a three-roll blending machine to obtain a grease composition of Example 3.

(5) The grease composition of Example 3 was subjected to the above tests (2) to (4). The results are summarized in Table 1.

Example 4

[0026]

(1) In a grease preparation vessel, a half amount of a base oil, 15 % by mass of lithium 12-hydroxystearate were charged and heated with stirring. When the temperature of 210°C was reached, the grease composition was further maintained at that temperature for 5 minutes.

(2) Then, the grease composition was added with the remaining half of the base oil and thereafter cooled to 80°C at a rate of 50°C per hour. Thereafter, an aralkylated diphenylamine and a phenol compound 1 were added to and mixed with the composition.

(4) The resulting mixture was allowed to spontaneously cool to room temperature and finished using a three-roll blending machine to obtain a grease composition of Example 4.

(5) The grease composition of Example 4 was subjected to the above tests (2) to (4). The results are summarized in Table 1.

[Table 1]

Example		1	2	3	4							
Comparative Example						1	2	3	4	5	6	7
Compounding Amount [% by mass]	Base oil1 *1	82.0	82.0	82.0	82.0	82.0	82.0	82.0	82.0	82.0	82.0	82.0
	Li Complex soap *2	15.0	15.0			15.0	15.0	15.0	15.0	15.0	15.0	15.0
	Urea compound *3			15.0								
	Li Soap *4				15.0							
	Aralkylated diphenylamine *5	1.0	1.0	1.0	1.0			1.0		1.0		
	Amine compound 1 *6					1.0	3.0				1.0	
	Amine compound 2 *7											1.0
	Phenol compound 1 *8	1.0		1.0	1.0				1.0		1.0	1.0
	Phenol compound 2 *9		1.0									
	Phenol compound 3 *10									1.0		
	Ca Sulfonate	1.0	1.0			1.0	1.0	1.0	1.0	1.0	1.0	1.0
Dropping point [°C]		260<	260<	260<	201	260<	260<	260<	260<	260<	260<	260<
Oxidation life (180°C) [hours]		121	115	130	82	7	23	28	22	28	33	35
Oil separation (180°C) [% by mass]		4	4	3	23	4	4	4	4	4	4	4

*1: Paraffin mineral oil (flush point: 226°C, kinematic viscosity (40°C): 90.5 mm^2/s, %C_A: < 0.1, sulfur content: 3 ppm)
*2: Refer to the method for preparing grease in Examples 1 and 2 and Comparative Examples 1 to 7
*3: Refer to the method for preparing grease in Example 3
*4: Refer to the method for preparing grease in Example 4
*5: 4,4'-Bis(α,α-dimethylbenzyl)diphenylamine
*6: p,p'-Dioctyldiphenylamine
*7: Phenyl-α-naphthylamine
*8: Octadecyl-3-(3,5-di-tert-butyl-4-hydroxyphenyl) propionate (molecular weight: 520.89)
*9: 2,2'-methylenebis(4-ethyl-6-tert-butylphenol) (molecular weight: 368.54)
*10: 2,6-di-tert-butyl-4-methylphenol (DBPC) (molecular weight: 220.36)

The grease compositions of Examples 1 and 2 and Comparative Examples 3 and 6 were each measured for the above-described bearing life. The bearing life was found to be 530 in the case of the grease composition of Example 1, 410 in the case of the grease composition of Example 2, 130 in the case of the grease composition of Comparative Example 3, and 145 in the case of the grease composition of Comparative Example 6. Thus, it was revealed that the grease composition of the present invention has a long bearing life.

Example 5 and Comparative Examples 8 to 10

[0027] As a base oil, 1-decene oligomer (kinematic viscosity (40°C): 30 mm^2/s) was used. As shown in Table 2, the base oil was compounded with an antioxidant, a metal deactivator, an anti-corrosive agent and an antifoaming agent to obtain four kinds of lubricating oil compositions. Each of the four lubricating oil compositions was measured for the above-described oil remaining percent (6) and fluidity (7). The results are summarized in Table 2.

