

High Viscosity Polyacrylate Base Fluids

The present invention is directed to low molecular weight polyalkyl acrylate polymers, a method for their preparation and their use as high viscosity base fluids. It is further directed to lubricant compositions comprising such low molecular weight polyalkyl acrylate polymers and to the use of such compositions as automatic transmission fluids, manual transmission fluids, continuously variable transmission fluids, gear oil formulations, industrial gear oil formulations, axle fluid formulations, dual clutch transmission fluids, dedicated hybrid transmission fluids or as hydraulic oils.

High viscosity base fluids are commonly used to lift the viscosity index (VI) and to thicken lubricant formulations with demanding shear stability requirements. A typical application are gear oils which have very demanding requirements due to high mechanical stress and a broad temperature range in operation.

High viscosity base fluids are known to have a kinematic viscosity at 100°C (KV100) of 30 to 1000 cSt.

Industrial gearboxes are expected to perform under conditions of high heat and heavy loads; and in environments often contaminated with dirt, process debris and water. Without adequate protection, gears will wear prematurely. That means that certain parts have to be replaced more frequently, the oil has to be changed more frequently, and worst of all, equipment downtime has to be expected.

Today's gear driven equipment is designed to perform in many applications, often having to withstand harsh environments. Typically, gear boxes are becoming smaller and are being made from lighter and more sophisticated materials, yet they must be more durable than ever before. As a result, greater demands are being placed upon the gear oil lubricant and greater consideration must be given to the use of high-performance base fluids and additives.

Typical products in this market are high viscosity polyalphaolefins (PAOs) and metallocene catalyzed PAOs (mPAOs), typically sold in viscosity ranges of 40 to 300 cSt at 100°C (Choudary et al. Lubr. Sci. 2012, 23-44). Formulations based on high viscosity PAOs are known to have the best performance at low temperatures, but their weakness is the low polarity. Due to the apolar nature of PAO base oils, dispersion inhibitor (DI) packages and ageing products are poorly dissolved in the oil causing various problems.

Higher polarity is provided by copolymers of alpha-olefins with maleates (US 5,435,928), oligomers of alpha-olefins with alkyl acrylates (US 3,968,148) or copolymers of alpha-olefins with alkyl methacrylates (US 5,691,284). Alternatively, PAOs with ester-functionalized monomers (EP2970532) or polyvinylethers (US 2013/0165360) can be applied. A big advantage of using polar high viscosity base fluids is that no polar low viscous fluids, such as esters, must be used as

compatibilizers for the DI package. Polar low viscous fluids are known to cause problems with coatings and seals which is less of an issue for high viscosity fluids.

Another class of high viscosity base fluids are polyalkyl (meth)acrylates (PAMAs) (US 2013/229016). PAMAs are well-known for their use as VI improvers in lubricants and can be tuned to reach the highest performance level.

US 2013/229016 is directed to lubricants for transmission systems and wind power plants, comprising at least 30% by weight of a polyalkyl methacrylate. The working examples disclosed do all consist of methacrylates containing alkyl side-chains with a minimum of 10 carbon atoms. Pure alkyl acrylates are not disclosed.

Alkyl acrylates are not used in VI improver application. 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 (WO 96/17517) exist, it is generally known that the performance of polyacrylates as VI improver is inferior to the one of polymethacrylates. Especially in WO 96/17517 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.

Branched alcohols are commonly used for the preparation of PAMA VI improvers. Among others, the mono-branched long-chain Guerbet alcohols are known to be one of the alcohol classes that provide a favorable branching pattern for use as VI improvers (US 2004/0077509). The branching inhibits crystallization of the alcohols; and when they are incorporated into a polymer, it will keep the polymer chains from crystallizing.

Short-chain alcohols with branching pattern, such as ethylhexanol and propylheptanol, are accessible via a reaction sequence involving hydroformylation and aldol condensation, starting from propene or butene, respectively. These alcohols are commercially highly attractive as they are produced on large industrial scale for a variety of applications. The use of polymers comprising ethylhexyl methacrylate (EP 0 937 769) and/or propylheptyl methacrylate (US 2012/245068) as PAMA VI improvers is described in the known literature.

