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(54) USE OF POLYCLYCERIN ESTERS AS FRICTION MODIFIERS IN LUBRICANT FORMULATIONS

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(57) **ABSTRACT**

The present invention relates to a lubricating oil composition comprising polyglycerol partial esters of polyfunctional carboxylic acids and saturated or unsaturated, linear or branched fatty acids and/or poly(hydroxystearic acid) and the use thereof to lubricate an engine and reduce friction.

Stribeck curve measurements after two hours of run in phase

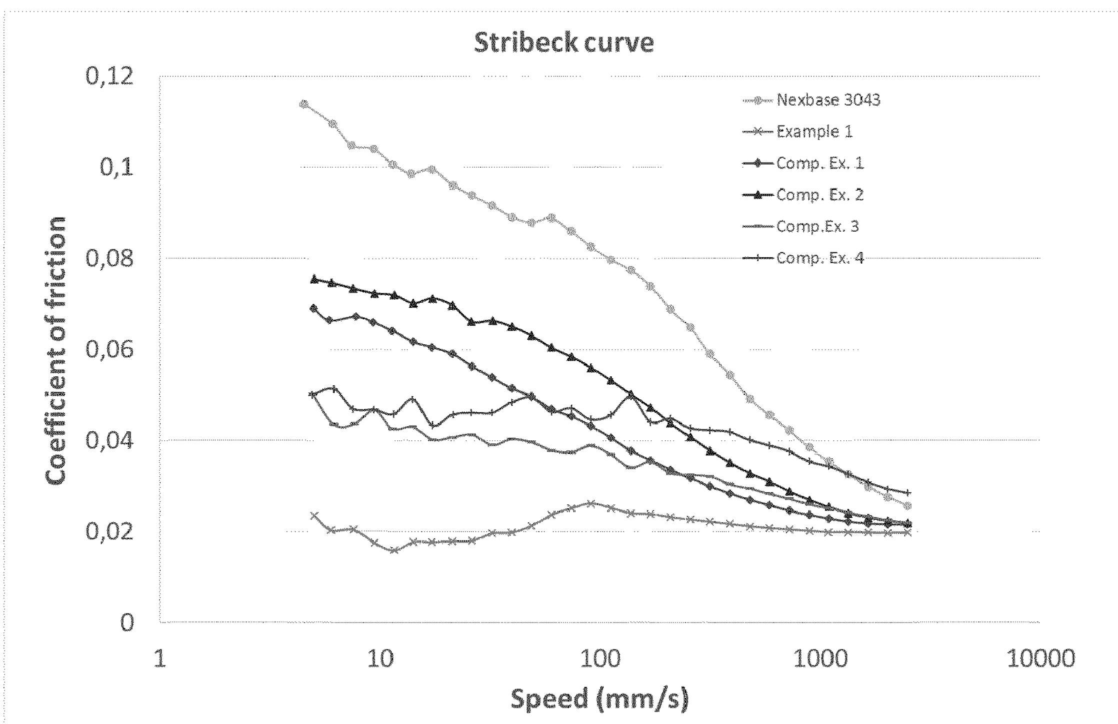
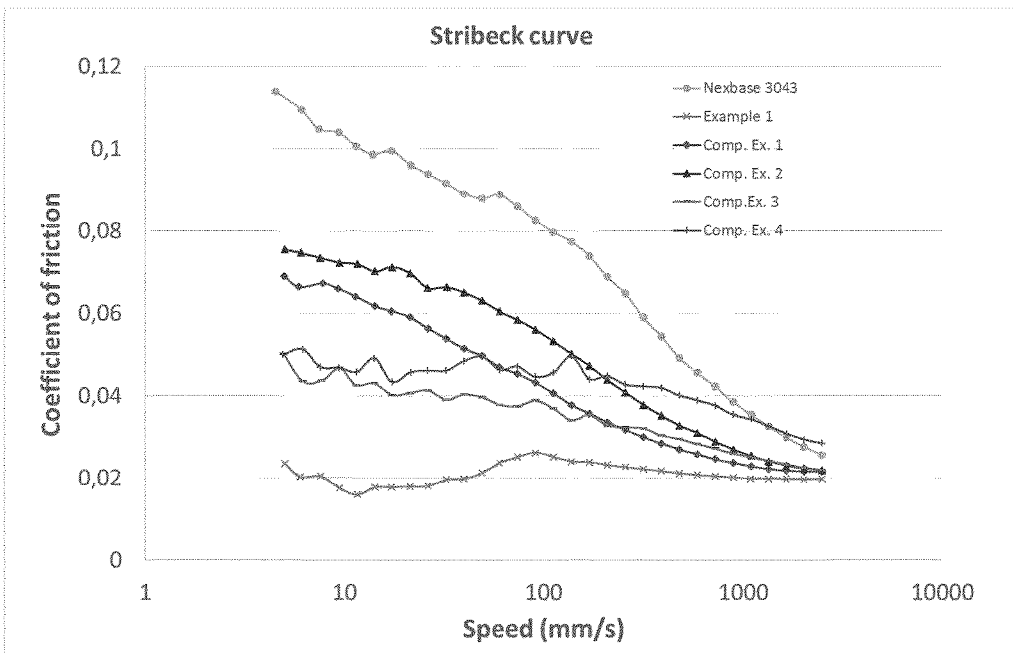


