Polyaziridine polymers as lubricating oil additives

TECHNICAL FIELD OF THE INVENTION

The invention relates to a lubricating oil composition comprising a polyaziridine polymer, a process for preparing such lubricating oil composition and the use thereof as a lubricating oil additive for reducing friction in a transmission fluid, an engine oil formulation, a gear oil formulation, an axle fluid or in a hydraulic fluid.

BACKGROUND OF THE INVENTION

The present invention relates to the field of lubrication. Lubricants are compositions that reduce friction between surfaces. In addition to allowing freedom of motion between two surfaces and reducing mechanical wear of the surfaces, a lubricant also may inhibit corrosion of the surfaces and/or may inhibit damage to the surfaces due to heat or oxidation. Examples of lubricant compositions include, but are not limited to, engine oils, transmission fluids, gear oils, industrial lubricating oils, greases and metalworking oils.

A typical lubricant composition includes a base fluid and optionally one or more additives. Conventional base fluids are hydrocarbons, such as mineral oils. The terminology base oil or base fluid is commonly used interchangeably. Here, base fluid is used as a general term.

A wide variety of additives may be combined with the base fluid, depending on the intended use of the lubricant. Examples of lubricant additives include, but are not limited to, viscosity index improvers, thickeners, oxidation inhibitors, corrosion inhibitors, dispersing agents, high pressure additives, anti-foaming agents and metal deactivators.

The currently biggest challenge for lube manufacturers and OEMs in the automotive industry are more and more stringent fuel economy targets. Two levers are used to improve the fuel economy of, e.g., transmissions: the use of lubricants with lower viscosities and downsizing of the hardware.

The use of low viscosity lubricants leads to a thinner oil film between the contact surfaces in e.g. gearings and roller bearings especially at high temperatures, thus leading to an increased level of damage caused by excessive local stress. Friction modifiers are used to protect the metal surfaces as they build up a protective film at the metal surfaces and in addition help to reduce friction.

The downsizing of the hardware leads to additional hurdles. The transmission and hydraulic pump are smaller, cooling is more difficult, and gears and bearings have to handle higher loads. Thus,

the tribological contact between two moving surfaces exhibits a reduced film thickness of the lubricant. The applied additives have to ensure a low friction loss and to protect the surface from wear and fatigue in these boundary conditions.

As of today, typical oil soluble friction modifiers in lubricants either adsorb at the metal surface of the tribological contact e.g. via van-der-Waals interactions or build up reacted layers. Typical classes of friction modifiers are (i) oxygen-containing organic compounds that have a polar head group capable of adsorption at surfaces including alcohols, esters and carboxylic acids, (ii) organic compounds which contain nitrogen groups either in combination with (i) or (iii), (iii) organic sulphur compounds which can form reacted films at surfaces, (iv) organic phosphorus compounds which can form reacted films at surfaces, (v) organic boron compounds which may form reacted films at surfaces, (vi) organic molybdenum compounds which can form MoS_2 film on surfaces, or (vii) ZDDPs which can form polymeric films on surfaces (R.M. Mortier et al. (eds.), *Chemistry and Technology of Lubricants*, 3rd edn., DOI 10.1023/b105569_3, Springer Science+Business Media B.V. 2010).

For the class of absorbing compounds, several factors are important such as they have to show a strong interaction with the surface also under high loads, they have to build up a protective film layer at the surface, they have to be oil-soluble in case they desorb from the surface, their tendency to interact with the surface must be higher than the interaction with the surrounding oil.

The synthesis of polyaziridine polymers is described in detail in many publications, such as “The living anionic polymerization of activated aziridines: a systematic study of reaction conditions and kinetics“, *Polym. Chem. 2017, 8*, 2824-2832; "Multihydroxy Polyamines by Living Anionic Polymerization of Aziridines“ *ACS Macro Lett., 2016, 5,* 195-198; or “Organocatalytic Ring-Opening Polymerization of N-Tosyl Aziridines by a N-Heterocyclic Carbene” *Chem. Commun., 2016, 72,* 9719-9722. These publications are silent on the problems of lubrication and oil solubility.

Based on the foregoing, there is still the need to find additional lubricating oil additives, in particular, new friction modifiers with excellent friction performances while having good oil compatibility with the lubricating oil compositions.

SUMMARY OF THE INVENTION

After an exhaustive investigation, the inventors of the present invention have surprisingly found that the polyaziridine polymers as defined in claim 1 provide excellent friction reduction performances when added to a lubricant oil composition.

Thus, a first object of the present invention is a lubricating oil composition comprising at least one base fluid and at least one polyaziridine polymer as defined in claim 1 and its dependent claims.

A second object of the present invention relates to a process for preparing the lubricating oil composition according to the present invention.

