

Lubricant formulations with acrylate-olefin copolymers as high viscosity base fluids**TECHNICAL FIELD OF THE INVENTION**

5 The invention relates to a lubricant formulation comprising a base oil and a functionalized acrylate-olefin copolymers, as well as a method for the preparation of these lubricant formulations. The present invention is also directed to the use of the lubricant formulation comprising a base oil and a functionalized acrylate-olefin copolymer as a lubricant formulation, preferably as a gear oil lubricating composition, a transmission oil lubricating composition, a hydraulic oil lubricating composition, an
10 engine oil lubricating composition, a marine oil lubricating composition, an industrial lubricating oil composition or a grease by using the functionalized acrylate-olefin copolymer of the invention in the lubricant formulation.

BACKGROUND OF THE INVENTION

15 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
20 compositions include, but are not limited to, engine oils, transmission fluids, gear oils, hydraulic fluids, industrial lubricating oils, greases and metalworking oils.

Lubricants typically contain a base fluid and variable amounts of additives. Conventional base fluids are hydrocarbons, such as mineral oils. The terminology base oil or base fluid is commonly used
25 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, pour point depressants, oxidation inhibitors, corrosion inhibitors, dispersing agents, high
30 pressure additives, anti-foaming agents and metal deactivators.

Typical non-polymeric base fluids are less effective as lubricants, because of their low viscosity and further decreased viscosity at higher operating temperatures. Therefore, polymeric additives are used to thicken the base oil and reduce the change in viscosity with change in temperature. The term
35 Viscosity Index (VI) is used to describe this change in viscosity with temperature. The lower the VI, the greater the change in viscosity with temperature, and vice versa. Thus, a high VI is desired for lubricant formulations. In order to improve the VI, polymeric additives or Viscosity Index Improvers (VII) may be added to a lubricant formulation.

40 It is well-known in the art that alkyl acrylates are not recommended in VI improver applications, and commercial VI improvers are usually based on methacrylates. While literature (Rashad et al. J. of Petr. Sci. and Engineering 2012, 173-177; Evin et al. J. of Sol. Chem 1994, 325-338) and patents

(WO96/17517) exist, it is generally known that the performance of polyacrylates as VI improver is inferior to the ones of polymethacrylates. Especially in WO96/17517, it is mentioned that it was unexpectedly found that poly(alkyl acrylate) esters typically fail to adequately reduce the effect of temperature on viscosity when used in the hydraulic fluids.

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The drawback of adding polymeric additives to a lubricant formulation is that they will undergo shear stress and will mechanically degrade over time. Higher molecular weight polymers are better thickeners but will be more prone to shear stress leading to polymer degradation. In order to decrease the amount of polymer degradation, the molecular weight of a polymer can be decreased, thereby obtaining a more shear stable polymer. However, these shear stable low molecular weight polymers are no longer very effective thickeners and must be used in larger concentrations in the lubricant in order to reach a desired viscosity. These low molecular weight polymers typically have molecular weights below 20,000 g/mol and are also called synthetic high viscosity base fluids. High viscosity base fluids are used to lift the VI and to thicken lubricant formulations with demanding shear stability requirements. A typical application are gear oils which have very demanding requirements due high mechanical stress and a broad temperature range in operation.

Typical products in this market are high viscosity polyalphaolefins (PAOs) and metallocene polyalphaolefins (mPAOs), typically sold in viscosity ranges from 40 to 300 cSt at 100°C (Choudary et al. Lubr. Sci. 2012, 23-44), whose key feature is good handling properties in term of viscosity since these base fluids are polymeric in nature and provide for an improved viscosity index. However, the apolar nature of the PAO base oils is a disadvantage as can lead to poor solubility of DI packages and ageing products in oil, which can cause subsequent problems.

It has been already described that higher polarity is provided by copolymers of alpha-olefins with maleates (DE3223694), copolymers of alpha-olefins and acrylates (DE2243064), copolymers of alpha-olefins and methacrylates (EP0471266) or terpolymers based on the aforementioned monomers (WO2020/078770). Another example is EP4015604, which describes acrylate-olefin copolymers for use as high viscosity base stocks or lubricant additives in a lubricating oil composition. The resulting lubricating oil compositions show good low temperature properties and good viscosity index level, when compared with methacrylate-olefin copolymers and pure polyacrylates. The document is silent on the problem of dispersancy and sludge sedimentation.

WO2017/139572 relates to copolymers prepared by a reaction of (1) an unactivated olefin, (2) an activated olefin, and (3) a hydroxyl functional activated olefin and/or a hydroxyl functional unactivated olefin. It is described that these copolymers are well suited for optically clear, pressure sensitive, polyurethane and/or barrier adhesives.

Dispersant additives can prevent sedimentation of sludge and contribute to better ratings in the test and finally longer lifetimes of the finished lubricants. The disadvantage of dispersing sludge is a viscosity increase of the lubricant. Keeping this viscosity increase as low as possible is a major performance parameter for a dispersant. Typical dispersants are for example end-functionalized

polyisobutylene (PIB) oligomers. PAMAs with nitrogen functionality are also well-known as dispersants additives (see for example US2015/0274875).

5 There is still the need to provide highly shear stable synthetic base fluids or lubricating oil additives, which, in lubricant oil compositions, have a positive influence on oil solubility and component solubility, as well as on low temperature performance. Furthermore, the new products should not only be able to thicken an oil to a desired viscosity, but should also improve the sludge sedimentation and dispersancy performance of the resulting lubricating oil composition.