[0028]

[Table 2]

Example		5			
Comparative Example			8	9	10
Compounding amount [% by mass]	Poly-α-olefin *1	97.795	97.795	97.795	98.795
	Phenol compound 3 *2		1		
	Phenol compound 4 *3	1		1	
	Aralkylated diphenylamine *4	1	1		1
	Amine compound 1 *5			1	
	Metal deactivator *6	0.1	0.1	0.1	0.1
	Anti-corrosive agent *7	0.1	0.1	0.1	0.1
	Antifoaming agent *8	0.005	0.005	0.005	0.005
Stability test at high temperature (170°C, 48 hours): Oil remaining percent [% by mass]		71.82	68.43	51.40	67.12
Fluidity		showed fluidity	no fluidity	no fluidity	no fluidity

*1: 1-Decene oligomer (flash point: 236°C, kinematic viscosity (40°C): 30 mm^2/s, %CA: 0)
*2: 2,6-Di-tert-butyl-4-methylphenol (DBPC) (molecular weight: 220.36)
*3: 4,4'-Methylenebis(2,6-di-tert-butylphenol) (molecular weight:424.68)
*4: 4,4'-Bis(α,α-dimethylbenzyl)diphenylamine
*5: p,p'-Dioctyldiphenylamine
*6: Benzotriazole
*7: Alkenylsuccinic acid ester of polyhydric alcohol
*8: Dimethylsilicone

[0029] As is apparent from Table 2, it is revealed that the lubricating oil composition of the present invention has a high oil remaining percent and fluidity and, therefore, is hardly decomposed or volatilized even at high temperatures and has a long oxidation life.

[Industrial Applicability]

[0030] The lubricating composition of the present invention, which has long oxidation life and can maintain its lubricating characteristics for a long time even when exposed to high temperatures, is suitably used, as a high temperature lubricating composition, particularly as a high temperature grease composition and as a high temperature lubricating oil composition, for lubrication of various machines and apparatuses such as automobiles, electric appliances, construction machines and machine tools as well as bearings. To be more specific, the lubricating composition is suitably used for lubrication in internal combustion engines, torque converters, fluid couplings, radial bearings, rolling bearings, oil retaining bearings, fluid bearings, compressors, chain drives, gears, oil hydraulic circuits, vacuum pumps, clock parts, hard disk apparatuses, refrigerators, cutting, rolling, metal drawing, form rolling, forging, heat treatment, heat media, washing, shock absorbers, corrosion prevention, brake members and sealing devices.

Claims

1. A lubricating composition comprising a base oil, an aralkylated diphenylamine, and a phenol compound having a molecular weight of not less than 340.

2. A lubricating composition as recited in claim 1, wherein the phenol compound has a molecular weight not less than

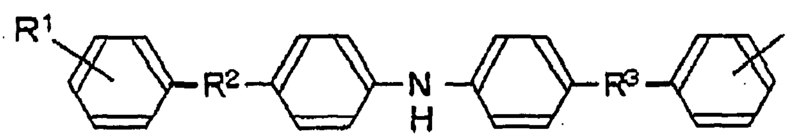
340 but not greater than 1,500.

3. A lubricating composition as recited in claim 1 or 2, wherein the base oil has a flash point of not lower than 180°C and wherein the lubricating composition is a grease composition which additionally comprises a thickening agent.

4. A lubricating composition as recited in claim 3, which contains 0.01 to 10 % by mass of the aralkylated diphenylamine, 0.01 to 10 % by mass of the phenol compound having a molecular weight of not less than 340 and 10 to 30 % by mass of the thickening agent, based on the grease composition.

5. A lubricating composition as recited in claim 1 or 2, which is a lubricating oil composition and contains 0.01 to 10 % by mass of the aralkylated diphenylamine and 0.01 to 10 % by mass of the phenol compound having a molecular weight of not less than 340, based on the lubricating oil composition.

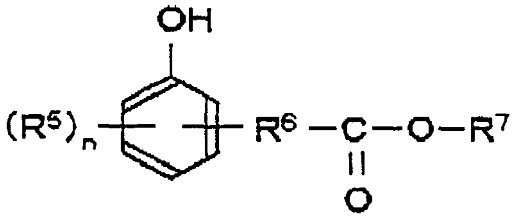
6. A lubricating composition as recited in any one of claims 1 to 5, wherein the aralkylated diphenylamine is represented by the following chemical formula (1):



------(1)

wherein R^1 and R^4 each independently represent a C_0 to C_{24} alkyl group and R^2 and R^3 each independently represent a C_1 to C_5 alkylene group,

7. A lubricating composition as recited in any one of claims 1 to 6, wherein the phenol compound having a molecular weight of not less than 340 is represented by the following chemical formula (2):



-------(2)

wherein R^5 represents a C_1 to C_{18} alkyl group, R^6 represents a C_1 to C_5 alkylene group, R^7 represents a C_1 to C_{24} alkyl group and n is 1 or 2.

8. A lubricating composition as recited in any one of claims 1 to 6, wherein the phenol compound having a molecular weight of not less than 340 is a bisphenol compound.