Figure 1: Stribeck curve measurements after two hours of run in phase



USE OF POLYCLYCERIN ESTERS AS FRICTION MODIFIERS IN LUBRICANT FORMULATIONS

[0001] The present invention relates to a lubricating oil composition comprising polyglycerol partial esters of polyfunctional carboxylic acids and saturated or unsaturated, linear or branched fatty acids and/or poly(hydroxystearic acid) and the use thereof to lubricate an engine and reduce friction.

[0002] Energy losses due to friction in lubricated contacts can be reduced by adding friction modifiers to the lubricant formulation. Friction modifiers are used especially in gear and engine oil formulations where lower viscosity formulations are applied in order to save energy. While reducing the energy losses in the fluid, lubricants with low viscosities struggle to keep the sliding surfaces completely apart from each other and require a friction modifier to maintain a lubricant film on the surfaces.

[0003] Friction modifiers work by forming adsorption layers on the metal surface. They are of high importance under mixed lubrication conditions when the sliding surfaces are not always separated by a lubricant film of sufficient thickness. Such conditions can be simulated with a mini traction machine (MTM) that is able to measure the friction coefficient over a broad range of conditions.

[0004] Friction reducing additives that have been used to improve fuel economy fall into three main chemically-defined categories, which are organic, metal organic and oil insoluble. The organic friction reducing additives themselves fall within four main categories which are (i) carboxylic acids or their derivatives, including partial esters, (ii) nitrogen-containing compounds such as amides, imides, amines and their derivatives, (iii) phosphoric or phosphonic acid derivatives and (iv) organic polymers.

[0005] In current commercial practice examples of friction reducing additives are glycerol monooleate and oleylamide, which are both derived from unsaturated fatty acids, or molybdenum dialkyldithiocarbamate. Also used are copolymers with blocks of polyethyleneglycol (WO 2011/107739 and WO 2015/065801) or other alkoxide polymers (WO 2014/139935). It is further known that polyglycerol solubilized by a long alkyl chain attached via an ether function (U.S. Pat. No. 7,803,745) or an ester function (WO 2015/044639) can be applied as a friction modifier.

[0006] It was now surprisingly found that polyglycerol partial esters of polyfunctional carboxylic acids and saturated or unsaturated, linear or branched fatty acids and/or poly(hydroxystearic acid) show superior performance as friction modifiers for lubricants. Superior means a larger reduction of the friction coefficient and/or more efficient friction reduction due to a lower treat rate and/or a better combination of oil compatibility and friction reducing performance.

[0007] In a first embodiment, the present invention is directed to a lubricating oil composition comprising a lubricating base oil and polyglycerol partial esters, characterized in that the polyglycerol partial esters are obtainable by esterification of a polyglycerol mixture with

[0008] (i) polyfunctional carboxylic acids and

[0009] (ii) saturated or unsaturated, linear or branched fatty acids and/or

[0010] (ii) poly(hydroxystearic acid).

[0011] Polyglycerol esters were found to work especially in apolar formulations containing mainly API Group II, Ill and/or IV as lubricating base oils.

[0012] The American Petroleum Institute (API) currently defines five groups of lubricant base stocks (API Publication 1509). Groups I, II and III are mineral oils which are classified by the amount of saturates and sulphur they contain and by their viscosity indices. The table below illustrates these API classifications for Groups I, II and III.

Group	Saturates	Sulphur content	Viscosity Index (VI)
I	<90%	>0.03%	80-120
II	at least 90%	not more than 0.03%	80-120
III	at least 90%	not more than 0.03%	at least 120

[0013] Group I base stocks are solvent refined mineral oils, which are the least expensive base stock to produce, and currently account for the majority of base stock sales. They provide satisfactory oxidation stability, volatility, low temperature performance and traction properties and have very good solvency for additives and contaminants.

[0014] Group II base stocks are mostly hydroprocessed mineral oils, which typically provide improved volatility and oxidation stability as compared to Group I base stocks.

[0015] Group III base stocks are severely hydroprocessed mineral oils or they can be produced via wax or paraffin isomerisation. They are known to have better oxidation stability and volatility than Group I and II base stocks but have a limited range of commercially available viscosities.

[0016] Group IV base stocks differ from Groups I, II and III in that they are synthetic base stocks comprising e.g. polyalphaolefins (PAOs). PAOs have good oxidative stability, volatility and low pour points. Disadvantages include moderate solubility of polar additives, for example antiwear additives.

[0017] Group II, II and IV oils are known for their exceptional stability towards oxidation and high temperatures, but they provide only limited solubility for polar additives such as friction modifiers. For this reason the lubricating oil compositions according the present invention may contain up to 10% of an ester base oil according to API Group V as solubilizer.