10 BRIEF SUMMARY OF THE INVENTION

The inventors of the present invention have surprisingly found that hydroxy-functionalized acrylate-olefin copolymers comprising a certain amount of hydroxy-functional (meth)acrylate ester, as defined in claim 1, are able to thicken very efficiently an oil to a desired viscosity, and simultaneously also
15 improve the sludge sedimentation and dispersancy performance of the resulting lubricating oil composition. As exemplified in the experimental part of the present invention, it has unexpectedly been found that the specific weight ratio combination of acrylate monomers, with C₈-C₁₄ alpha-olefins and hydroxy-functional (meth)acrylate ester monomers, as defined in claim 1, are crucial to achieve a combination of good thickening properties and excellent sludge sedimentation reduction, while still
20 maintaining good low temperature properties. Furthermore, these copolymers are highly shear stable and have a high viscosity index to reduce the effect of changes in viscosity with temperature.

Accordingly, a first aspect of the invention is a lubricant formulation comprising a base oil and a hydroxy-functionalized acrylate-olefin copolymer comprising hydroxy-functional (meth)acrylate ester
25 monomer units as defined in claim 1 and its dependent claims.

A second aspect of the invention is a method for preparing the lubricant formulation according to the invention.

30 A third aspect of the invention is a method of thickening lubricant formulation and improving the dispersancy and/or reducing the sludge sedimentation of a lubricant formulation, by adding a hydroxy-functionalized acrylate-olefin copolymer according to the present invention, as a lubricant additive or a synthetic base fluid, to said lubricant formulation.

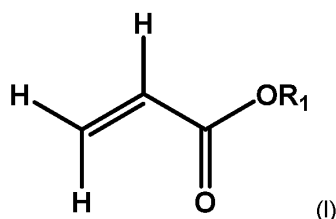
35 DETAILED DESCRIPTION OF THE INVENTION

Lubricant formulation according to the invention

The present invention relates to a lubricant formulation comprising a base oil and a hydroxy-functionalized acrylate-olefin copolymer,
40 wherein the copolymer has a weight-average molecular weight from 5,000 to 30,000 g/mol according to DIN 55672-1 and comprises:

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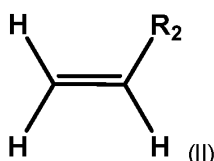
- a) 60 to 99.8% by weight, based on the total weight of the copolymer, of monomer units derived from at least one acrylate of formula (I),



wherein R_1 means a linear or branched alkyl group having from 8 to 15 carbon atoms,

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- b) 0.1 to 39.9% by weight, based on the total weight of the copolymer, of monomer units derived from at least one non-functionalized alpha-olefin of formula (II),



wherein R_2 means a linear alkyl group having from 8 to 14 carbon atoms, and

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- c) 0.1 to 5% by weight, based on the total weight of the copolymer, of monomer units derived from at least one hydroxy-functional (meth)acrylate monomer c),

and

wherein the lubricant formulation has a content of hydroxy-functional (meth)acrylate monomer c) in

- 15 formulation of less than 100, calculated with the formula (III)

$$[\text{wt}\% \text{ of monomer c)}] \times \text{TR} < 100 \quad (\text{III})$$

wherein [wt% of monomer c)] is the total weight content of monomers c) in the polymer and wherein TR is the polymer treat rate in weight percent in the lubricant formulation.

- 20 The terms "polymer" and "copolymer" are used interchangeably to define the copolymer according to the present invention.

The terms "lubricant formulation" and "lubricating oil composition" are used interchangeably to define the lubricant formulation according to the present invention.

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In the present invention, the term "alkyl methacrylate" refers to esters of methacrylic acid and the term "alkyl acrylate" refers to esters of acrylic acid. The term "(meth)acrylate" refers to esters of acrylic acid, esters of methacrylic acid or a mixture of esters of acrylic acid and methacrylic acid.

- 30 In formula (III) above, the polymer treat rate (TR) corresponds to the total amount in weight percent of polymer in the lubricant formulation, based on the total weight of the lubricant formulation.

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

The base oils 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 oil with a VI of greater than or equal to 120 and a saturates level greater than or equal to 90%. Group IV base oils are polyalphaolefins (PAO). Group V base oils are esters and any other base oils not included in Group I to IV base oils. These base oils can be used individually or as a mixture.

Preferably, the base oil included in the lubricating oil composition of the present invention is selected from the group consisting of an API Group II base oil, an API Group III base oil, API Group IV base oil, or a mixture thereof. Most preferably, the lubricant composition comprises an API Group III base oil or a mixture thereof.

Preferably, the lubricant formulation comprises from 0.1 to 99.9% by weight, more preferably from 3 to 99% by weight, of the hydroxy-functionalized acrylate-olefin copolymer according to the invention, based on the total weight of the lubricant formulation.

In a preferred embodiment of the invention, the lubricant formulation comprises from 0.1 to 99.9% by weight, preferably from 1 to 97% by weight, of at least one base oil and from 0.1 to 99.9% by weight, preferably from 3% to 99% by weight, of at least one copolymer according to the present invention, based on the total weight of the lubricating composition.

All preferred aspects of the polymer, base oil and amounts as listed above apply for this lubricating oil composition.

The lubricating oil compositions according to the present invention may also comprise any other additional additives suitable for use in the formulations. These additives include additional viscosity index improvers, pour point depressants, dispersants, demulsifiers, defoamers, lubricity additives, friction modifiers, antioxidants, detergents, dyes, corrosion inhibitors and/or odorants.

According to a preferred aspect of the invention, the total content of the copolymer according to the invention and base oil in the lubricant composition sums up from 90% by weight or more, more preferably sums up from 95% by weight or more, based on the total weight of the lubricant composition.