It was now surprisingly found that high viscosity base fluids prepared from low molecular weight polyalkyl acrylates perform remarkably different than low molecular weight polyalkyl methacrylates. Polyalkyl acrylates comprising at least 95% by weight of acrylates show excellent oil solubility, even at lower temperatures, compared to corresponding polyalkyl methacrylates, although the polyalkyl acrylates have a lower ratio of carbon to oxygen.

A first object of the present invention is therefore directed to polyalkyl acrylates, comprising:

- (a) 95 to 100% by weight of branched C₈₋₁₀-alkyl acrylates; and
- (b) 0 to 5% by weight of C₁₋₂₀-alkyl (meth)acrylates,

characterized in that the weight-average molecular weight is in the range of 7,000 to 25,000 g/mol and the residual monomer content is 0.1% or lower.

5 The content of each component (a) and (b) is based on the total composition of the polyalkyl acrylate. In a particular embodiment, the proportions of components (a) and (b) add up to 100% by weight.

10 The molar ratio of carbon to oxygen in the polyalkyl acrylates are preferably in the range of 4.5:1 to 7.5:1, more preferably in the range of 5:1 to 7:1, and even more preferably in the range of 5.5:1 to 6.5:1.

The weight-average molecular weight M_w of the polyalkyl acrylate polymers according to the present invention is preferably in the range from 10,000 to 20,000 g/mol.

15 Preferably, the polyalkyl acrylate polymers according to the present invention have a polydispersity index (PDI) M_w/M_n in the range of 1.5 to 3.5, more preferably in the range of 1.5 to 3.

20 M_w and M_n are determined by size exclusion chromatography (SEC) using commercially available polymethylmethacrylate standards. The determination is affected by gel permeation chromatography with THF as eluent.

The term "acrylate" refers to esters of acrylic acid; the term "(meth)acrylate" refers to both, esters of acrylic acid and esters of methacrylic acid.

25 The branched C_{8-10} alkyl acrylates for use in accordance with the invention are esters of acrylic acid and branched alcohols having 8 to 10 carbon atoms. The term " C_{8-10} alkyl acrylates" encompasses individual acrylic esters with an alcohol of a particular length, and likewise mixtures of acrylic esters with alcohols of different lengths.

30 The suitable branched C_{8-10} alkyl acrylates include, for example, 2-ethylhexyl acrylate, 3-isopropylheptyl acrylate and iso-decyl acrylate.

35 The C_{1-20} alkyl (meth)acrylates for use in accordance with the invention are esters of (meth)acrylic acid and straight chain or branched alcohols having 1 to 20 carbon atoms and are different to the branched C_{8-10} alkyl acrylates as described further above. The term " C_{1-20} alkyl methacrylates" encompasses individual (meth)acrylic esters with an alcohol of a particular length, and likewise mixtures of (meth)acrylic esters with alcohols of different lengths.

40 Suitable C_{1-20} alkyl (meth)acrylates include, for example, methyl (meth)acrylate, ethyl (meth)acrylate, *n*-propyl (meth)acrylate, *iso*-propyl (meth)acrylate, *n*-butyl (meth)acrylate, *iso*-butyl (meth)acrylate, *tert*-butyl (meth)acrylate, pentyl (meth)acrylate, hexyl (meth)acrylate, heptyl (meth)acrylate, octyl (meth)acrylate, nonyl (meth)acrylate, decyl (meth)acrylate, undecyl

(meth)acrylate, 5-methylundecyl (meth)acrylate, dodecyl (meth)acrylate, 2-methyldodecyl (meth)acrylate, tridecyl (meth)acrylate, 5-methyltridecyl (meth)acrylate, tetradecyl (meth)acrylate, pentadecyl (meth)acrylate, hexadecyl (meth)acrylate, heptadecyl (meth)acrylate, octadecyl (meth)acrylate, nonadecyl (meth)acrylate and eicosyl (meth)acrylate.