[0018] Group V base stocks are all base stocks that are not included in the other Groups. Examples include alkyl naphthalenes, alkyl aromatics, vegetable oils, esters (including polyol esters, diesters and monoesters), polycarbonates, silicone oils and polyalkylene glycols.

[0019] The friction modifier performance of polyglycerol partial esters according to the present invention can be achieved in formulations with and without the additional ester base stock.

[0020] In a preferred embodiment, the lubricating oil compositions according to the present invention are characterized in that they comprise

[0021] (a) 90-100% by weight of an apolar oil selected from the group consisting of API Group II, III and IV and/or mixtures thereof and

[0022] (b) 0-10% of a polar ester oil of Group V according to the definition of the American Petroleum Institute (API),

based on the total weight of the lubricating oil composition.

[0023] Polyglycerol partial esters of poly(hydroxystearic acid) and polyfunctional carboxylic acids are known as W/O emulsifiers in cosmetic or pharmaceutical formulations and as auxiliaries for dispersing inorganic micropigments in oily dispersions (EP 1 500 427 B1 and EP 1 683 781 B1). For best performance as friction modifiers the parameters surface activity or polarity and oil solubility have to be balanced and adjusted to the polarity of the respective oil mixture used as base stock. The balance of polar and apolar parts in the polymer is described by the HLB value that is calculated. This can be done by selection of a polyglycerol characterized by a certain degree of polymerization and selection of carboxylic acids and polycarboxylic acids. Especially the amount of polycarboxylic acids has a major influence on the molecular weight (measured by SEC) of the resulting component. The ratio of acid and alcohol functions is important as it determines the degree of esterification and thus the amount of unreacted OH-functions (described by the OH-number determined by titration). Free acid functions are unwanted and should be kept at a minimum level (described by the acid value, determined by titration).

[0024] The superior performance relative to other friction modifiers is attributed to the high polarity of the polyglycerol moieties, the free OH-functions due to the partial esterification and the polymeric nature of the substances which provides multiple interaction sites between the surface and the friction reducing component. The polymeric nature of the described friction modifiers is especially important for the solubility of the component as very polar moieties in the molecule have to be kept in solution.

[0025] These polyglycerol partial esters of polyfunctional carboxylic acids and saturated or unsaturated, linear or branched fatty acids and/or poly(hydroxystearic acid) are obtainable by esterification of a polyglycerol mixture with saturated or unsaturated, linear or branched fatty acids having 8 to 22 carbon atoms, preferably 12 to 18 carbon atoms, and polyfunctional carboxylic acids having 4 to 54 carbon atoms, preferably 6 to 36 carbon atoms, more preferably 6 to 18 carbon atoms and even more preferably 6 to 12 carbon atoms, and a mean functionality of from 2 to 4, preferably 2 to 3 and more preferably 2 to 2.5, the degree of esterification of the polyglycerol mixture being between 30 and 75% of the OH groups.

[0026] The mean functionality of a mixture of polyfunctional carboxylic acids can be determined using the following formula:

$$\overline{N} = \sum_i \frac{x_i}{100} \cdot N_i$$

with $\overline{N}$=mean functionality of a mixture of polyfunctioal carboxylic acids

[0027] x_i=mass fraction [%] of individual polyfunctional carboxylic acid i

[0028] N_i=functionality of individual polyfunctional carboxylic acid i

[0029] Particularly suitable linear or branched saturated fatty acid components are selected from the group consisting of caprylic acid, capric acid, lauric acid, tridecanoic acid, myristic acid, palmitic acid, margaric acid, stearic acid, isostearic acid, arachidic acid, behenic acid and mixtures thereof. A suitable saturated fatty acid is also 12-hydroxy stearic acid. Naturally occurring mixtures are, for example, the coconut fatty acids, which contain lauric acid as the main constituent and also contain saturated C14- to C18-fatty acids and possibly small amounts of saturated C8- to C18-fatty acids and unsaturated fatty acids, and tallow fatty acids, which are essentially a mixture of palmitic acid and stearic acid.

[0030] Suitable unsaturated fatty acid components are monoolefinically unsaturated acids, for example hexadecenoic acids, octadecenoic acids, such as oleic acid (cis-9-octadecenoic acid) or eladidic acid (trans-9-octadecenoic acid), eicosenoic acids and docosenoic acids, such as erucic acid (cis-13-docosenoic acid) or brassidic acid (trans-13-docosenoic acid), poly-unsaturated fatty acids, for example octadecadienoic acids and octadecatrienoic acids, such as linoleic acid and linolenic acid, ricinoleic acid and mixtures thereof.

[0031] The liquid fatty acids which contain 18 to 22 carbon atoms, namely oleic, ricinoleic, erucic and isostearic acids, are particularly suitable. Because of branching solidification points are below 35 DEG C. It is also possible to use fatty acid mixtures, which can also contain wax-like components, such as hydrogenated ricinoleic acid.