A third object of the present invention is the use of a polyaziridine polymer in a lubricating oil composition as defined in claim 1 or its dependent claims as a lubricating oil additive in an automatic transmission fluid, a manual transmission fluid, a continuously variable transmission fluid, a dual clutch transmission fluid, a dedicated hybrid transmission fluid, an engine oil formulation, a gear oil formulation, an industrial gear oil formulation, an axle fluid or in a hydraulic fluid. In a preferred embodiment, the present invention is directed to the use of a polyaziridine polymer according to the present invention as a friction modifier for reducing friction in a lubricating oil composition.

BRIEF DESCRIPTION OF THE DRAWINGS

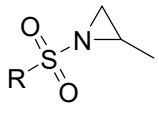
For better illustrating the advantages and properties of a lubricating oil composition comprising the polyaziridine polymer of the invention, a graph is attached as a non-limiting example:

Figure 1 is a graph comparing the Stribeck curve obtained with a pure naphthenic API Group V base fluid and the Stribeck curve obtained with the same base fluid (API group V base fluid) treated with the polymer 2 according to the present invention.

DETAILED DESCRIPTION OF THE INVENTION

Lubricating oil compositions of the invention

According to a first aspect of the invention, the invention relates to a lubricating oil composition comprising at least one base fluid; and at least one polyaziridine polymer obtainable by polymerizing a monomer composition consisting of one or more aziridine monomer of formula (I)



(I)

wherein R is a linear or branched alkyl group with 15 to 30 carbon atoms.

According to a preferred embodiment of the invention, the lubricating oil composition comprises between 95 and 99.95 % by weight of the at least one base fluid and between 0.05 and 5 % by weight of the at least one polyaziridine polymer, based on the total weight of the lubricating composition.

According to another preferred embodiment of the invention, the lubricating oil composition may further comprise an additive selected from the group consisting of a viscosity index improver, a pour point improver, a dispersant, a demulsifier, a lubricity additive, a detergent, a defoamer, a corrosion inhibitor, an antioxidant, an antiwear additive, an extreme pressure additive, an antifatigue additive, a dye, an odorant or a mixture thereof.

Polyaziridine polymers

According to the present invention, the polyaziridine polymer as defined in claim 1 bares a nitrogen in every monomer unit of the linear or branched polymer backbone, thus enabling good adhesion to the metal surface. In contrast to the existing carbon acid compound friction modifiers, they work as multidentate compound giving good adhesion also under high load.

The polyaziridine polymer may be prepared by cationic ring opening polymerization, in which case the polyaziridine polymer according to the present invention has a branched polymer backbone. The polymer backbone of the polyaziridine polymer corresponds to the longest series of covalently bonded atoms that together create the continuous chain of the polyaziridine polymer.

The polyaziridine polymer may also be prepared by anionic ring opening polymerization, in which case the polyaziridine polymer according to the present invention has a linear polymer backbone. The polyaziridine polymers of the invention can be prepared for example according to the process as described in Section B of the supporting information of the publication “Sequence-Controlled Polymers via Simultaneous Living Anionic Copolymerization of Competing Monomers“, E. Rieger, Macromol. Rapid Commun., 2016, 37, 833-839.

The nitrogen atom in every monomer unit makes the structure very polar. The inventors of the present invention surprisingly came to the conclusion that this structure favors to attach to the metal surface, rather than staying in the oil phase. It seems to favor a fast and strong adhesion of the polymer to the surface, which allows to reduce the friction between metal parts.

The aziridine monomer has two sites where side groups can be attached: the nitrogen atom or one of the carbon atoms. This allows to tailor the properties and also to attach long carbon side-chains

making this structure oil soluble. It was found that the polyaziridine polymers according to the invention must be prepared using aziridine monomers of formula (I) with an alkyl group R having between 15 and 30 carbon atoms, preferably between 15 and 20 carbon atoms, more preferably 16 carbon atoms. This seems to ensure oil solubility in the lubricating oil composition as shown in the experimental part.

The inventors of the present invention have surprisingly found that lubricating oil compositions comprising at least one oil-soluble polyaziridine polymer according to the present invention have an improved friction coefficient compared to a pure base fluid. Thus, the oil-soluble polyaziridine polymer according to the present invention can be used as friction modifier in lubricating oil compositions.

According to a preferred embodiment of the present invention, the oil-soluble polyaziridine polymer is poly-2-methyl-N-hexadecasylaziridin, in which case the alkyl group R of the aziridine monomer is a linear alkyl group having 16 carbon atoms.

According to a preferred embodiment of the invention, the at least one polyaziridine polymer has a linear polymer backbone.

