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(54) LUBRICATING OIL COMPOSITION FOR GEAR.

(57) A lubricating oil composition for gear which contains as a base oil polyoxyalkylene glycol ester obtained by reacting a polymer prepared by ring-opening polymerisation or ring-opening copolymerization of one or more members selected from among alkylene oxides having 2 to 4 carbon atoms with a carboxylic acid having 1 to 10 carbon atoms. This lubricating oil composition has remarkably good oxidation stability and abrasion resistance at high temperatures and flowability at low temperatures.

EP 0 340 302 A1

GEAR LUBRICANT OIL COMPOSITION

FIELD OF THE INVENTION

This invention relates to a gear lubricant oil composition comprising polyoxyalkylene glycol ester(s) (also simply called polyglycol ester(s)) as a base oil. More particularly, it relates to a gear oil composition whose wear resistance properties and oxidation stability are improved by incorporating specific polyoxyalkylene glycol ester(s) as a base oil.

BACKGROUND OF THE INVENTION

Mechanical devices using gears have been used in a variety of industrial fields because they steadily transmit power to a driven device. These gear devices are broadly classified, depending on their uses, into industrial devices and those for use in automobiles. An appropriate gear oil suitable for the particular purpose is used in each case.

A gear oil is a lubricant oil that reduces friction between at least one pair of gears transmitting power from a driving device, e.g., a motor, to a driven one, thereby decreasing power loss and inhibiting damage to the gears, thus prolonging the life span of the gears. Presently, mineral oils are exclusively used as the base oils of gear oils. Gear oils further contain about 0.1 to 10 % by weight of various additives such as antioxidants, extreme pressure agents, rust preventives and anti-foaming agents.

Recently, machines made in Japan have been exported to various countries, including the USA and various European countries, and their shipments have been increasing yearly. It is now a usual practice to supply lubricants, e.g., gear oils, for such exported machines, in the manufacturing plant, before their shipment. Therefore it is necessary to take into consideration the properties of these lubricants in light of the working conditions in the customer's country. Thus the machine manufacturers have requested the lubricant oil manufacturers to supply products possessing properties that meet the trends of the demand (the market circumstances). In compliance with the wishes of the former, the latter have attempted to develop products satisfying these requirements.

In Japan, gear oils mainly employ base oils comprising mineral oils. When gears must be used at, for example, high temperatures or high loads, a gear oil composition comprising such a base oil, as well as specific additives such as extreme-pressure agents or antioxidants, is usually used.

An example of these gear oils is the lubricant oil composition disclosed in Japanese Patent Laid-Open No. 59-75995, which proposes improving the wear resistance, extreme-pressure qualities, and friction properties of a lubricant oil, by introducing an organo molybdenum compound of a specific structural formula and an acid phosphite ester or an acid phosphate ester as essential ingredients into, for example, a mineral oil having a lubricant viscosity. The mineral oil used is a refined mineral oil which is obtained by, for example, distilling a naphthene crude oil in vacuo to give a crude lubricant oil, and removing impurities such as unsaturated hydrocarbons or metallic components therefrom by solvent-refining or hydrogenation.

There have been attempts to use synthetic lubricant oils comprising, for example, esters, poly-α-olefins, and polyglycol oils. Generally, a synthetic lubricant oil of the desired lubricant properties may be obtained by controlling the synthesis conditions. Thus it is believed that synthetic lubricant oils can exhibit better anti-friction and anti-oxidation properties than mineral oils. As for polyglycol oils, Japanese Patent Publication No. 49-1339 has disclosed a lubricant which is prepared by adding, for example, an aromatic amine, an aliphatic phenol, and an organic phosphate, to a base oil. This lubricant composition has improved oxidation stability, load resistance, and rust resistance, at high working temperatures.

Japanese Patent Laid-Open No. 49-18821 discloses a polyglycol ester which is obtained by esterifying polyethylene glycol with an unsaturated carboxylic acid useful as a surfactant or a stain remover for fabrics.

Recently, the property requirements, particularly the wear resistance and oxidation stability at high working temperatures, of gear oils, have become more stringent. Presently, gear oils comprising mineral oils as base oils have an overwhelming share in the machine industries. However, gear oils which comprise a mineral base oil containing additives compensating for the shortcomings of the mineral base oil will not satisfy the various requirements of future markets. Thus it is impossible to provide gear oils possessing excellent properties unless the properties of the mineral oils, which are contained therein in an amount of 70 to 95 % as base oils, are improved.