[0032] The poly(hydroxystearic acids) co-used according to the invention are prepared, for example, by polycondensation of hydroxystearic acid, preferably 12-hydroxystearic acid, which is obtained by hardening of ricinoleic acid or technical-grade castor oil fatty acid, by known processes. They have a mean degree of polymerization of 1 to 10 units, preferably 2 to 8 units and in particular 2 to 5 units.

[0033] The polyfunctional carboxylic acids can be dicarboxylic acids, tricarboxylic acids or polycarboxylic acids. The polyfunctional carboxylic acids may be unsubstituted or optionally substituted by one, two or three hydroxyl groups, preferably by one hydroxyl group.

[0034] The aliphatic dicarboxylic acids used for the esterification should have a chain length of 3 to 18 carbon atoms. They can be straight-chain or branched, such as, for example, malonic acid, succinic acid, fumaric acid, maleic acid, dimethylglutaric acid, adipic acid, trimethyladipic acid, azelaic acid, sebacic acid, dodecanedioic acid, hecadecanedioic acid, octadecanedioic and their anhydrides.

[0035] The dicarboxylic acids used can also be dimeric fatty acids. As is known, these are mixtures of acyclic and cyclic dicarboxylic acids which are obtained by a catalyzed dimerization reaction of unsaturated fatty acids having 12 to 22 carbon atoms.

[0036] For the preparation and use of dimer acids and their physical and chemical properties, reference is made to the publication "The Dimer Acids: The chemical and physical properties, reactions and applications", Ed. E. C. Leonard; Humko Sheffield Chemical, 1975, Memphis, Tenn.

[0037] The dicarboxylic acids can also contain, to a lesser extent, tri-and polyfunctional carboxylic acids. The functionality of the mixture should not exceed a value of 2 to 2.5 molar average.

[0038] Furthermore, as polyfunctional carboxylic acids can be used phthalic acid, trimellitic acid and pyromellitic acid.

[0039] Under the term "polyglycerol" according to the present invention encompasses a polyglycerol comprising glycerol. Therefore, for the calculation of amounts, masses etc. the glycerol content has to be taken into account. The term glycerol oligomers or polyglycerol(s) encompasses linear as well as cyclic structures.

[0040] Suitable polyglycerols are in particular those having a mean degree of condensation of >2, preferably from 3 to 6. These are technical-grade polyglycerol mixtures which are obtained, for example, by alkali-catalyzed condensation of glycerol at elevated temperatures and from which fractions with the desired degree of condensation can be obtained if desired by distillation methods. Also suitable are polyglycerols obtained by other methods, e.g. from epichlorohydrin or glycidol. Commercial polyglycerols can be obtained from companies like Solvay, Spiga Nord, Daicel or Lonza.

[0041] In the polyglycerol partial esters according to the invention, from 30 to 75%, preferably from 50 to 65%, of the hydroxyl groups of the polyglycerol are esterified. They are initially esterified to a degree of esterification of from 25 to 60%, preferably from 35 to 50%, using fatty acid and in a second step, using dicarboxylic acids to an overall degree of esterification of from 30 to 75%, preferably from 50 to 65%. Through suitable selection of the hydrophilic and lipophilic molecular proportions, an HLB value of from 3 to 7 is aimed at in order to obtain favorable products.

[0042] The HLB value is a measure of the degree to which the molecule is hydrophilic or lipophilic, determined by calculating values for the different regions of the molecule. For the purpose of the present invention, the HLB value of the polyglycerol partial esters is calculated as follows:

$$HLB=(mp/(mp+ma))*20,$$

where mp is the mass of polyglycerol, and ma is the mass of carboxylic acid mixture comprising mono-, di- and polycarboxylic acids as well as polyhydroxy fatty acids used in the synthesis of the polyglycerol ester. For example, esterification of 100 g polyglycerol with 90 g mono-carboxylic acid and 10 g dicarboxylic acid would result in an HLB of (100 g 1(90 g+10 g+100 g))*20=10, independent of the degree of polymerization of the polyglycerol and the type of carboxylic acids used.

[0043] For the present invention it is essential that the polyglycerol backbone of the polyglycerol partial ester comprises an average degree of polymerization of from 2 to 8, preferred from 2.5 to 6, particularly preferred from 3 to 4.5. A suitable method for determining the oligomer distribution of the polyglycerol in a given polyglycerol partial ester comprises hydrolysis or alcoholysis of the partial ester, separation of the resulting polyglycerol from the formed carboxylic acid compounds, and analysis by gas chromatography after derivatization.