Within the meaning of the present invention, the monomer composition corresponds to the monomers used to prepare the polymer according to the present invention (not including other reactants such as initiators, stabilizers).

According to the present invention, the copolymer of the invention comprises 60 to 99.8% by weight, based on the total weight of the copolymer, of monomer units a) derived from acrylate monomer of formula (I). Preferably, the copolymer comprises from 65.5 to 95% by weight, more preferably from 74.2 to 90% by weight, of monomer units a) derived from acrylate monomer of formula (I), based on the total weight of the copolymer.

The acrylates a) of formula (I) refer to esters of acrylic acid with straight chain or branched alcohols having 8 to 15 carbon atoms. The term encompasses individual acrylic esters with an alcohol of a particular length, and likewise mixtures of acrylic esters with alcohols of different lengths.

Particularly preferred acrylates a) of formula (I) are selected from the group consisting of n-octyl acrylate, 2-ethylhexyl acrylate, 2-propylheptyl acrylate, isononyl acrylate, isodecyl acrylate, isotridecylacrylate, n-decyl acrylate, lauryl acrylate, or a mixture thereof.

According to the present invention, the copolymer of the invention comprises 0.1 to 39.9 % by weight, based on the total weight of the copolymer, of monomer units b) derived from at least one non-functionalized alpha-olefin of formula (II), wherein R₂ means a linear alkyl group having from 8 to 14 carbon atoms. According to one aspect of the invention, it is preferred that the copolymer comprises from 4.5 to 35% by weight, preferably from 4.9 to 30% by weight, more preferably from 9.2 to 25% by weight, of monomer units b) derived from at least one non-functionalized alpha-olefin of formula (II), based on the total weight of the copolymer.

Most preferred non-functionalized alpha-olefins b) of formula (II) are selected from the group consisting of decene, dodecene, tetradecene, hexadecene, or a mixture thereof.

According to the present invention, the copolymer of the invention also comprises 0.1 to 5% by weight, based on the total weight of the copolymer, of monomer units c) derived from at least one hydroxy-functional (meth)acrylate ester of formula (III). Preferably, the copolymer comprises from 0.5 to 5% by weight, preferably from 0.8 to 5% by weight, of monomer units c) derived from at least one non-functionalized alpha-olefin of formula (II), based on the total weight of the copolymer.

Preferred hydroxy-functional (meth)acrylate ester c) of formula (III) are selected from the group consisting of 2-hydroxyethyl (meth)acrylate, 2-hydroxypropyl (meth)acrylate, 2,3-dihydroxypropyl (meth)acrylate, 4-hydroxybutyl (meth)acrylate, 2-hydroxybutyl (meth)acrylate, 3-hydroxybutyl (meth)acrylate, trimethylolpropane mono(meth)acrylate, 2-ethoxy ethyl (meth)acrylate, 2-(2-ethoxyethoxy)ethyl (meth)acrylate, 2-hydroxy-2-methylpropyl (meth)acrylate, or a mixture thereof. Most preferred hydroxy-functional (meth)acrylate esters c) of formula (III) are selected from the group consisting of 2-hydroxyethyl (meth)acrylate, 2-hydroxypropyl (meth)acrylate, 2,3-dihydroxypropyl (meth)acrylate, or a mixture thereof.

According to another aspect of the invention, it is preferred that the copolymer has a kinematic viscosity from 100 to 1,000 mm²/s at 100°C according to ASTM D 445, more preferably from 120 to

700 mm²/s at 100°C according to ASTM D 445, even more preferably from 150 to 500 mm²/s at 100°C according to ASTM D 445.

5 According to another preferred aspect of the invention, the total content of monomer units derived from monomers a), b) and c) in the copolymer of the invention sums up to 90 % by weight or more, more preferably sums up to 95% by weight or more, even more preferably sums up to 98 % by weight or more, most preferably sums up to 100 % by weight, based on the total weight of the copolymer.

10 According to the present invention, the copolymer has a weight-average molecular weight from 5,000 to 30,000 g/mol, preferably from 8,000 to 30,000 g/mol, more preferably from 10,000 to 25,000 g/mol, even more preferably from 12,000 to 20,000 g/mol, according to DIN 55672-1.

15 According to the present invention, the weight-average molecular weight (M_w) and the number-average molecular weight (M_n) of the polymers is determined by gel permeation chromatography (GPC) according to DIN 55672-1 using polymethylmethacrylate (PMMA) calibration standard using the following measurement conditions:

Eluent: tetrahydrofuran (THF) including 0.02M 2-diethylamino ethylamine

Operation temperature: 35 °C

20 Columns: the column set consists of one pre-column (SDV 10μ; 8 x 50 mm) and four columns: SDV 106 Å, SDV 105 Å and 2 x SDV 103 Å (PSS Standards Service GmbH, Mainz, Germany), all four columns have a size of 300 x 8 mm and an average particle size of 10 μm.

Flow rate: 1mL/min

Injected volume: 100 μL

Instrument: Agilent 1100 series consisting of an autosampler, pump and column oven

25 Detection device: a refractive index detector from the Agilent 1260 series.

30 Preferably, the copolymers of the invention have a very low degree of cross-linking and a narrow molecular weight distribution, which further contributes to the shear resistance. The low degree of crosslinking and the narrow molecular weight are reflected in the polydispersity index of the copolymers. Preferably, the polydispersity index (PDI) of the copolymers according to the invention is in the range of 1.0 to 5.0, more preferably of 1.0 to 4.0, even more preferably of 1.0 to 3.5, most preferably in the range of 1.5 to 3.0. A polydispersity index in the range of 1.0 to 3.5 is considered optimal for most industrial applications with regard to the shear resistance of the copolymers. The polydispersity index is defined as the ratio of weight-average molecular weight to number-average molecular weight (M_w/M_n).