Under these circumstances it is necessary to reconsider the use of synthetic lubricant oils as base oils of gear oils. However, there is presently no commercially available synthetic lubricant oil which has the requisite satisfactory properties and is also inexpensive. Regarding polyglycol oil, the relationship between its properties as a base oil and its molecular structure is not yet fully understood. Thus, efforts in this area have been directed to identifying suitable types and amounts of additives for conventional base oils. In addition, a polyglycol gear oil is liable to exhibit poor cold viscosity properties when used in a machine in a cold environment, resulting in failure during the normal operation of the transmission device.

DISCLOSURE OF THE INVENTION

It is an object of this invention to provide a low cost gear oil comprising a synthetic lubricant oil which, without requiring additives, has high wear resistance, excellent stability at high temperatures, high- or moderate-speed rotation, and high flowability at low temperatures.

Under these circumstances, we have attempted to overcome the above problems, and consequently found that a gear oil comprising specific polyoxyalkylene glycol ester(s) as a base oil exhibits not only a remarkably improved wear resistance and oxidation stability, even at high temperatures, but also improved viscosity properties at low temperatures.

Accordingly, this invention relates to a gear lubricant oil composition characterized by comprising polyoxyalkylene glycol ester(s) as a base oil in which the polyoxyalkylene glycol ester(s) are ester(s) obtained by reacting polymer(s) that are obtainable by ring opening (co)polymerization of one or more alkylene oxides selected from the group of alkylene oxide(s) having two to four carbon atoms with carboxylic acid(s) having one to ten carbon atoms.

We first describe the polyoxyalkylene glycol ester(s) of this invention: The polyglycol ester(s) of this invention are ester(s) of polyglycol(s) and carboxylic acid(s). The polyglycols are polymers obtained by ring-opening (co)polymerization of one or more alkylene oxides selected from the group of alkylene oxides having two to four carbon atoms, i.e., ethylene oxide, propylene oxide, butylene oxide, and isobutylene oxide. Therefore, the polyglycols include, for example, polyethylene glycol, polypropylene glycol, polybutylene glycol, polyisobutylene glycol, a ring-opening copolymer of ethylene oxide and propylene oxide, and a ring-opening copolymer of propylene oxide and butylene oxide. The average molecular weight of these polyalkylene oxides is about 800 to 4000. For example, a polypropylene glycol of an average molecular weight of 1000 to 3000 may be used in this invention.

The carboxylic acid(s) used in this invention are those having one to ten carbon atoms. Any straight-chain, branched, or cyclic carboxylic acids may be used, unless they contain unsaturated bond(s). Examples include formic, acetic, propionic, -butyric, isobutyric, valeric, trimethylacetic, caproic, enanthic, caprylic, pelargonic, capric, cyclohexylcarboxylic, and methylhexylcarboxylic acids. Among these carboxylic acids, those having five to ten carbon atoms are particularly preferred. The polyoxyalkylene glycol esters have a viscosity of 5 mm^2/s to 40 mm^2/s at 100 °C. A polyoxyalkylene glycol ester having a viscosity of less than 5 mm^2/s at 100 °C is undesirable, because of its poor wear resistance and low oxidation stability at high temperatures. On the other hand, one having a viscosity of more than 40 mm^2/s is also undesirable, since its poor flowability at low temperatures results in insufficient lubricating effects. A gear oil that is to be used in a machine in a cold area is particularly required to have satisfactory viscosities at low temperatures. It is possible to achieve a good lubricating effect by using polyoxyalkylene glycol(s) having a viscosity of 6 x 10^4 mpa.s to 95 x 10^4 mpa.s at -40 °C in this invention. A particularly preferred base oil for the gear oil of this invention comprises polypropylene glycol ester or polyethylene glycol ester having a viscosity of 8 mm^2/s to 25 mm^2/s at 100 °C and 10 x 10^4 mpa.s to 60 x 10^4 mpa.s at -40 °C.