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A further first object of the present invention is directed to polyalkyl acrylates, consisting of 100% by weight of branched C₈₋₁₀-alkyl acrylates.

10 A further first object of the present invention is directed to polyalkyl acrylates, wherein the C₈₋₁₀-alkyl acrylate is selected from the group consisting of ethylhexyl acrylate and propylheptyl acrylate.

A further first object of the present invention is directed to polyalkyl acrylates, wherein the C₈₋₁₀-alkyl acrylate is ethylhexyl acrylate.

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A further first object of the present invention is directed to poly-ethylhexyl acrylate, having a weight-average molecular weight is in the range of 10,000 to 20,000 g/mol and being characterized by a residual monomer content of 0.1% or lower.

20 A second object of the present invention is directed to the use of the polyalkyl acrylates as described herein before as base oils in lubricant formulations, especially in industrial gear oil formulations.

25 The use is preferably directed to the preparation of ISO 220 formulations or ISO 320 formulations, wherein the KV₄₀ of the lubricant formulation is 220 mm²/s $\pm$ 10% or 320 mm²/s $\pm$ 10%, respectively. The ISO 220 formulation such prepared are characterized by a VI of 125 or higher, preferably in the range of 130 to 150.

The ISO 320 formulation such prepared are characterized by a VI of 140 or higher, preferably in the range of 150 to 180.

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A further second object of the present invention is directed to a method of lubricating an industrial gear, comprising the steps of:

- 35 (i) using at least one polyalkyl acrylate as described further above as a base oil;
 (ii) optionally combining the polyalkyl acrylate with another base oil selected from the group consisting of API Group II oils, API Group III oils, API Group IV oils, and mixtures thereof;
 and
 (iii) applying the formulation prepared under (ii) to an industrial gear.

A third object of the present invention is directed to a base oil composition, comprising:

- 40 (A) 70 to 95% by weight of at least one polyalkyl acrylate, comprising:
 (a) 95 to 100% by weight of branched C₈₋₁₀-alkyl acrylates; and

- (b) 0 to 5% by weight of C₁₋₂₀-alkyl (meth)acrylates, characterized in that the weight-average molecular weight is in the range of 7,000 to 25,000 g/mol and the residual monomer content is 0.1% or lower; and
- (B) 5 to 30% by weight of a base oil selected from the group consisting of API Group II oils, API Group III oils, API Group IV oils, and mixtures thereof.

The content of each component (A) and (B) is based on the total weight of the base oil composition. In a particular embodiment, the proportions of components (A) and (B) add up to 100% by weight.

- The content of each component (a) and (b) is based on the total composition of the polyalkyl acrylate. In a particular embodiment, the proportions of components (a) and (b) add up to 100% by weight.

- A further third object of the present invention is directed to a base oil composition, wherein the polyalkyl acrylates (A) consist of 100% by weight of branched C₈₋₁₀-alkyl acrylates.

- A further third object of the present invention is directed to a base oil composition, wherein the C₈₋₁₀-alkyl acrylate is selected from the group consisting of ethylhexyl acrylate and propylheptyl acrylate.

- A further third object of the present invention is directed to a base oil composition, wherein the C₈₋₁₀-alkyl acrylate is ethylhexyl acrylate.

- A further third object of the present invention is directed to a base oil composition, comprising:
- (A) 70 to 95% by weight of poly-ethylhexyl acrylate, having a weight-average molecular weight is in the range of 10,000 to 20,000 g/mol and being characterized by a residual monomer content of 0.1% or lower; and
- (B) 5 to 30% by weight of a base oil selected from the group consisting of API Group II oils, API Group III oils, API Group IV oils, and mixtures thereof.

- A fourth object of the present invention is directed to the use of a base oil composition as described further above for the preparation of an industrial gear oil.