According to a preferred aspect of the present invention, the polymer of the invention has a COC flashpoint above 250°C according to ASTM D92.

40 According to an aspect of the present invention, the monomer composition may also comprise further monomers d), other than the monomers a), b) and c), as long as the properties of the hydroxy-functionalized acrylate-olefin copolymer are not negatively affected.

According to the invention, the copolymer is a statistical copolymer, wherein the monomer units a), b) and c), and optionally any other monomer units d), are distributed randomly, and sometimes unevenly, in the copolymer.

- 5 Surprisingly, it has been observed that the combination of monomer units a) of formula (I) with alpha olefin monomer units b) of formula (II) and hydroxy-functional (meth)acrylate ester c) of formula (III), allows to prepare copolymers with great properties when used as an additive or a base fluid in thickening a lubricant oil formulation. As shown in the experimental part of the present invention, the lubricant formulations of the present invention, shows great thickening properties and improved
10 dispersancy and/or reduction in the sludge sedimentation of a lubricant formulation.

Method for preparing the copolymer according to the invention

- According to the present invention, the above-mentioned polymers are prepared following the
15 method comprising the steps of:

- i) providing a monomer composition as described above;
- ii) initiating radical polymerization in the monomer composition to obtain a copolymer.

- Standard free-radical polymerization is detailed, inter alia, in Ullmann's Encyclopedia of Industrial
20 Chemistry, Sixth Edition. In general, a polymerization initiator and optionally a chain transfer agent are used for this purpose.

- The polymerization step ii) can be conducted under standard pressure, reduced pressure or elevated pressure. In the context of the present invention, the term "standard pressure" means no added
25 pressure, but ambient or atmospheric pressure.

- For the radical copolymerization of olefins with acrylates, the polymerization temperature is critical. In general, the copolymerization temperature is in the range from 130 to 180°C, preferably from 140 to 170°C.
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The polymerization step ii) may be performed with or without dilution in oil or any solvent. Preferably, the polymerization step ii) is made without dilution in oil or any solvent.

- Preferably, step ii) comprises the addition of a radical initiator. Preferably, the radical initiator is
35 selected from di-tert-amyl-peroxide, 2,2-di-(tert-butylperoxy) butane, 1,1-di-tert-butylperoxy-3,3,5-trimethylcyclohexane, dicumyl peroxide or di-tert-butyl-peroxide. Preferably, the total amount of radical initiator relative to the total weight of the monomer mixture is 0.01 to 5 % by weight, more preferably 0.1 to 1 % by weight. Preferably, the total amount of radical initiator is added continuously over the course of the copolymerization reaction ii).

- 40 Preferably, the copolymerization step ii) is made by feeding the acrylate monomers a), and the monomers c) and optionally any other comonomers, together with the initiator to the non-

functionalized alpha-olefin monomers b). Preferably, the total reaction time of the radical polymerization is 2 to 5 hours, more preferably 2 to 4 hours, most preferably 3 hours.

5 In another preferred aspect of the invention, a further step after step ii) is optionally performed, corresponding to a distillation step to remove the unreacted alpha-olefin monomer b). Preferably, residual unreacted alpha-olefin monomer b) is removed by distillation at a temperature from 140 to 180°C and pressures as low as 5 mbar using a rotary evaporator.

Method for preparing the lubricant formulation according to the invention

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According to the present invention, the above-mentioned lubricant formulations are prepared following the method the steps of:

- i) providing a monomer composition as defined above,
- 15 ii) initiating radical polymerization in the monomer composition of step i) to obtain the copolymer,
- iii) mixing the copolymer of step ii) with a base oil.

All preferred aspects of the copolymer, preparation of the copolymer, base oil and amounts as listed above apply to the lubricant formulation according to the invention and to the preparation thereof.

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Applications for the lubricant formulation of the invention

The invention also relates to the use of a lubricant formulation according to the present invention as a lubricant formulation by adding the hydroxy-functionalized acrylate-olefin copolymer as defined
25 herein to said lubricant formulation.

The invention also relates to a method of thickening a lubricant formulation and improving the dispersancy and/or reducing the sludge sedimentation of a lubricant formulation, by adding a hydroxy-functionalized acrylate-olefin copolymer as defined in the present invention, as a lubricant
30 additive or a synthetic base fluid, to said lubricant formulation.

Preferably, the lubricating oil composition is a gear oil composition, a transmission oil composition, a hydraulic oil composition, an engine oil composition, a marine oil composition, an industrial lubricating oil composition or in grease.

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EXPERIMENTAL PART

The invention is further illustrated in detail hereinafter with reference to examples and comparative examples, without any intention to limit the scope of the present invention. All percentages in relation to monomers or base fluids given in the tables below are weight percentages (wt%).