The polyoxyalkylene glycol ester(s) of this invention can be produced by any known method. Namely, a polyglycol and a carboxylic acid may be esterified under any known and conventional esterification condition. The polyglycol is reacted with a nearly equi-molar or slight excess of carboxylic acid, i.e., at a molar ratio of 1 : 1 to 1 : 1.5. These reactants are introduced into a reactor and allowed to react in it in the presence of a catalyst at about 80 to 150 °C, preferably about 100 °C to 120 °C, under a pressure of about 1 to 5 atm, preferably about 1 to 3 atm. Either a continuous or batch-type reactor may be used, although the latter is preferred from the operational standpoint. An acid catalyst such as phosphoric acid may be used. An inert gas such as nitrogen gas is passed through the reactor to inhibit the oxidation of the reaction product. Alkylbenzene(s) such as benzene or toluene are used as solvent(s) to prevent the water formed during the reaction from returning to the reactor. When the amount of water thus formed reaches, on a mole basis, that of the starting materials, heating is terminated and any excess acid is neutralized with an alkali

such as caustic soda. Finally, the reaction product is distilled in vacuo and the solvent(s) and excess starting materials are distilled off to obtain the polyglycol ester. Polypropylene glycol may be prepared by polymerizing propylene oxide in the presence of a metal alcoholate as a catalyst, and water or an alcohol as an initiator, under a pressure of 1 to 10 atm at 100 to 150 ° C.

As the polyoxyalkylene glycol ester(s) of this invention, polypropylene glycol ester may be used alone. Alternately, a base oil that is a mixture of a polypropylene glycol ester and a polyethylene glycol ester, or a polybutylene glycol ester, may be used. It is very effective to use as a base oil comprising such a mixture of polyalkylene glycol esters to achieve the desired viscosity properties as defined above. That is to say, a polyoxyalkylene glycol ester base oil having the appropriate viscosity properties can be readily obtained by blending a polypropylene glycol ester, which has a high molecular weight and high viscosity at low temperatures, with a polyethylene glycol ester, which has a relatively low molecular weight and is highly flowable at low temperatures. Similarly, the polyoxyalkylene glycol ester of this invention may contain other esters. Examples of these esters are monoesters, diesters, and polyesters, i.e., those having three or more ester bonds. The monoesters include aliphatic esters having 15 or more carbon atoms: the diesters include those formed by esterifying aliphatic dibasic acids having 4 to 14 carbon atoms with monoalcohols having 4 to 14 carbon atoms; and the polyesters include triesters formed from trihydric alcohols having 4 to 13 carbon atoms and fatty acids having 3 to 13 carbon atoms, and tetraesters formed from tetrahydric alcohols having 5 to 10 carbon atoms and fatty acids having 5 to 10 carbon atoms. Among these esters, diesters such as diisodecyl adipate, dioctyl sebacate, and dioctyl azelate, and triesters such as trimethylolpropane triheptanoate, and trimethylolpropane trioctanoate, are particularly preferred. These esters enhance the oxidation stability of polyalkylene glycol esters. In particular, the addition of about 10 to 50 % by weight, preferably 20 to 40 % by weight, of the ester(s), can significantly enhance the lubricant properties of a gear oil comprising polyalkylene glycol ester(s), of low viscosity, i.e., 5 to 20 mm^2/s at 100 ° C as a base oil.

The polyglycol ester synthetic lubricant oil of this invention can be used as a gear oil. It exhibits remarkable properties, particularly when used as an industrial gear oil. Namely, it can be advantageously used as a gear oil at high temperatures, high loads, and high rotation speeds, or as a gear oil for machines used under changing temperature conditions, i.e., varying widely from low to high temperatures. The polyglycol ester base oil may additionally contain a suitable amount of conventional additives, depending on its use. Suitable additives include antioxidants such as aromatic amines (0.3 to 5 % by weight); extreme pressure agents such as tricresyl phosphate (0.3 to 13 % by weight); metal inactivators (0.01 to 3 % by weight); rust preventtives (0.05 to 2 % by weight); oiliness improvers (0.01 to 3 % by weight); and anti-foaming agents (0.0005 to 0.02 % by weight). These additives may be added in a total amount of 3 to 15 % by weight and, unlike a mineral base oil, no viscosity index additive is required.

Since the polyoxyalkylene glycol ester(s) of this invention are obtained by esterifying with carboxylic acid(s) the terminal alcohol group of polyethers that are obtained by polymerizing oxyalkylene through a ring-opening mechanism, the polyoxyalkylene glycol ester(s) of this invention have high oxidation stability and flowability, even at high temperatures. Further, they can act as viscosity index improvers since they have specific viscosities at both high and low temperatures. Unlike polyoxyalkylene glycol(s), they contain no terminal hydroxyl group. Thus their oxidation stability is not adversely affected, even at high temperatures. Furthermore, they exhibit excellent compatibility with antiwear agents such as tricresyl phosphate, which results in highly preferred lubricant properties for use as gear oil compositions.