9. A lubricating composition as recited in claim 3, 4, 6, 7 or 8, wherein the thickening agent is a complex soap or a urea compound.

10. A lubricating composition as recited in any one of claims 3 to 8, wherein the base oil has a flash point of not less than 200°C.

11. A lubricating composition as recited in claim 1, 2, 3, 4, 6, 7, 8 or 9, which has a dropping point of not less than 230°C.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/JP2006/319293

A. CLASSIFICATION OF SUBJECT MATTER
See extra sheet.

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

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
C10M141/06, 115/08, 117/00-117/10, 129/10-129/14, 129/76, 133/12-133/14, 169/06, C10N20/00, 20/04, 30/06-30/10, 40/00-40/04, 40/08, 50/10

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

Jitsuyo Shinan Koho	1922-1996	Jitsuyo Shinan Toroku Koho	1996-2006
Kokai Jitsuyo Shinan Koho	1971-2006	Toroku Jitsuyo Shinan Koho	1994-2006

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

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X Y	JP 11-228981 A (Ethyl Corp.), 24 August, 1999 (24.08.99), & CA 2240973 A1 & CN 1206041 A & CN 1296063 A & DE 69802148 T2 & EP 892037 A1 & JP 2001-89782 A & US 5840672 A	1-2,5,7-8,10 6
X Y	JP 2000-119675 A (Ethyl Corp.), 25 April, 2000 (25.04.00), & AU 9953518 A & BR 9904933 A & CA 2286235 A1 & CN 1251859 A & EP 994175 A2 & KR 2000029082 A & US 6326336 B1	1-2,5,7-8,10 6
Y	JP 5-179275 A (Tonen Corp.), 20 July, 1993 (20.07.93), (Family: none)	1-2,5-8,10

☒ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

* Special categories of cited documents:
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"O" document referring to an oral disclosure, use, exhibition or other means
"P" document published prior to the international filing date but later than the priority date claimed
"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"&" document member of the same patent family

Date of the actual completion of the international search
05 January, 2007 (05.01.07)

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Name and mailing address of the ISA/
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Facsimile No.

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INTERNATIONAL SEARCH REPORT

International application No.
PCT/JP2006/319293

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	JP 6-41572 A (Tonen Corp.), 15 February, 1994 (15.02.94), (Family: none)	1-2,5-8,10
Y	JP 4-292694 A (Mitsubishi Oil Co., Ltd.), 16 October, 1992 (16.10.92), (Family: none)	1-2,5-8,10
Y	JP 2003-183686 A (Nippon Oil Corp.), 03 July, 2003 (03.07.03), & AU 2002336287 A & EP 1439217 A1 & JP 2003-277781 A & JP 2003-277782 A & JP 2003-277783 A & US 2004/0242434 A1 & WO 2003/0033629 A1	1-2,5-8,10
Y	JP 2005-42070 A (Petroleum Energy Center et al.), 17 February, 2005 (17.02.05), (Family: none)	1-2,5-8,10
Y	JP 2001-3074 A (Seiko Instruments Inc.), 09 January, 2001 (09.01.01), (Family: none)	1-6,8-11
Y	JP 9-53087 A (Seiko Chemical Co., Ltd.), 25 February, 1997 (25.02.97), (Family: none)	1-11

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INTERNATIONAL SEARCH REPORT

International application No.
PCT/JP2006/319293

Continuation of A. CLASSIFICATION OF SUBJECT MATTER (International Patent Classification (IPC))

C10M141/06(2006.01)i, *C10M169/06*(2006.01)i, *C10M115/08*(2006.01)n, *C10M117/00*(2006.01)n, *C10M129/10*(2006.01)n, *C10M129/14*(2006.01)n, *C10M129/76*(2006.01)n, *C10M133/12*(2006.01)n, *C10N20/00*(2006.01)n, *C10N20/04*(2006.01)n, *C10N30/06*(2006.01)n, *C10N30/08*(2006.01)n, *C10N30/10*(2006.01)n, *C10N40/00*(2006.01)n, *C10N40/02*(2006.01)n, *C10N40/04*(2006.01)n, *C10N40/08*(2006.01)n, *C10N50/10*(2006.01)n

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

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REFERENCES CITED IN THE DESCRIPTION

Patent documents cited in the description

- JP H0586392 B **[0004]**
- JP H11228985 B **[0004]**
- JP H11256184 B **[0004]**
- JP 2000026877 A **[0004]**
- JP 2000319681 A **[0004]**
- JP H0953087 B **[0004]**
- JP 2005029647 A **[0004]**