Abbreviations

	Acr.	acrylate
	Anglamol 6043	additive package commercially available from Lubrizol
10	BF-40	Brookfield viscosity measured at -40°C in accordance with ASTM D2983
	BV	bulk viscosity
	BV100	bulk viscosity @100°C in accordance with ASTM D445
	cSt	centistokes corresponding to mm ² /s in SI units
	cP	centipoise corresponding to mPa s in SI units
15	DBPO	di-tert-butyl peroxide
	Dec	1-decene
	DMAEMA	2-dimethylamino ethyl methacrylate
	DMAPMAM	dimethylamino propyl methacrylamide
	EHA	2-ethylhexyl acrylate
20	GMMA	2,3-dihydroxypropyl methacrylate (glycerol monomethacrylate)
	HEMA	2-hydroxyethyl methacrylate
	HPMA	2-hydroxypropyl methacrylate
	IDA	isodecyl acrylate
	Ini	initiator
25	KRL	Tapered Roller Bearing Shear Stability Test according to CEC L-45-A-99
	KV	kinematic viscosity measured according to ASTM D445
	KV40	kinematic viscosity measured @40°C to ASTM D445
	KV100	kinematic viscosity measured @100°C to ASTM D445
	LA	lauryl acrylate or dodecyl acrylate
30	M _n	number-average molecular weight
	M _w	weight-average molecular weight
	n.m.	not measured
	PDI	polydispersity index
	PHA	2-propylheptyl acrylate
35	PPD	pour point depressant
	SL	shear loss determined at 100°C after KRL (20 hours run at 60°C)
	TAN	total acid number according to ASTM D664
	TBN	total base number according to ASTM D2896
	TR	treat rate (polymer content in weight percent in the formulation)
40	VI	viscosity index
	VPL 1-300	Evonik VISCOPLEX® 1-300, polyalkylmethacrylate pour point depressant

	wt% of monomer c)	content of monomer c) in % by weight based on the total weight of the copolymer
	Yubase 4	Group III base oil from SK Lubricants with a KV100 of 4 mm ² /s
	Yubase 6	Group III base oil from SK Lubricants with a KV100 of 6 mm ² /s
5	Yubase 8	Group III base oil from SK Lubricants with a KV100 of 8 mm ² /s

Test methods

	KV	ASTM D445
	VI	ASTM D2270
10	KRL	CEC L-45-A-99
	BF	ASTM D2983
	TAN	ASTM D664
	TBN	ASTM D2896

15 In the present invention, the bulk viscosity (BV) of the polymer (product obtained from polymerization reaction) corresponds to the kinematic viscosity (KV) of the resulting product of the polymerization measured in accordance with ASTM D445. Thus, the bulk viscosity of the polymers (BV100) as shown in Table 1 below, were measured as kinematic viscosity at 100°C in accordance with ASTM D445.

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The oxidative performance of the inventive and comparative examples in the present invention were evaluated using an oxidation test (CEC SG-L-048 Oxidation Stability of Lubricating Oils used in Automotive Transmissions by Artificial Ageing). The performance of a lubricating oil composition in the oxidation test according to CEC SG-L-48 is an important criteria for automotive gear oils. Parts of this test are a visual inspection of residues in the glass tube and a chromatographic test which both indicate how well the lubricant can prevent the sedimentation of insoluble oxidation products. The method is conducted at 160°C for 192 hours. The kinematic viscosity at 40 and 100°C as well as the acid number (TAN, ASTM D 664) of the fresh formulation is measured before the oxidation test (fresh oil) and compared to the corresponding values after oxidation (oxidized oil). The difference of the KV100 and TAN values between the fresh oil and the oxidized oil are termed as “delta KV100” and “delta TAN”, respectively. Additionally, a blotterspot test is performed to evaluate the dispersancy performance by placing a single drop of the formulation after oxidation (80°C) on a patch of blotter paper and evaluating size of the spot. A higher value for the blotterspot area corresponds to a better dispersant.

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Examples

Synthesis procedure of the inventive copolymer Ex. 1

2.72 g of DBPO (0.5 wt% relative to the monomers in the feed) dissolved in 521.25 g EHA and 22.5 g HEMA (3 wt% relative to all monomers) was slowly fed to 206.25 g of 1-decene (27.5 wt% relative to all monomers) under nitrogen at 150°C for 3 hours. After stirring for another 1.2 hours, the resulting clear polymer was cooled down. Subsequently, the residual decene was removed by distillation at 160°C and pressures as low as 5 mbar using a rotary evaporator. The amount of decene incorporated

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in the polymer is determined gravimetrically assuming that no residual (meth)acrylate monomer is present.

5 All examples were prepared in the same way as inventive example Ex.1, except that the amounts of reactants and other reaction conditions were changed as listed in Table 1. For Ex.2 to Ex.6, Ex.8 and Ex.9, 0.2 wt% of stabilizer (4-methyl-2,6-di-tert-butylphenol) relative to the reaction mixture was added before the distillation step.

10 Further details regarding the synthetic procedures of the individual examples are provided in Table 1 together with basic properties of the polymers. The alpha-olefin monomers are always first charged to the reactor. The acrylate and dispersant monomers and the initiator are then fed over a set period of time. For acrylate-olefin copolymers with acrylate (mixtures) and dispersant monomer, all of them were mixed with the initiator before feeding to the olefin. For all examples, 0.5 wt% of DBPO as initiator relative to the monomers in the feed was used. The temperatures given in Table 1 correspond to the reaction temperature during the feed.

It is observed that all inventive polymers Ex.1 to Ex.12 are colorless, which is a further advantage looked for in the industry in comparison to comparative N-dispersant polymers Ex.15* to Ex.16*, which are yellowish-colored.

20 Furthermore, the total base number (TBN) according to ASTM D2896 was evaluated. The TBN of the inventive polymers Ex.7 to Ex.12 is always below 0.15, whereas the comparative Ex.15* containing DMAEMA exhibits a significantly higher TBN of 15.6. A lower TBN of the thickener offers more flexibility in the lubrication formulation and is beneficial for the long-term performance as a lower impact of acidic oxidation products on dispersancy performance is expected.

Formulations comprising the inventive and comparative polymers of Table 1 were prepared. The ratio of the different components is provided in Tables 2 to 4. The properties of the different formulations using inventive examples such as viscosity index, kinematic viscosity, Brookfield viscosity and shear loss are shown along with the results from the oxidation test.

