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(71) Applicant: **NIPPON OIL CO., LTD.
3-12, 1-chome, Nishi-shimbashi Minato-ku
Tokyo(JP)**

(72) Inventor: **Takashima, Hiroyuki
1-29-3-214, Higashinagaya, Konan-ku
Yokohama-shi, Kanagawa-ken(JP)**
Inventor: **Ishida, Noboru
340, Idanakanomachi, Nakahara-ku
Kawasaki-shi, Kanagawa-ken(JP)**

(74) Representative: **Silverman, Warren et al
HASELTINE LAKE & CO. Hazlitt House 28
Southampton Buildings Chancery Lane
London WC2A 1AT(GB)**

(54) **Lubricating oil compositions.**

(57) A lubricating oil composition having excellent oxidation stability and reduced sludge formation which comprises (I) a base oil which is a mineral oil having an aromatic content of up to 30 wt.%, a synthetic oil having no aromatic rings in the structural units or a mixture thereof, and, as essential additives, (II) an N-p-alkylphenyl-alpha-naphthylamine and (III) a p,p'-dialkyldiphenylamine each in a specific minor amount.

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LUBRICATING OIL COMPOSITIONS

This invention relates to lubricating oil compositions utilizable as a lubricant in various industrial fields and more particularly to lubricating oil compositions which have good oxidation stability and in which sludges only form with difficulty.

As is well known in the art, mineral oils having a low aromatic content and synthetic oils, e.g. poly-alpha-olefin oils, which are free of aromatic rings in the structural units, have poor oxidation stability. When antioxidants are added to the mineral oils or synthetic oils, however, the resulting lubricating oil compositions will exhibit high oxidation stability. However, an undesirable problem involved in these compositions is that the solubility of antioxidants in the oils is low. Antioxidants will invariably be degraded when they are oxidized during their use, and the degradation products formed by oxidation will raise a problem if they are left as a sludge.

For the development of long-life lubricating oils, importance should be placed on how to balance the degree of formation of sludge with their service life, which conflict with each other, under oxidizing conditions.

Although phenyl-alpha-naphthylamine is known as a good antioxidant, it has the drawback that its own solubility is low; further, the substances produced by its oxidation, as well as dimers, trimers and other oligomers of the naphthylamine are also disadvantageous because of low solubility. Accordingly, even when high oxidation stability is required, the naphthylamine which has high oxidation stability cannot be used in large amounts in order to improve the oxidation stability of lubricating oils.

In order to improve the solubility of phenyl-alpha-naphthylamine GB-A-1,552,720 discloses a process of alkylating the phenyl group of the naphthylamine with a propylene trimer. Alternatively, United States Patent No. 3,696,851 discloses a process of alkylating with a propylene dimer or an isobutylene dimer or trimer. The alkylated N-alkylphenyl-alpha-naphthylamines obtained by alkylation of the phenyl groups with a propylene or isobutylene dimer or trimer exhibit an improved solubility in oils, but they have the disadvantage that the solubility of the substances produced by oxidation is still low.

Diphenylamines are also excellent antioxidants, e.g. p,p'-di-t-octyldiphenylamine having a t-octyl group is known for this purpose. However, its oligomers like phenyl-alpha-naphthylamine have insufficient solubility.

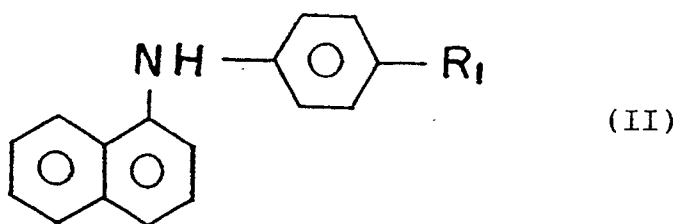
Japanese Patent Laid-Open Gazette No. Sho. 59-5146 discloses an alkylidiphenylamine having a branched chain dodecyl group, a method for the production thereof and compositions including said amine. Said alkylidiphenylamines and compositions are also insufficiently effective in preventing oxidation and suppressing sludge formation.