THE OPTIMUM EMBODIMENTS OF THE INVENTION

Examples 1 - 6

A base oil for a gear oil (A) of this invention was prepared in the following manner: 1000 g of polypropylene glycol of an average molecular weight of 1,000, 144g (approximately 1.2 mol per mol of the polyglycol) of caproic acid (having six carbon atoms), and 100 g of toluene, were put in a flask. After adding to it 0.4 % by weight of phosphoric acid as a catalyst, the mixture was heated to 130 ° C, and then allowed to react at 100 to 120 ° C under atmospheric pressure and a nitrogen atmosphere. When the water formed during the reaction reached about one mol, the heating was stopped. Alkali (caustic soda) was then added to the reaction product to neutralize the unreacted carboxylic acid. The toluene was distilled off in vacuo, thereby giving an ester of polypropylene glycol with caproic acid.

Similarly, base oils for gear oils (B to F) of this invention were prepared. To the base oils A to F, an extreme-pressure agent (tricresylphosphate), and an antioxidant (an aromatic amine compound) were added. The gear lubricant oil compositions of this invention as shown in Table 1 were obtained.

The wear resistance of each gear oil composition of this invention as thus prepared was determined in the following manner: a four-ball wear tester (Shell type) was operated at an oil temperature of 150 °C , at a rate of 1800 rpm under a load of 25 kg for 30 minutes, and then the wear diameter of a roller (1/2 inch) was determined. Table 2 shows the results.

Then an IEA gear tester was operated at an oil temperature of 140 °C at a gear rate of 7000 rpm under a load of 60 lbs for three hours. Subsequently the weight loss in the large and small gears was determined. Table 2 shows the results.

Further, the oxidation stability of each gear oil composition of this invention was determined according to Fed. 791 b. 5308 at an oil temperature of 150 °C mentioned for 200 hours. The change in viscosity (% @ 100 °C), the total acid number gain (mg KOH/g), insoluble matters in oil (% by weight; determined by the pentane-B method), and the change in the weight of the metals, i.e., iron and copper (mg/cm^2), were determined. Table 2 shows the results.

Comparative Examples 1 - 5

Comparative gear oils (a to e) were prepared by adding the appropriate amounts of various additives such as a viscosity index improver, an antiwear agent, and an antioxidant, to various commercially available base oils. They were ATF-D II, ATF-D II′, Gear Oil 75W-90, a diester oil (DIDA: diisodecyl adipate), and polyglycol (polypropylene glycol), although no viscosity index improver was added to the diester and polyglycol oil. Table 1 shows the composition and properties of each gear oil thus obtained.

These comparative gear oils were also subjected to the same procedures as those stated in Examples 1 to 6, to determine the wear resistance and oxidation stabilities thereof. Table 2 shows the lubricant properties.

The above Examples 1 to 6 and Comparative Examples 1 to 5 indicate that the polyglycol ester gear oils of this invention are superior to conventional oils such as ATF-DII or Gear Oil 75 W-90 in their viscosity properties, wear resistance, and oxidation stability. Further, it was found that the polyglycol ester gear oils of this invention exhibited remarkably improved wear resistances and viscosity properties as compared to the diester oil (DIDA).

Table 1

Gear oil composition									
	Base Oil (**)				Additive *(% by wt.)	Viscosity			
	Glycol ester		Mineral Oil	Synthetic Oil		100 ° C (mm^2/S)		-40 ° C (mPa • s)	
	PPGE	PEGE				Base oil	Product	Base oil	Product
A	90(1100)				10	8.45	8.10	10×10^4	15×10^4
B	90(1200)				10	9.30	9.01	13×10^4	19×10^4
C	90(1600)				10	16.2	15.3	26×10^4	38×10^4
D	90(1800)				10	21.4	19.3	37×10^4	53×10^4
E		90(900)			10	8.75	8.95	-	-
F		90(1400)			10	15.95	14.1	-	-
a			85		15	4.0	7.21	solidified	4.2×10^4
b			85		15	4.5	8.50	do.	10×10^4
c			70		30	4.0	14.20	do.	14.8×10^4
d				90	10	3.68	3.80	0.345×10^4	0.48×10^4
e				90(500)	10	4.9	5.3	6.1×10^4	8.3×10^4
Note:									

*: A to F, and d and e, contain tricresyl phosphate and an aromatic amine, but no viscosity index improver.
a and b contain 7 % by weight of a viscosity index improver.
c contains 20 % by weight of a viscosity index improver.
**: The value in parentheses is an average molecular weight.