35 Tables 2 to 4 also list the content of hydroxy-functional monomer c) (OH-functional monomer c) content) in formulation which corresponds to the weight content (wt%) of monomer c) in the polymer multiplied by the treat rate (TR). For example, formulation example F-1 contains 30.2 wt% polymer Ex.1 with 3.2 wt% HEMA. Thus, wt% of monomer c) is 3.2 and TR is 30.2, resulting in a OH-functional monomer c) content in formulation of $3.2 \times 30.2 = 97$. As shown in Tables 2 and 3, all inventive formulations according to the invention have a OH-functional monomer c) content in formulation of less than 100.

40 The target was to obtain formulations fulfilling SAE 75W-90 (Table 2) or 75W-80 (Table 3) standard (SAE is the organization Society of Automotive Engineers). Table 4 gives comparative examples of 75W-90 and 75W-80 formulations and their oxidative performance.

Table 1: Polymer properties of the prepared acrylate-olefin copolymers

Ex#	Acr.	Acr. [wt%]	Olefin	Olefin input* [wt%]	Olefin inc* [wt%]	Dispersant	Dispersant [wt%]	T [°C]	Mn [g/mol]	Mw [g/mol]	PDI	BV100 [mm²/s]
Ex.1	EHA	74.4	Dec	27.5	22.4	HEMA	3.2	150	6,400	15,300	2.38	324.4
Ex.2	EHA / LA	45.7 / 30.5	Dec	25	20.8	HEMA	3.0	150	7,030	18,000	2.57	245.1
Ex.3	EHA / LA	30.6 / 45.9	Dec	25	20.6	HEMA	3.0	150	7,130	17,900	2.51	202.7
Ex.4	IDA	76.3	Dec	25	20.7	HEMA	3.0	150	6,680	17,100	2.57	275.1
Ex.5	EHA / LA	60.6 / 15.1	Dec	25	21.3	HEMA	2.9	150	6,710	17,400	2.59	289.9
Ex.6	PHA	75.9	Dec	25	21.2	HEMA	2.9	150	6,000	14,100	2.34	246.6
Ex.7	EHA	75.2	Dec	27.5	22.9	HEMA	1.9	150	6,490	15,500	2.39	316.8
Ex.8	EHA	76.5	Dec	25	21.6	HPMA	1.9	150	6,600	17,400	2.63	380.3
Ex.9	EHA	76.3	Dec	25	21.8	GMMA	1.9	150	6,550	17,200	2.63	363.1
Ex.10	EHA	78.1	Dec	25	21.0	HEMA	0.9	150	6,940	17,500	2.53	349.8
Ex.11	EHA	74.7	Dec	25	21.9	HEMA	3.9	150	6,650	16,700	2.51	360.5
Ex.12	EHA	74.5	Dec	25	20.6	HEMA	4.9	150	6,840	16,800	2.45	403.1
Ex.13*	EHA	77.5	Dec	27	22.5	-	-	149	6,720	16,500	2.46	307.2
Ex.14*	EHA	71.0	Dec	27.5	23.8	HEMA	5.3	150	6,120	14,900	2.43	330.9
Ex.15*	EHA	76.3	Dec	27	18.6	DMAEMA	5.1	147	5,600	12,300	2.20	321.7
Ex.16*	EHA	76.5	Dec	25	21.6	DMAPMAM	1.9	150	6,390	15,400	2.41	334.9

* Amount of olefin monomer in wt% added to the reaction vessel (Olefin input) and incorporated in the final polymer (Olefin inc)

Table 3: 75W-80 formulations of acrylate-olefin copolymers according to the present invention

Formulation Examples	F-11	F-12	F-13	F-14	F-15	F-16	F-17
Ex.2 [wt%]	5.0						
Ex.3 [wt%]		5.2					
Ex.4 [wt%]			5.2				
Ex.5 [wt%]				5.1			
Ex.6 [wt%]					5.6		
Ex.8 [wt%]						5.0	
Ex.12 [wt%]							4.9
Anglamol 6043 [wt%]	6.5	6.5	6.5	6.5	6.5	6.5	6.5
VPL 1-300 [wt%]	1.0	1.0	1.0	1.0	1.0	1.0	1.0
Yubase 8 [wt%]	87.5	87.3	87.3	87.4	86.9	87.5	87.6
OH-functional monomer c) content in formulation (wt% of c) x TR)	15	15	15	15	16	10	24
KV40 [mm ² /s]	54.8	55.21	55.34	55.19	54.85	55.33	55.59
KV100 [mm ² /s]	8.989	9.039	9.01	9.01	8.939	9.02	9.045
VI	144	144	142	143	142	143	142
BF-40 [mPa·s]	73,000	72,000	75,000	74,000	71,000	75,000	72,000
SL 100°C [%]	2.8	3.1	2.9	2.7	2.9	2.4	3.5
Fresh oil TAN [mg KOH/g]	1.0	1.0	1.0	1.0	0.99	1.0	1.0
Oxidized oil TAN [mg KOH/g]	2	2.1	2.1	2.1	2.0	2.1	2.1
delta TAN [mg KOH/g]	1.00	1.10	1.10	1.10	1.01	1.10	1.10
delta KV100 [mm ² /s]	1.68	2.00	1.94	1.73	1.81	2.03	2.14
Blotterspot area [%]	70.23	73.47	71.35	66.82	70.31	61.83	65.33

Table 4: Comparative examples of 75W-90 and 75W-80 formulations of acrylate-olefin copolymers