The present inventors previously filed an application (Japanese Patent Laid-Open Gazette No. Sho. 62-181396 and corresponding U.S. Patent No. 4,770,802) after they had found that an alkylphenyl-alpha-naphthylamine having at least one alkyl group of a specified structure has high oxidation stability while suppressing sludge formation.

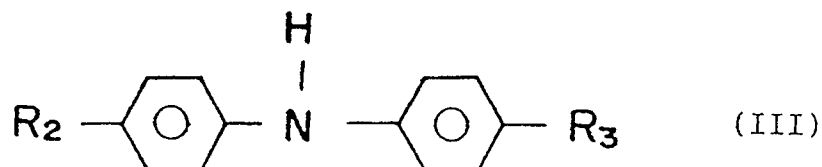
An object of the present invention is to provide a lubricating oil composition which has higher oxidation stability than such compositions have had hither to and to suppress the formation of sludges.

The present inventors have made intensive studies to improve the sludge formation suppressing effect and oxidation stability of antioxidant by products and, as the result of the studies, they found that a lubricating oil composition including as additives an alkylphenyl-alpha-naphthylamine and alkylidiphenylamine respectively having specific structures and used in respective amounts has very high oxidation stability and lessens sludge formation therein, thus completing the present invention.

The above object can be achieved by the provision of a lubricating oil composition which comprises (I) a base oil selected from mineral oils having an aromatic content not higher than 30 wt.%, synthetic oils having no aromatic rings in the structural units, and mixtures thereof, (II) 0.01 to 5.0 wt.%, based on the total composition, of an N-p-alkylphenyl-alpha-naphthylamine of the general formula



10 in which R₁ represents a branched alkyl group having 12 or 15 carbon atoms and is derived from an oligomer of propylene, and (III) 0.01 to 5.0 wt.%, based on the total composition, of a p,p'-dialkyl-diphenylamine of the general formula



20 in which R₂ and R₃ may be identical with, or different from, each other and each represents a branched alkyl group having 12 or 15 carbon atoms which is derived from oligomers of propylene.

The present invention will be further explained in detail.

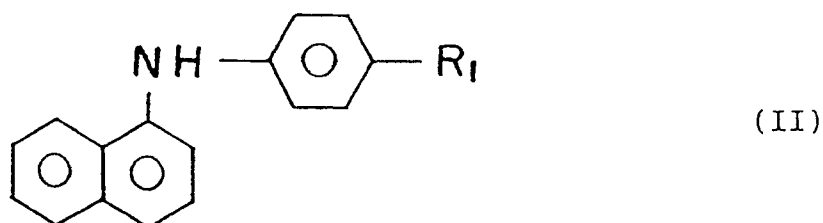
25 The base oils used in the present invention should be mineral oils having an aromatic content of 30 wt.% or less and/or synthetic oils which do not contain any aromatic rings in the structural units.

The mineral oils suitable for the purpose of the invention have generally a kinematic viscosity at 40°C of from 5 to 10,000 centistokes, preferably from 10 to 10,000 centistokes, more preferably 20 to 1,000 centistokes. In general, the preferable mineral oils used herein are those produced by subjecting lubricating oil fractions obtained by distillation of crude oils, to a suitable refining treatment such as refining with a solvent, treatment with sulfuric acid, refining by hydrogenation or treatment with clay.

30 The preferable mineral oils should not have an aromatic content of more than 30 wt.%, preferably not more than 20 wt.%. The aromatic content defined herein is intended to mean a value which is determined according to the method prescribed in ASTM D 2549-81.