[0044] The polyglycerol partial esters according to the invention can be prepared in a manner known per se by heating the reaction components and removing the resultant water of reaction by distillation. The reaction can be accelerated by means of acidic catalysts such as sulfonic acids, phosphoric acid or phosphorous acid or basic catalysts such as alkali metal or alkaline earth metal oxides or hydroxides, alcoholates or salts, or Lewis acids, such as tin salts,. However, the addition of a catalyst is not absolutely necessary. The polyglycerol partial esters are preferably prepared in a two-step process, which again is carried out in a manner known per se. In a first step, the polyglycerol is esterified using the monofunctional fatty acid or some of the fatty acid. After most, or all, of the fatty acid has reacted, the polyfunctional carboxylic acid is then added and the esterification reaction is continued. The progress of the reaction can be monitored, for example, via the water of reaction removed, by measuring the acid number or by infrared spectroscopy. In general, an acid number in the end product of <20, preferably <10, is desired. Products with an acid number of <5 are particularly preferred. The acid number is measured according to DIN EN ISO 2114.

[0045] The weight average molecular weight M_w of the claimed polyglycerol partial esters determined via SEC versus polymethylmethacrylate (PMMA) standard is in the range of 2,000 to 15,000 g/mol, preferably in the range of 4,000 to 10,000 g/mol, with a polydispersity index of 1.5 to 5, preferably 2 to 4.

[0046] The OH-number of the polyglycerol partial esters according to the present invention is in the range of 50 to 180 mg KOH/g, preferably 80 to 170 mg KOH/g and most preferred in the range of 110 to 150 mg KOH/g. The OH-number is measured according to DIN 53 240-2.

[0047] For engine oils the organic polymeric friction reducing additive is present at levels of 0.2 to 5% by weight, preferably 0.3 to 3% by weight, and even more preferably 0.5 to 2% by weight in an automotive engine oil, based on the total weight of the lubricating oil composition.

[0048] Accordingly, a preferred embodiment of the present invention is directed to a lubricating oil composition, comprising

[0049] (a) 0.2 to 5% by weight, preferably 0.3 to 3% by weight, even more preferably 0.5 to 2% by weight, of a polyglycerol partial ester, based on the total weight of the lubricating oil composition,

[0050] (b) 85 to 99.8% by weight, preferably 87 to 99.7% by weight, even more preferably 88 to 99.5% by weight, of an apolar base stock selected from the group consisting of API Group II, III and IV and/or mixtures thereof, based on the total weight of the lubricating oil composition, and

[0051] (c) 0 to 10% by weight of a polar ester oil of Group V according to the definition of the American Petroleum Institute (API), based on the total weight of the lubricating oil composition.

[0052] In a preferred embodiment (a), (b) and (c) add up to 100% by weight.

[0053] In addition to the polyglycerol partial esters in accordance with the invention, the lubricant oil compositions detailed herein may also comprise one or more further additive(s). These additives include viscosity index (VI) improvers, pour point depressants and dispersant inhibitor (DI) additives selected from the group consisting of dispersants, detergents, defoamers, corrosion inhibitors, antioxidants, antiwear and extreme pressure additives and further friction modifiers.

[0054] Suitable viscosity index improvers are, for example, polyalkyl(meth)acrylate polymers, ethylene-propylene copolymers, styrene-isoprene copolymers, hydrogenated styrene-isoprene copolymers, polyisobutylene, and dispersant type viscosity index improvers.

[0055] Suitable pour point depressants are, for example, polyalkyl(meth)acrylate polymers.

[0056] Suitable dispersants are, for example, alkenyl succinimides, alkenyl succinate esters, alkenyl succinimides modified with other organic compounds, alkenyl succinimides modified by post-treatment with ethylene carbonate or boric acid, pentaerythritols, phenatesalicylates and their post-treated analogs, alkali metal or mixed alkali metal, alkaline earth metal borates, dispersions of hydrated alkali metal borates, dispersions of alkaline-earth metal borates, polyamide ashless dispersants and the like or mixtures of such dispersants.

[0057] Suitable detergents are, for example, metal detergents which include oil-soluble neutral and overbased sulfonates, phenates, sulfurized phenates, thiophosphonates, salicylates, and naphthenates and other oil-soluble carboxylates of a metal, particularly the alkali or alkaline earth metals, as for example barium, sodium, potassium, lithium, calcium, and magnesium. The most commonly used metals are calcium and magnesium, which may both be present in detergents used in a lubricant, and mixtures of calcium and/or magnesium with sodium. Particularly convenient metal detergents are neutral and overbased calcium sulfonates having TBN of from 20 to 450, neutral and overbased calcium phenates and sulfurized phenates having TBN of from 50 to 450 and neutral and overbased magnesium or calcium salicylates having a TBN of from 20 to 450. Combinations of detergents, whether overbased or neutral or both, may be used as well.

[0058] Suitable defoamers are, for example, selected from the group consisting of alkyl (meth)acrylate polymers, silicone oil and dimethyl silicone polymers.