Formulation Examples	F-1*	F-2*	F-3*	F-4*	F-5*	F-6*
Ex.13* [wt%]	30.6					
Ex.14* [wt%]		30.0				
Ex.12 [wt%]			29.3			
Ex.15* [wt%]				31.0		5.3
Ex.16* [wt%]					30.0	
Anglamol 6043 [wt%]	6.5	6.5	6.5	6.5	6.5	6.5
VPL 1-300 [wt%]	0.5	0.5	0.5	0.5	0.5	1.0
Yubase 4 [wt%]	19.4	27.0	30.7	22.0	23.0	-
Yubase 6 [wt%]	43.0	36.0	33.0	40.0	40.0	-
Yubase 8 [wt%]	-	-	-	-	-	87.7
OH-functional monomer c) content in formulation (wt% of c) x TR)	0	159	144	0	0	0
KV40 [mm ² /s]	91.73	91.18	88.43	95.11	89.00	55.07
KV100 [mm ² /s]	14.55	14.25	14.22	14.54	14.15	8.993
VI	165	162	167	159	164	143
BF-40 [mPa·s]	116,000	128,000	118,000	144,000	116,000	73,000
SL 100°C [%]	4.3	2.9	5.4	5.4	4.3	3.1
Fresh oil TAN [mg KOH/g]	1.0	1.1	1.0	1.5	1.1	1.1
Oxidized oil TAN [mg KOH/g]	2.9	3	2.6	7.9	3.7	2.6
delta TAN [mg KOH/g]	1.90	1.90	1.60	6.40	2.60	1.50
delta KV100 [mm ² /s]	6.66	279.9 - 296.5	134.7 - 138.1	16.25	11.38	3.88
Blotterspot area [%]	10.52	100.00	100.0	100.00	100.00	54.74

Comparative Ex.13* of the present patent application is similar to example 5 of EP401604 comprising EHA and 1-decene. These copolymers comprising EHA, which are consequently rather polar due to the short side-chain, show poor performance in the dispersancy rating of the oxidation test according to CEC SG-L-48 as shown in formulation example F-1* in Table 4. Better performance in sludge
5 handling is achieved with lubricant formulations comprising the inventive hydroxy-functionalized acrylate-olefin copolymers according to the invention. Indeed, as shown in Table 2 above, the oxidation tests of the 75W-90 formulations comprising the hydroxy-functionalized acrylate-olefin copolymers according to the invention (F-1 to F-10) deliver good oxidative performance with 100% dispersancy rating in the blotterspot test (blotterspot area). Even at lower treat rates as in the 75W-80
10 formulations shown in Table 3 (F-11 to F-17), the dispersancy is surprisingly still above 60%.

Furthermore, comparative formulation examples F-2* and F-3* demonstrate that high amounts of OH-functional groups in the formulation result in a high viscosity increase in the oxidation test. For these cases, it was not even possible to clearly determine the values for the increase of the KV100
15 between fresh and oxidized oil but only a range for the increase can be given. For both formulations F-2* and F-3*, an increase of the KV100 higher than 130 mm²/s was found. The polymer composition of comparative example Ex.14* used in F-2* comprises > 5 wt% of the OH-functional monomer HEMA. The polymer Ex.12 used for F-3* comprises 4.9 wt% HEMA and therefore the concentration of OH-functional monomer in the final formulation is also higher than allowed by the restriction of
20 [wt% of monomer c)] x TR < 100. However, the same polymer (Ex.12) used in a 75W-80 formulation (F-7) which only requires 4.9 wt% of polymer treat rate shows good oxidative performance. Here, the restriction [wt% of monomer c)] x TR < 100 is fulfilled.

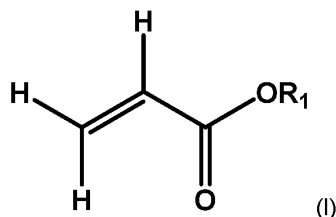
The hydroxy-functionalized polymers perform on the level of the nitrogen-containing ones regarding
25 dispersancy, which is quite unexpected because nitrogen functionality is more typical in dispersants (US20150274875, US10428292). Even more surprising is the lower acid number after oxidation of the formulations containing the hydroxy-functional monomers and especially the lower acid number increase. The basic nitrogen functionalities were expected to perform better in both tests. Polymers containing N-dispersant functions such as comparative examples Ex.15* and Ex.16* exhibit this
30 higher increase of the acid number after the oxidation test. These comparative examples in 75W-90 formulations show an increase in acid number (delta TAN) of 2.6 mg KOH/g (F-5*) up to 6.4 mg KOH/g (F-4*), while the increase of the inventive examples in the 75W-90 formulation are at 2.0 mg KOH/g or below (F-1 to F-10).

35 The inventive polymers comprising hydroxy-functional dispersant monomers exhibit good oxidative performance with good dispersancy and low increase in acid number due to oxidation compared to similar polymers comprising N-functional dispersant monomers. Polymers outside the claimed composition with higher contents of hydroxy-functional monomers or formulations which contain high amounts of hydroxy-functional monomers due to a high treat rate, exhibit a large increase of the
40 kinematic viscosity at 100°C after oxidation. Thus, the type and amount of dispersant monomer is crucial for the oxidative performance of the polymer, and consequently of the lubricant formulation thereof.