According to another preferred embodiment of the invention, the at least one polyaziridine polymer has a number-average molecular weight comprised in the range between 1,000 g/mol and 20,000 g/mol, preferably in the range between 1,000 g/mol and 10,000 g/mol, more preferably in the range between 2,000 g/mol and 8,000 g/mol, even more preferably in the range between 3,000 g/mol and 6,000 g/mol.

In the present invention, all number-average molecular weights are calculated by measuring the ratio of ^{1}H NMR absorptions of the polymer chain and the initiator signals. Nuclear magnetic resonance (NMR) measurements were conducted on a Bruker AVANCE 300 spectrometer operating with 300 MHz frequencies at 298 K.

According to a preferred embodiment of the invention, the at least one polyaziridine polymer is obtainable by polymerizing a monomer composition consisting of one or more aziridine monomer of formula (I), wherein R is a linear alkyl group with 15 to 20 carbon atoms, preferably 16 carbon atoms.

Base fluids

As indicated above, the present invention relates to a lubricating oil composition comprising a base fluid and at least one polyaziridine polymer of the present invention as defined in claim 1.

The base fluids correspond to lubricant base fluids, mineral, synthetic or natural, animal or vegetable oils suited to their use/chosen depending on the intended use.

The base fluids used in formulating the lubricating oil compositions according to the present invention include, for example, conventional base stocks selected from API (American Petroleum Institute) base stock categories known as Group I, Group II, Group III, Group IV and Group V. The Group I and II base stocks are mineral oil materials (such as paraffinic and naphthenic oils) having a viscosity index (or VI) of less than 120. Group I is further differentiated from Group II in that the latter contains greater than 90% saturated materials and the former contains less than 90% saturated material (that is more than 10% unsaturated material). Group III is considered the highest level of mineral base fluid with a VI of greater than or equal to 120 and a saturates level greater than or equal to 90%. Group IV base fluids are polyalphaolefins (PAO). Group V base fluids are esters and any other base fluids not included in Group I to IV base fluids. These base fluids can be used individually or as a mixture. Preferably, the lubricant composition comprises an API Group V base fluid.

Additional additives

The lubricating oil compositions according to the present invention may also further comprise any other additional additives suitable for use in the formulations. These additives are selected from the group consisting of a viscosity index improver, a pour point improver, a dispersant, a demulsifier, a lubricity additive, a detergent, a defoamer, a corrosion inhibitor, an antioxidant, an antiwear additive, an extreme pressure additive, an antifatigue additive, a dye, an odorant or a mixture thereof.

Process for preparing a lubricating oil composition according to the invention

The invention also relates to a process for preparing a lubricating oil composition comprising at least one polyaziridine polymer as defined above, wherein the process comprises:

(i) preparing one or more polyaziridine polymer, and

(ii) mixing with one or more base fluid.

Reference is made to the base fluids as described above.

Use of the polymer according to the invention

The invention also relates to the use of the polymer as described in detail above as a lubricating oil additive in a lubricating oil composition.

The invention relates to the use of the polymer as described in detail above as a friction modifier for a lubricating oil composition.

The lubricating oil compositions are, among others, an automatic transmission fluid, a manual transmission fluid, a continuously variable transmission fluid, a dedicated hybrid transmission fluid, a dual clutch transmission fluid, a gear oil formulation, an industrial gear oil formulation, an axle fluid, an engine oil formulation or a hydraulic fluid.

As shown in the experimental part, due to the presence of the polyaziridine polymer as defined in the present invention, the lubricating oil compositions show excellent antifriction properties.

EXPERIMENTAL PART

The invention is illustrated by the following examples.

Abbreviations

M_n	number-average molecular weight
MTM	mini traction machine
Poly(HDsMAz)	Poly-2-methyl-N-hexadecasylaziridine
Poly(OsMAz)	Poly-2-methyl-N-octasylaziridine
SRR	Slide-Roll-Ratio

Test method

The polymers were dissolved with a treat rate of 0.5 wt% in a naphthenic API Group V base fluid and the friction coefficient measured on a Mini Traction Machine with the following conditions: scanning from 2500 to 5 mm/s at 30N, 80° C and 50% Slide-Roll-Ratio (SRR) with 4 repeats per sample.