[0059] Suitable corrosion inhibitors are, in many cases, divided into antirust additives and metal passivators/deactivators. The antirust additives used may, inter alia, be sulphonates, for example petroleumsulphonates or (in many cases overbased) synthetic alkylbenzenesulphonates, e.g. dinonylnaphthenesulphonates; carboxylic acid derivatives, for example lanolin (wool fat), oxidized paraffins, zinc naphthenates, alkylated succinic acids, 4-nonylphenoxyacetic acid, amides and imides (N-acylsarcosine, imidazoline derivatives); amine-neutralized mono- and dialkyl phosphates; morpholine, dicyclohexylamine or diethanolamine. The metal passivators/deactivators include benzotriazole, tolyltriazole, tolutriazole (such as Vanlube® 887 or 887E), 2-mercaptobenzothiazole, dialkyl-2,5-dimercapto-1,3,4-thiadiazole; N,N'-disalicylideneethylenediamine, N,N'-disalicylidenepropylenediamine; zinc dialkyldithiophosphates and dialkyl dithiocarbamates.

[0060] Suitable anti-oxidants are, for example, phenol type (phenolic) oxidation inhibitors, such as 4,4'-methylene-bis(2,6-di-tert-butylphenol), 4,4'-bis(2,6-di-tert-butylphenol), 4,4'-bis(2-methyl-6-tert-butylphenol), 2,2'-methylene-bis(4-methyl-6-tert-butyl-phenol), 4,4'butylidene-bis(3-methyl-6-tert-butylphenol), 4,4'-isopropylidene-bis(2,6-ditertbutylphenol), 2,2'-methylene-bis(4-methyl-6-nonylphenol), 2,2'-isobutylidene-bis(4,6-dimethylphenol), 2,2'-methylene-bis(4-methyl-6-cyclohexylphenol), 2,6-di-tert-butyl-4-methylphenol, 2,6-di-tert-butyl-4-ethylphenol, 2,6-di-tert-butylphenol, 2,4-dimethyl-6-tert-butyl-phenol, 2,6-di-tert-1-dimethylamino-p-cresol, 2,6-di-tert-4-(N,N'dimethylamino-methylphenol), 4,4'-thiobis(2-methyl-6-tert-butylphenol), 2,2'-thiobis(4-methyl-6-tert-butylphenol), bis (3-methyl-4-hydroxy-5-tert-butylbenzyl)-sulfide, and bis(3,5-di-tert-butyl-4-hydroxybenzyl). Other types of oxidation inhibitors include alkylated diphenylamines (e.g., Irganox L-57 from BASF), metal dithiocarbamate (e.g., zinc dithiocarbamate) and methylenebis(dibutyldithiocarbamate).

[0061] Suitable antiwear additives are, for example, phosphates, phosphites, carbamates, esters, sulfur containing compounds and molybdenum complexes.

[0062] Suitable extreme pressure additives are, for example, zinc dialkyldithiophosphate (primary alkyl, secondary alkyl, and aryl type), sulfurized oils, diphenyl sulfide, methyl trichlorostearate, chlorinated naphthalene, fluoroalkylpolysiloxane and lead naphthenate.

[0063] A second embodiment of the present invention is directed to an engine oil comprising the lubricating oil composition as described hereinbefore.

[0064] A third embodiment of the present invention is directed to a method of lubricating an engine using the lubricating oil composition as described hereinbefore.

[0065] A fourth embodiment of the present invention is directed to a method of reducing friction in an engine by applying/by the addition of the lubricating oil composition as described hereinbefore.

[0066] The invention has been illustrated by the following non-limiting examples.

EXPERIMENTAL PART

EXAMPLE 1

Polycarboxylic Acid Ester Prepared from polyglycerol, isostearic acid, sebacic acid and poly(hydroxystearic acid) according to synthesis example 2 of EP 1 500 427 B1

[0067] A mixture of isostearic acid (91.1 g, 0.320 mol) and poly(hydroxystearic acid) (141.7 g, 0.120 mol, acid number of 47 mg KOH/g) was esterified with polyglycerol (61.9 g, 0.121 mol, hydroxyl value of 950 mg KOH/g) at 240° C. while nitrogen flowing through. After 2 h at this temperature, the acid number of the reaction mixture was <10. Then, the mixture was cooled to 130° C., sebacic acid (20.2 g, 0.100 mol) was added and the mixture was heated again to 240° C. After 3 h at this temperature, a viscous product having an acid number of <5 was obtained.

COMPARATIVE EXAMPLE 1

Polycarboxylic Acid Ester Prepared from Ethoxylated Soybean Oil, Oleic Acid and Dimer Acid

[0068] A mixture of epoxidized soybean oil (300 g, 0.302 mol) with an oxirane-[O] content of 6.3%, oleic acid (331 g, 1.18 mol) and dimer acid (57.5 g; 0.101 mol, comprising about 2% monobasic acids, about 96% dimer acids and about 2% trimer acids and higher polyacids) was heated to 240° C. until the acid value was <10 mg KOH/g.

[0069] The structure of this polymer is different to polyglycerol partial ester according to the present invention and therefore not encompassed by the present invention.

COMPARATIVE EXAMPLE 2

Polycarboxylic Acid Ester Prepared from Polyglycerol, Isostearic Acid and Sebacic Acid

[0070] A mixture of 72 g isostearic acid and 11 g sebacic acid was esterified with 17 g polyglycerol (average degree of polymerization=3) at 240° C. while nitrogen flowing through. Reaction was cooled down when an acid number of 12 was reached.