- A further fourth object of the present invention is directed to a method of preparing an industrial gear oil composition, the method comprising:
- combining 70 to 95% by weight of at least one polyalkyl acrylate, comprising:
- (a) 95 to 100% by weight of branched C₈₋₁₀-alkyl acrylates; and
- (b) 0 to 5% by weight of C₁₋₂₀-alkyl (meth)acrylates, characterized in that the weight-average molecular weight is in the range of 7,000 to 25,000 g/mol and the residual monomer content is 0.1% or lower, with

5 to 30% by weight of a base oil selected from the group consisting of API Group II oils, API Group III oils, API Group IV oils, and mixtures thereof.

A further fourth object of the present invention is directed to a method of lubricating an industrial gear, comprising the steps of:

- (i) preparing a base oil composition as described further above; and
- (ii) applying the base oil composition prepared under (i) to an industrial gear.

A fifth object of the present invention is directed to a lubricating composition, comprising:

- 10 (A) 20 to 60% by weight of at least one polyalkyl acrylate, comprising:
 - (a) 95 to 100% by weight of branched C₈₋₁₀-alkyl acrylates; and
 - (b) 0 to 5% by weight of C₁₋₂₀-alkyl (meth)acrylates, characterized in that the weight-average molecular weight is in the range of 7,000 to 25,000 g/mol and the residual monomer content is 0.1% or lower;
- 15 (B) 40 to 80% by weight of a base oil selected from the group consisting of API Group II oils, API Group III oils, API Group IV oils, and mixtures thereof; and
- (C) 0 to 5% by weight of one or more additives.

The content of each component (A), (B) and (C) is based on the total weight of the lubricating composition. In a particular embodiment, the proportions of components (A), (B) and (C) add up to 100% by weight.

The content of each component (a) and (b) is based on the total composition of the polyalkyl acrylate. In a particular embodiment, the proportions of components (a) and (b) add up to 100% by weight.

25 In apolar formulations based on Group II, III and IV base oils and polyolefin thickeners, it is common practice to add a Group V base oil, such as esters or alkylated naphthalenes, in order to dissolve the additives. Due to the solvency provided by the highly polar polyacrylates of the present invention, no further compatibilizer is added to the formulations described in the present invention.

30 The base oil to be used in the lubricating composition comprises an oil of lubricating viscosity. Such oils include natural and synthetic oils, oils derived from hydrocracking, hydrogenation, and hydrofinishing, unrefined, refined, re-refined oils or mixtures thereof.

The base oil may also be defined as specified by the American Petroleum Institute (API) (see April 35 2008 version of "Appendix E-API Base Oil Interchangeability Guidelines for Passenger Car Motor Oils and Diesel Engine Oils", section 1.3 Sub-heading 1.3. "Base Stock Categories").

The API currently defines five groups of lubricant base stocks (API 1509, Annex E - API Base Oil Interchangeability Guidelines for Passenger Car Motor Oils and Diesel Engine Oils, September 40 2011). 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; Group IV are polyalphaolefins; and Group V are all others, including e.g. ester oils. The table below illustrates these API classifications.

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
IV	All polyalphaolefins (PAOs)		
V	All others not included in Groups I, II, III or IV (e.g. ester oils)		