Table 2

Properties											
	Example						Comp. Ex.				
	1	2	3	4	5	6	1	2	3	4	5
	A	B	C	D	E	F	a	b	c	d	e
	PPGE				PEGE		ATF-DII	ATF-DII′	75W90	DIDA	PPG
Viscosity properties	○	○	○	○	○	○	×	×	×	△	△
4-ball wear test Wear diameter (*mm*)	0.35	0.32	0.30	0.28	0.34	0.30	0.48	0.46	0.42	0.50	0.49
IAE gear test Gear weight loss (*mg*)	84	61	16	8	65	18	100	75	34	200	150
Change in viscosity (%) @ 100°C	0.95	0.95	0.97	0.96	0.97	0.98	1.06	1.06	1.12	1.01	1.02
Total acid number gain (*mg* KOH/ *g*)	0.4	0.3	0.2	0.2	0.3	0.2	1.50	1.40	2.50	0.10	0.80
Insoluble matters in oil (wt. %)	0.01	0.01	0.005	0.005	0.01	0.01	0.05	0.05	3.40	0.01	0.05
Change in metal weight											
Fe (*mg/cm²*)	-0.01	-0.01	+0.00	+0.00	+0.01	+0.00	-0.03	+0.01	-0.03	+0.01	-0.03
Cu (*mg/cm²*)	+0.00	+0.00	+0.00	+0.00	-0.05	-0.05	-1.40	-1.35	-61.2	-0.01	-0.30

EP 0 340 302 A1

INDUSTRIAL APPLICATION

The polyoxyalkylene glycol ester synthetic lubricant oils of this invention, which exhibit high oxidation stability and wear resistance at high temperatures, and high flowability at low temperatures, undergo less denaturation than conventional mineral-oil-based, polyglycol-based, or other synthetic, lubricant oils. Thus they can be used at a low cost with little or no maintenance for machines.

Claims

A gear lubricant oil composition characterized by comprising polyoxyalkylene glycol ester(s) as a base oil wherein said polyoxyalkylene glycol ester(s) are ester(s) obtained by reacting polymer(s) that are obtainable by ring-opening polymerization or copolymerization of one or more alkylene oxides selected from the group of alkylene oxides having 2 to 4 carbon atoms, with carboxylic acid(s) having 1 to 10 carbon atoms.

INTERNATIONAL SEARCH REPORT

International Application No PCT/JP87/00763

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all) [3]

According to International Patent Classification (IPC) or to both National Classification and IPC

Int.Cl[4] C10M105/40, 107/34, C10N40:04

II. FIELDS SEARCHED

Minimum Documentation Searched [4]

Classification System	Classification Symbols
IPC	C10M105/38, 105/40, 107/32, 107/34, C10N40:04

Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched [5]

III. DOCUMENTS CONSIDERED TO BE RELEVANT [14]

Category *	Citation of Document, [16] with indication, where appropriate, of the relevant passages [17]	Relevant to Claim No. [18]
Y	JP, A, 52-127484 (Kao Soap Co., Ltd.) 26 October 1977 (26. 10. 77) Column 1, lines 5 to 16, column 7, lines 4 to 8, column 7, line 20 to column 8, line 2 (Family: none)	1
Y	JP, A, 62-201995 (Toa Nenryo Kogyo Kabushiki Kaisha) 5 September 1987 (05. 09. 87) Column 1, lines 5 to 11 (Family: none)	1
E	JP, A, 62-241996 (Toa Nenryo Kogyo Kabushiki Kaisha) 22 October 1987 (22. 10. 87) Column 1, lines 5 to 11 (Family: none)	1

* Special categories of cited documents: [16]

"A" document defining the general state of the art which is not considered to be of particular relevance

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"P" document published prior to the international filing date but later than the priority date claimed

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"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step

"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

IV. CERTIFICATION

Date of the Actual Completion of the International Search [2]	Date of Mailing of this International Search Report [2]
December 10, 1987 (10.12.87)	December 21, 1987 (21.12.87)
International Searching Authority [1]	**Signature of Authorized Officer [20]**
Japanese Patent Office	