[0071] The OH-value of this polymer is much lower than the favorable range according to the present invention.

COMPARATIVE EXAMPLE 3

[0072] Polymeric friction modifier Perfad™ 3006, which is commercially available by Croda Inc. (see US 2013/0079536, WO 2011/107739 A1 for structure and Lube Magazine No. 120, April 2014, page 27 for physical properties).

[0073] The structure of this polymer is different to polyglycerol partial ester according to the present invention and therefore not encompassed by the present invention.

COMPARATIVE EXAMPLE 4

[0074] Polymeric friction modifier Perfad™ 3057, diluted form of Perfad™ 3050, which is commercially available by Croda Sucursal Colombia (see US 2013/0079536, WO 2011/107739 A1 for structure and Lube Magazine No. 120, April 2014, page 27 for physical properties).

[0075] The structure of this polymer is different to polyglycerol partial ester according to the present invention and therefore not encompassed by the present invention.

TABLE 1

physical data of examples and comparative examples

	HLB value	acid number [mg KOH/g]	OH-number [mg KOH/g]	M_n [g/mol]	M_w [g/mol]
Ex 1	~5	≤5	125-145	2600	6100
Comp. Ex 1	—	9	24	4600	16000
Comp. Ex. 2	—	12	10-20	3200	10600
Comp. Ex. 3	—	1.2	—	—	—
Comp. Ex. 4	—	4*)	—	—	—

M_n and M_w are measured via GPC using PMMA (polymethyl methacrylate) as standard
*)value given for Perfad™ 3050; Perfad™ 3057 is a diluted form of Perfad™ 3050

[0076] All polymers were diluted in Nexbase 3043 which is a Group III oil according to the American Petroleum Institute (API). The final blends have a similar kinematic viscosity at 100° C. (KV_{100}) of about 4.45 cSt.

[0077] For Comparative Examples 3 and 4 treat rates of 0.5% are recommended by the manufacturer.

TABLE 1

Viscosity values of the tested blends

Comparative Example 1	[% wt]	1				
Comparative Example 2	[% wt]		1			
Comparative Example 3	[% wt]			0.5		
Comparative Example 4	[% wt]				0.5	
Example 1	[% wt]					1
Reference Nexbase 3043	[% wt]	99	99	99.5	99.5	99
KV_{100}	mm^2/s	4.49	4.45	4.48	4.43	4.48

(KV_{100} = Kinematic Viscosity @ 100° C.)

[0078] Determination of Friction-Reducing Action:

[0079] The measurements of the coefficient of friction at 100° C. were performed on a Mini Traction Machine (MTM) from PCS Instruments. The test consist of evaluating the friction level occurring in a lubricated contact formed by a steel ball and a steel disc. The speeds of the ball and the disc are driven independently. The ball is loaded and rubbed in rolling sliding conditions against the steel disc, the contact being fully immersed in oil.

[0080] For each sample, the test was performed in two steps:

[0081] 1) Run In phase

[0082] For this phase, the conditions described in Table 2 below have been applied, SRR referring to Sliding Roll Ratio. This parameter was maintained constant during the 2 hours testing and is defined as:

$$\frac{|U\text{Ball} - U\text{Disc}|}{U}$$

where U Ball−U Disc represents the sliding speed and U the entrainment speed, given by U=(U Ball+U Disc)/2

TABLE 2

test parameters for run in phase

Test Rig	MTM 2 von PCS Instruments
Disc	Highly polished stainless Steel AISI 52100 Disc diameter 46 mm
Ball	Highly polished stainless Steel AISI 52100 Ball diameter 19.05 mm
Mean Speed	100 mm/s
Temperature	100° C.
Duration	2 hours
Load	30 N
SRR	50%

[0083] 2) Stribeck Curve Evaluation

[0084] A Stribeck was then obtained by measuring the friction coefficient under the conditions shown in Table 3.

TABLE 3

conditions for Stribeck curve evaluation

Test Rig	MTM 2 von PCS Instruments
Disc	Highly polished stainless Steel AISI 52100 Disc diameter 46 mm
Ball	Highly polished stainless Steel AISI 52100 Ball diameter 19.05 mm
Mean Speed	from 5 to 2500 mm/s
Temperature	100° C.
Load	30 N
SRR	50%

[0085] The Stribeck curves are plotted in FIG. **1**. The curve NB3043-Ref refers to the formulation containing 100% of Group III oil named Nexbase 3043.

[0086] FIG. **1**: Stribeck curve measurements after two hours of run in phase

[0087] To express in % the friction reduction obtained by working Example 1, a quantifiable result can be expressed as a number is obtained as follows:

[0088] Integration of the friction value curves in the range of sliding speed 0.005-2.5 m/s using the trapezoidal rule. The area corresponds to the "total friction" over the entire speed range examined. The smaller the area, the greater the friction-reducing effect of the polymer examined.

[0089] The percentage friction reductions calculated therefrom in relation to the reference oil are compiled in Table 4 below.