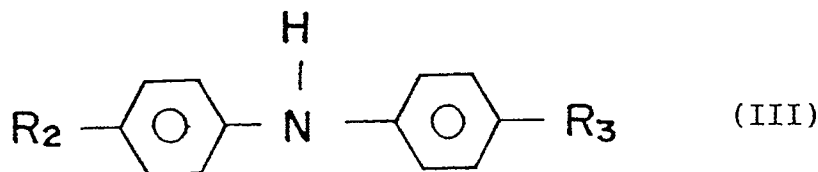
35 The synthetic oils generally used in the practice of the invention should be those which are free of any aromatic rings in their structural units and which generally will have a kinematic viscosity at 40°C of from 10 to 10,000 centistokes. Examples of the synthetic oils include: poly-alpha-olefin oils, such as polybutene and decene-1-oligomers, obtained by homopolymerization or copolymerization of alpha-olefins having from 4 to 30 carbon atoms; monoesters of aliphatic monocarboxylic acids and aliphatic monohydric alcohols, typical monoesters being butyl stearate and methyl laurate; diesters of aliphatic dibasic acids and aliphatic monohydric alcohols, such as di-2-ethylhexyl sebacate, dioctyl adipate and ditridecyl glutarate; aliphatic monocarboxylic acid esters of aliphatic polyhydric alcohols, typified by trimethylolpropane caprylate, trimethylolpropane pelargonate and pentaerythritol 2-ethyl-hexanoate pentaerythritol and pelargonate; poly-alkylene glycols such as polyethylene glycol and polypropylene glycol, their monoalkyl ethers, dialkyl ethers, monoalkyl esters and dialkyl esters; cycloparaffins such as cyclododecane, hydrindane, bicyclohexyl and tercyclohexyl; alkylcycloparaffins such as dicyclohexylbutane and dicyclohexylpropane; and mixtures thereof.

45 The N-p-alkylphenyl-alpha-naphthylamine used in the present invention is a compound of the general formula



in which R₁ represents a branched alkyl group having 12 or 15 carbon atoms which is derived from an oligomer (tetramer or pentamer) of propylene.

The p,p'-dialkyldiphenylamine used in the present invention is a compound of the general formula



in which R₂ and R₃ may be identical with, or different from, each other and each represent a branched alkyl group having 12 or 15 carbon atoms which is derived from an oligomer of propylene.

15 In the practice of the invention, it is important that each of R₁, R₂ and R₃ be a branched alkyl group derived from an oligomer of propylene. If such a branched alkyl group is derived from an alpha-olefin, the anti-oxidizing property of the resulting product will be very inferior to that of N-p-alkylphenyl-alpha-naphthylamine as the component (II) or p,p'-dialkyldiphenylamine as the component (III) used in the present invention. In addition, when such a branched alkyl group is derived from oligomers of olefins other than propylene, e.g. isobutylene, the resulting product itself is likely to precipitate by oxidation as a sludge when used in lubricating oils.

20 Moreover, when such a branched alkyl group has fewer carbonate than those defined in the invention, even if it is derived from a propylene oligomer, the resultant product is also likely to precipitate undesirably sludge in lubricating oils as a result of oxidation. On the other hand, when the number of carbon atoms in the oligomer exceeds the range of the invention, the resulting product will have a decreased proportion of functional groups in the molecule thereby undesirably weakening its anti-oxidant property.

25 The N-p-alkylphenyl-alpha-naphthylamine used as the component (II) and p,p'-dialkyldiphenylamine used as the component (III) in the practice of the invention can be prepared by any known techniques. In view of the ease of preparation, it is preferred to use a Friedel-Crafts alkylation reaction between phenyl-alpha-naphthylamine or diphenylamine and a propylene oligomer. The catalysts usable in this reaction include metal halides such as aluminiumchloride, zinc chloride and iron chloride, as well as acid catalysts such as sulphuric acid, phosphoric acid, phosphorus pentoxide boron fluoride, acid clay and activated Clay.

30 Methods for the preparation of the N-p-alkylphenyl-alpha-naphthylamine and for the preparation of the p,p'-dialkyldiphenylamine are disclosed respectively in Japanese Patent Laid-Open Gazettes Nos. sho 62-181396 and 59-5146.