Material

Two polyaziridine polymers were used, both provided by the Max-Planck-Institute for Polymer Research in Mainz and prepared via anionic polymerization according to the process as described on page 14 in Section B of the supporting information of the publication "Sequence-Controlled Polymers via Simultaneous Living Anionic Copolymerization of Competing Monomers", E. Rieger, Macromol. Rapid Commun., 2016, 37, 833-839:

Polymer 1: Poly-2-methyl-N-octasylaziridine (Poly(OsMAz)) with 14 repeat units
Starting material: 2-methyl-N-octasylaziridine monomer (12.5 g, 64.28 mmol), N-benzyl-sulfonamide as initiator (1.00 g, 5.40 mmol), potassium bis(trimethylsilyl)amide as a deprotonation agent (969.57 mg, 4.86 mmol)
M_n (NMR) = 3,400 g/mol

Polymer 2: Poly-2-methyl-N-hexadecasylaziridine (Poly(HDsMAz)) with 15 repeat units
Starting material: 2-methyl-N-hexadecasylaziridine monomer (250 mg, 725 µmol), N-benzyl-sulfonamide as initiator (8.93 mg, 36.15 µmol), potassium bis(trimethylsilyl)amide as a deprotonation agent (6.5 mg, 33 µmol)
M_n (NMR) = 5,400 g/mol

Evaluation of friction modifier properties

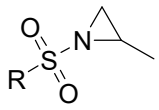
To test the solubility in oil which is the key criteria for an application in lubricants, both polymers were added to a naphthenic base fluid with a treat rate of 0.5 wt%, based on the total weight of the lubricating oil composition. Polymer 1 with a C8 side chain was not soluble in oil. In contrast, inventive Polymer 2 with a C16 side chain was soluble in oil at elevated temperatures (80 to 100 °C).

Thus, for the further evaluation of the friction modifier properties only Polymer 2 was used.

In Figure 1, a comparison of the Stribeck curves measured with the MTM of the pure naphthenic API Group V fluid and of the same base fluid comprising polymer 2 is shown. It can be seen that the friction coefficient for the base fluid comprising polymer 2 is lower over the full speed range compared to the pure base fluid, thus proving a positive effect of the polyaziridine structure on friction and a possible application as friction modifier in lubricants.

Claims

1. A lubricating oil composition comprising at least one base fluid and at least one polyaziridine polymer obtainable by polymerizing a monomer composition consisting of one or more aziridine monomer of formula (I)



(I)

wherein R is a linear or branched alkyl group with 15 to 30 carbon atoms.

2. The lubricating oil composition according to claim 1, wherein the at least one polyaziridine polymer has a linear polymer backbone.

3. The lubricating oil composition according to claim 1 or 2, wherein the at least one polyaziridine polymer has a number-average molecular weight comprised in the range between 1,000 g/mol and 20,000 g/mol.

4. The lubricating oil composition according to claim 3, wherein the at least one polyaziridine polymer has a number-average molecular weight comprised in the range between 1,000 g/mol and 10,000 g/mol.

5. The lubricating oil composition according to claim 3, wherein the at least one polyaziridine polymer has a number-average molecular weight comprised in the range between 2,000 g/mol and 8,000 g/mol.

6. The lubricating oil composition according to claim 3, wherein the at least one polyaziridine polymer has a number-average molecular weight comprised in the range between 3,000 g/mol and 6,000 g/mol.

7. The lubricating oil composition according to any one of claims 1 to 6, wherein the at least one polyaziridine polymer is obtainable by polymerizing a monomer composition consisting of one or more aziridine monomer of formula (I), wherein R is a linear alkyl group with 15 to 20 carbon atoms, preferably 16 carbon atoms.

8. The lubricating oil composition according to any one of claims 1 to 7, wherein the lubricating oil composition comprises between 95 and 99.95 % by weight of the base fluid and

between 0.05 and 5 % by weight of the at least one polyaziridine polymer, based on the total weight of the lubricating composition.

9. The lubricating oil composition according to any one of claims 1 to 8, wherein the lubricating oil composition further comprises an additive selected from the group consisting of a viscosity index improver, a pour point improver, a dispersant, a demulsifier, a lubricity additive, a detergent, a defoamer, a corrosion inhibitor, an antioxidant, an antiwear additive, an extreme pressure additive, an antifatigue additive, a dye, an odorant or a mixture thereof.

10. The lubricating oil composition according to any one of claims 1 to 9, wherein the at least one base fluid is selected from the group consisting of API Group I base fluid, API Group II base fluid, API Group III base fluid, API Group IV base fluid, API Group V base fluid or a mixture thereof, preferably an API Group V base fluid.

11. Process for preparing the lubricating oil composition comprising the at least one polyaziridine polymer as defined in any one of claims 1 to 10, wherein the process comprises:

(i) preparing one or more polyaziridine polymer, and

(ii) mixing with one or more base fluid.

12. Use of a polyaziridine polymer in a lubricating oil composition as defined in any one of claims 1 to 10 as a lubricating oil additive in an automatic transmission fluid, a manual transmission fluid, a continuously variable transmission fluid, a dual clutch transmission fluid, a dedicated hybrid transmission fluid, an engine oil formulation, a gear oil formulation, an industrial gear oil formulation, an axle fluid, or in a hydraulic fluid.

13. Use of a polyaziridine polymer according to claim 12 as a friction modifier for reducing friction in a lubricating oil composition.