TABLE 4

Quantitative evaluation of the reduction in friction						
	Reference	Ex. 1	Comp. Ex. 1	Comp. Ex. 2	Comp. Ex. 3	Comp. Ex. 4
Area in mm/s	99.239	51.079	62.675	71.354	65.109	86.581
reduction in friction relative to reference [%]	0	48.53	36.84	28.10	34.39	12.75

[0090] The data in Table 4 and FIG. **1** show clearly that the inventive polymers have a much better effect with regard to the reduction in friction than the corresponding comparative polymers of the prior art using different chemistry. The effect is even more pronounced in the low speed regime as revealed in Table 5 below.

[0091] Since the low speeds are of particular economic interest for the use of the lubricant compositions in accordance with the, Table 5 shows the integration data of the friction value curves within the sliding speed range from 0.005 to 0.090 m/s.

[0092] The areas determined and the percentage reductions in friction calculated therefrom in relation to the reference oil are compiled in Table 5 in an analogous manner to Table 4.

TABLE 5

Quantitative evaluation of the reduction in friction at low frequency (from 0.005 to 0.090 m/s)						
	Reference	Ex. 1	Comp. Ex. 1	Comp. Ex. 2	Comp. Ex. 3	Comp. Ex. 4
Area [mm/s]	7.863	1.855	4.429	5.464	3.405	4.025
reduction in friction relative to reference in low speed regime [%]	0	76.41	43.67	30.51	56.70	48.81

[0093] The data in Table 5 show clearly that the inventive polymers have a much better effect once again with regard to the reduction in friction than the corresponding comparative polymers of the prior art.

[0094] Compared to the results as shown in Table 4, it is found that the friction-increasing action of lubricant composition for use in accordance with the invention is very clearly marked specifically within the range of low sliding speeds.

1. A lubricating oil composition comprising
(a) 0.2 to 5% by weight of one or more polyglycerol partial esters, based on a total weight of the lubricating oil composition, wherein the polyglycerol partial esters are obtained by esterification of a polyglycerol mixture with
(i) one or more polyfunctional carboxylic acids and
(ii) one or more saturated or unsaturated, linear or branched fatty acids and/or
(ii) poly(hydroxystearic acid),
wherein a degree of esterification of the poly-glycerol mixture is between 30 and 75% of the OH goups;
(b) 85 to 99.8% by weight of an apolar base stock selected from the group consisting of API Group II, III and IV and mixtures thereof, based on the total weight of the lubricating oil composition; and
(c) 0 to 10% by weight of a polar ester oil of API Group V, based on the total weight of the lubricating oil composition.

2. The lubricating oil composition according to claim **1**, wherein the polyglycerol has a mean degree of condensation of from 3 to 6.

3. The lubricating oil composition according to claim **1**, wherein the fatty acids are saturated or unsaturated, linear or branched having 8 to 22 carbon atoms.

4. The lubricating oil composition according to claim **1**, wherein the saturated fatty acids are one or more selected from the group consisting of caprylic acid, capric acid, lauric acid, tridecanoic acid, myristic acid, palmitic acid, margaric acid, stearic acid, isostearic acid, arachidic acid, behenic acid, and 12-hydroxy stearic acid.

5. The lubricating oil composition according to claim **1**, wherein the unsaturated fatty acids are one or more selected from the group consisting of hexadecenoic acids, octadecenoic acids, eicosenoic docosenoic acids, octadecadienoic acids, octadecatrienoic acids, and ricinoleic acid.

6. The lubricating oil composition according to claim **1**, wherein the polyfunctional carboxylic: acids have 4 to 54 carbon atoms, and a mean functionality of from 2 to 2.5.

7. The lubricating oil composition according to claim **1**, wherein the polyfunctional carboxylic acids are aliphatic dicarboxylic acids which are selected from the group consisting of malonic acid, succinic acid, furmaric acid, maleic acid, dimethylgiutaric acid, adipic acid, trimethyladipic acid, azelaic acid, sebacic acid, dodecanedioic acid and their anhydrides.

8. The lubricating oil composition according to claim **1**, wherein the polyglycerol partial esters have HLB values of from 3 to 7.

9. The lubricating oil composition according to claim **1**, wherein the polyglycerol partial esters have an OH-number in the range of 50 to 180 mg KOH/g.

10. The lubricating oil composition according to claim **1**, further comprising an additive.

11. The lubricating oil composition according to claim **10**, wherein the additive is at least one selected from the group consisting of viscosity index (VI) improvers, pour point depressants, dispersants, detergents, defoamers, corrosion inhibitors, antioxidants, antiwear and extreme pressure additives and fiction modifiers.

12. The lubricating oil composition according to claim **1**, wherein the polyglycerol partial esters have a weight-average molecular weight of 2,000 to 15,000 g/mol.

13. A method of lubricating an engine, comprising adding the lubricating oil composition according to claim **1** to the engine.

14. A method of reducing friction in an engine, comprising applying the lubricating oil composition according to claim **1** to the engine.

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