35 The amount of each of the naphthylamine (II) and the diphenylamine (III) added should be from 0.01 to 5.0 wt.%, preferably from 0.1 to 3 wt.%, of the total composition. Amounts less than 0.01 wt.% are not desirable because hardly any effect is obtained. On the other hand, when the amount exceeds 5 wt.%, no further advantage is obtained and economical disadvantage is also incurred.

40 If necessary, the lubricating oil composition of the invention may be incorporated with other additives ordinarily used for various purposes including, for example, antioxidants, detergent-dispersants, pour point depressants, viscosity index improvers, oiliness improvers, wear resistant agents, extreme pressure agents, corrosion inhibitors, metal-deactivators, antifoamers, emulsifiers, demulsifiers, bactericides and colorants. These additives are described in detail, for example, in "The Lubrication Journal, Vol. 15, No. 6" and "Additives For Petroleum Products", written by Toshio Sakurai and published by Saiwai Bookstore.

45 The lubricating oil compositions of the invention are utilizable as lubricating oils requiring oxidation stability including, for example, motorcar engine oils, engine oils for agricultural machines, diesel engine oils, diesel engine oils, industrial multipurpose lubricating oils, turbine oils, hydraulic oils, spindle oils, film forming oils, refrigerator oils, gear oils, automatic transmission oils, cylinder oils dynamo oils, machine oils, cutting oils, and metal processing oils.

50 The following non-limiting example illustrates the present invention.

Inventive Example and Comparative Examples 1 - 4

55 The N-p-alkylphenyl-alpha-naphthylamine as the component (II) and the p,p'-dialkyldiphenylamine as the component (III) according to this invention, indicated in the following Table 1, were added in the respective amounts shown in Table 1 to a refined mineral oil (kinematic viscosity 34.4 cSt at 40°C) whose aromatic content was 7 wt.% to obtain a lubricating oil composition which was then subjected to the

following evaluation test to find its service life and sludge formation under oxidizing conditions with the results being shown in Table 1 (Inventive Example).

For the sake of comparison, various other compounds were added to the same mineral oil as above to obtain oil compositions which were then evaluated for their service life and sludge formation under oxidizing conditions in the same manner as above with the results being also shown in Table 1 (Comparative Examples 1 - 4).

Evaluation Test for Service Life under Oxidizing Conditions

A rotary bomb oxidation test was carried out at a test temperature of 150°C and an oxygen pressure of 6.3 kg/cm² at ambient temperature in the presence of a copper wire catalyst in accordance with JIS K 2514 3.3. The service life under oxidizing conditions was evaluated in terms of a time during which the oxygen pressure decreased by 1.75 kg/cm².

Test for Service Life and Sludge Formation Service Life

Using a water cooler-equipped rotary air compressor (motor output 5.5 kw) as typical apparatus with which the oil compositions might be used in practice, the oil compositions of the Example and Comparative Examples were tested for service life at an oil temperature of 80°C and an operating pressure of 7.5 kg f/cm². The service life of each oil composition was determined in terms of time which elapsed from the start of the test until one of the following points (when the oil composition properties changed) was reached:

- 1) a point at which the residual oxidation value is 15 min. or less (in accordance with JIS K-2514 3.3),
- 2) an indication point at which the total acid value is rapidly increased (in accordance with JIS-2501),
- 3) an induction point at which the viscosity is rapidly increased (in accordance with JIS K-2283)

Sludge Formation

The procedure of the above test was followed except that the same compressor as above was operated for 3000 hours, after which visual inspection to see whether sludges had stuck to the oil cooler was carried out.