CLAIMS

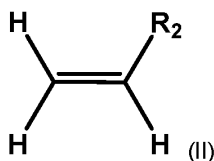
1. A lubricant formulation comprising a base oil and a hydroxy-functionalized acrylate-olefin copolymer,
 5 wherein the copolymer has a weight-average molecular weight from 5,000 to 30,000 g/mol according to DIN 55672-1 and comprises:

- a) 60 to 99.8% by weight, based on the total weight of the copolymer, of monomer units derived from at least one acrylate of formula (I),



- 10 wherein R₁ means a linear or branched alkyl group having from 8 to 15 carbon atoms,

- b) 0.1 to 39.9% by weight, based on the total weight of the copolymer, of monomer units derived from at least one non-functionalized alpha-olefin of formula (II),



- 15 wherein R₂ means a linear alkyl group having from 8 to 14 carbon atoms, and

- c) 0.1 to 5% by weight, based on the total weight of the copolymer, of monomer units derived from at least one hydroxy-functional (meth)acrylate monomer c),

and

- 20 wherein the lubricant formulation has a content of hydroxy-functional (meth)acrylate monomer c) in formulation of less than 100, calculated with the formula (III)

$$[\text{wt}\% \text{ of monomer c)}] \times \text{TR} < 100 \quad (\text{III})$$

wherein [wt% of monomer c)] is the total weight content of monomers c) in the polymer and wherein TR is the polymer treat rate in weight percent in the lubricant formulation.

25

2. The lubricant formulation according to claim 1, wherein the copolymer comprises from 65.5 to 95% by weight, preferably from 74.2 to 90% by weight, of monomer units a) derived from at least one acrylate of formula (I), based on the total weight of the copolymer.
- 30 3. The lubricant formulation according to claim 1 or 2, wherein the copolymer comprises from 4.5 to 35% by weight, preferably from 4.9 to 30% by weight, more preferably from 9.2 to 25% by weight, of monomer units b) derived from at least one non-functionalized alpha-olefin of formula (II), based on the total weight of the copolymer.

4. The lubricant formulation according to any one of the previous claims, wherein the copolymer comprises from 0.5 to 5% by weight, preferably from 0.8 to 5% by weight, of monomer units c) derived from at least one hydroxy-functional (meth)acrylate, based on the total weight of the copolymer.
5. The lubricant formulation according to any one of the previous claims, wherein the copolymer has a kinematic viscosity from 100 to 1,000 mm²/s at 100°C according to ASTM D445, preferably from 120 to 700 mm²/s at 100°C according to ASTM D445, more preferably from 150 to 500 mm²/s at 100°C according to ASTM D445.
6. The lubricant formulation according to any one of the previous claims, wherein the acrylate a) of formula (I) is selected from the group consisting of n-octyl acrylate, 2-ethylhexyl acrylate, 2-propylheptyl acrylate, isononyl acrylate, isodecyl acrylate, isotridecylacrylate, n-decyl acrylate, lauryl acrylate, or a mixture thereof.
7. The lubricant formulation according to any one of the previous claims, wherein the non-functionalized alpha-olefin b) of formula (II) is selected from the group consisting of decene, dodecene, tetradecene, hexadecene or a mixture thereof.
8. The lubricant formulation according to any one of the previous claims, wherein the hydroxy-functional (meth)acrylate c) is selected from the group consisting of 2-hydroxyethyl (meth)acrylate, 2-hydroxypropyl (meth)acrylate, 2,3-dihydroxypropyl (meth)acrylate, 4-hydroxybutyl (meth)acrylate, 2-hydroxybutyl (meth)acrylate, 3-hydroxybutyl (meth)acrylate, trimethylolpropane mono(meth)acrylate, 2-ethoxy ethyl (meth)acrylate, 2-(2-ethoxyethoxy)ethyl (meth)acrylate, 2-hydroxy-2-methylpropyl (meth)acrylate, or a mixture thereof.
9. The lubricant formulation according to any one of the previous claims, wherein the total amount of monomer units derived from monomers a), b) and c) in the copolymer sums up to 90% by weight or more, preferably sums up to 95% by weight or more, more preferably sums up to 98 % by weight or more, based on the total weight of the copolymer.
10. The lubricant formulation according to any one of the previous claims, wherein the copolymer has a weight-average molecular weight from 8,000 to 30,000 g/mol, preferably from 10,000 to 25,000 g/mol, even more preferably from 12,000 to 20,000 g/mol, according to DIN 55672-1.
11. The lubricant formulation according to any one of the previous claims, wherein the copolymer has a polydispersity index from 1.0 to 3.5, preferably from 1.5 to 3.0.
12. The lubricant formulation according to any one of the previous claims, wherein the lubricant formulation comprises from 0.1 to 99.9% by weight, more preferably from 3 to 99% by weight, of the copolymer, based on the total weight of the lubricant formulation.

13. A method for the preparation of a lubricant formulation as defined in any one of claims 1 to 12, wherein the method comprises the steps of:
- i) providing a monomer composition according to any one of claims 1 to 4 and 6 to 9,
 - ii) initiating radical polymerization in the monomer composition of step i) to obtain the
 - 5 copolymer according to any one of claims 1 to 11,
 - iii) mixing the copolymer of step ii) with a base oil.
14. Use of a formulation as defined in any one of claims 1 to 12 as a lubricant formulation, preferably a gear oil lubricating composition, a transmission oil lubricating composition, a hydraulic oil lubricating
- 10 composition, an engine oil lubricating composition, a marine oil lubricating composition, an industrial lubricating oil composition or a grease, by adding a copolymer as defined in any one of claims 1 to 12 to the lubricant formulation.
15. Method of thickening a lubricant formulation and improving the dispersancy and/or reducing the
- 15 sludge sedimentation of a lubricant formulation by adding a copolymer as defined in any one of claims 1 to 12, as a lubricant additive or a synthetic base fluid, to said lubricant formulation.