Table 1

				Existing Machine Tests	
Compounds Added		Amount (wt.%)	Service Life (min.)	Service Life (hr)	Sludges Formed
Ex.1	N-p-branched dodecylphenyl-alpha-naphthylamine	1.0	2300	9000	none
	p,p -di branched dodecyldiphenylamine	1.0	-	-	-
Comp. Ex.1	N-p-branched dodecylphenyl-alpha-naphthylamine	2.0	2000	6000	none
Comp. Ex.2	p,p -di branched dodecyldiphenylamine	2.0	500	7500	large amount
Comp. Ex.3	p,p -di branched octyldiphenylamine	2.0	500	6000	large amount
Comp. Ex.4	N-p-branched dodecylphenyl-alpha-naphthylamine	1.0	2300	9000	large amount
	p,p -di branched dodecyldiphenylamine	1.0	-	-	-

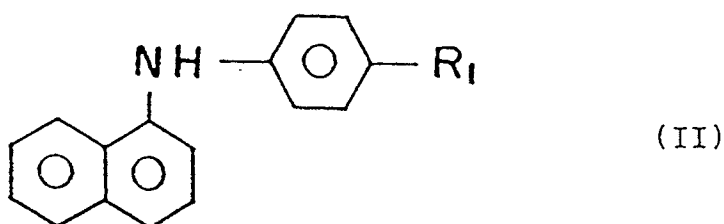
It is apparent from Table 1 that the lubricating oil composition of the inventive Example has excellent properties in exhibiting a synergistically extended service life without sludge formation as compared with those (Comparative Examples 1 - 3) wherein the component (II), the component (III) and the other compound were respectively used alone as additive. Further, the oil composition of Comparative Example 4, wherein one of the compounds added had an alkyl group outside of the range prescribed in the present invention, exhibited the same service life as that obtained in the inventive Example, but it formed sludges in

a large amount; thus, the composition of Comparative Example 4 showed very inferior performance to the composition of the inventive Example.

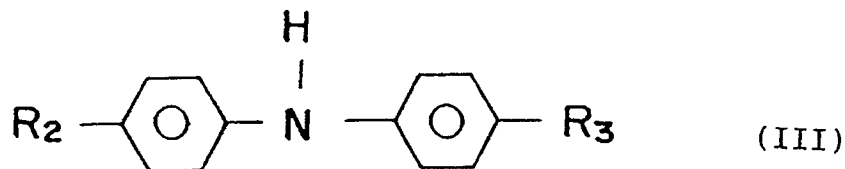
In summary, thus, the lubricating oil compositions obtained by incorporating in the base oil (I) an alkylphenyl-alpha-naphthylamine (II) and an alkyldiphenylamine (III) in respective specific amounts, each of the amines having a specific structure, have very excellent oxidation stability with reduced sludge formation.

Claims

10 A lubricating oil composition which is obtained by incorporating in (I) a base oil selected from mineral oils having an aromatic content not higher than 30 wt.%, synthetic oils having no aromatic rings in the structural units, and mixtures thereof, with, as essential components, (II) 0.01 to 5.0 wt.%, based on the total composition, of an N-p-alkylphenyl-alpha-naphthylamine of the general formula



25 in which R₁ represents a branched alkyl group having 12 or 15 carbon atoms and is derived from an oligomer of propylene, and (III) 0.01 to 5.0 wt.%, based on the total composition, of a p,p'-dialkyldiphenylamine of the general formula



40 in which R₂ and R₃ may be identical with, or different from, each other and each represents a branched alkyl group having 12 or 15 carbon atoms which is derived from an oligomer of propylene.



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EUROPEAN SEARCH REPORT

Application Number

EP 90 30 9748

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.5)
D,Y	EP-A-0 232 154 (NIPPON OIL) * Whole document * - - -	1	C 10 M 169/04 C 10 M 133/12 // (C 10 M 169/04
D,Y	EP-A-0 097 118 (CIBA-GEIGY) * Claims 1-3,9-12; abstract; page 5; page 6, lines 1-5; example 1 * - - -	1	C 10 M 133:12 C 10 M 133:12) C 10 N 30:10 C 10 N 40:00
A	US-A-4 096 078 (YAFFE) * Whole document * - - - - -	1	
The present search report has been drawn up for all claims			
Place of search		Date of completion of search	Examiner
The Hague		10 December 90	DE LA MORINERIE B.M.
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			