- 5 The kinematic viscosity at 100°C (KV₁₀₀) of appropriate apolar base oils used to prepare a lubricating composition in accordance with the present invention is preferably in the range of 5 mm²/s to 15 mm²/s, more preferably in the range of 6 mm²/s to 113 mm²/s, and even more preferably in the range of 8 mm²/s to 12 mm²/s, determined to ASTM D445.
 - 10 Particularly preferred lubricants of the present invention comprise at least one base oil selected from the group consisting of API Group II oils, API Group III oils, polyalphaolefins (PAO) and mixtures thereof.
- Further base oils which can be used in accordance with the present invention are Group II-III
- 15 Fischer-Tropsch derived base oils.
- Fischer-Tropsch derived base oils are known in the art. By the term "Fischer-Tropsch derived" is meant that a base oil is, or is derived from, a synthesis product of a Fischer-Tropsch process. A Fischer-Tropsch derived base oil may also be referred to as a GTL (Gas-To-Liquids) base oil.
- Suitable Fischer-Tropsch derived base oils that may be conveniently used as the base oil in the
- 20 lubricating composition of the present invention are those as for example disclosed in EP 0 776 959, EP 0 668 342, WO 97/21788, WO 00/15736, WO 00/14188, WO 00/14187, WO 00/14183, WO 00/14179, WO 00/08115, WO 99/41332, EP 1 029 029, WO 01/18156, WO 01/57166 and WO 2013/189951.
 - 25 Especially for industrial gear oil formulations are used base oils of API Group II, III, IV or mixtures thereof.
- The lubricating composition according to the invention may also contain, as component (C), further additives selected from the group consisting of pour point depressants, dispersants, defoamers,
- 30 detergents, demulsifiers, antioxidants, antiwear additives, extreme pressure additives, friction modifiers, anticorrosion additives, dyes and mixtures thereof.
- Preferred pour point depressants are, for example, selected from the group consisting of alkylated naphthalene and phenolic polymers, polyalkyl methacrylates, maleate copolymer esters and
- 35 fumarate copolymer esters, which may conveniently be used as effective pour point depressants.

The lubricating oil composition may contain 0.1% by weight to 0.5% by weight of a pour point depressant. Preferably, not more than 0.3% by weight of a pour point depressant is used.

- Appropriate dispersants include poly(isobutylene) derivatives, for example
- 5 poly(isobutylene)succinimides (PIBSIs), including borated PIBSIs; and ethylene-propylene oligomers having N/O functionalities.

Suitable defoaming agents include, for example, silicone oils, fluorosilicone oils, and fluoroalkyl ethers.

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- The preferred detergents include metal-containing compounds, for example phenoxides; salicylates; thiophosphonates, especially thiopyrophosphonates, thiophosphonates and phosphonates; sulfonates and carbonates. As metal, these compounds may contain especially calcium, magnesium and barium. These compounds may preferably be used in neutral or
- 15 overbased form.

Preferred demulsifiers include alkyleneoxide copolymers and (meth)acrylates including polar functions.

- 20 The suitable antioxidants include, for example, phenols, for example 2,6-di-tert-butylphenol (2,6-DTB), butylated hydroxytoluene (BHT), 2,6-di-tert-butyl-4-methylphenol, 4,4'-methylenebis(2,6-di-tert-butylphenol); aromatic amines, especially alkylated diphenylamines, N-phenyl-1-naphthylamine (PNA), polymeric 2,2,4-trimethyldihydroquinone (TMQ); compounds containing sulfur and phosphorus, for example metal dithiophosphates, for example zinc dithiophosphates (ZnDTPs),
- 25 "OOS triesters" = reaction products of dithiophosphoric acid with activated double bonds from olefins, cyclopentadiene, norbornadiene, α -pinene, polybutene, acrylic esters, maleic esters (ashless on combustion); organosulfur compounds, for example dialkyl sulfides, diaryl sulfides, polysulfides, modified thiols, thiophene derivatives, xanthates, thioglycols, thioaldehydes, sulfur-containing carboxylic acids; heterocyclic sulfur/nitrogen compounds, especially
- 30 dialkyldimercaptothiadiazoles, 2-mercaptobenzimidazoles; zinc bis(dialkyldithiocarbamate) and methylene bis(dialkyldithiocarbamate); organophosphorus compounds, for example triaryl and trialkyl phosphites; organocopper compounds and overbased calcium- and magnesium-based phenoxides and salicylates.
- 35 The preferred antiwear and extreme pressure additives include phosphorus compounds, for example trialkyl phosphates, triaryl phosphates, e.g. tricresyl phosphate, amine-neutralized mono- and dialkyl phosphates, ethoxylated mono- and dialkyl phosphates, phosphites, phosphonates, phosphines; compounds having sulfur and phosphorus, for example metal dithiophosphates, e.g. zinc di-C₃₋₁₂-alkyldithiophosphates (ZnDTPs), ammonium dialkyldithiophosphates, antimony
- 40 dialkyldithiophosphates, molybdenum dialkyldithiophosphates, lead dialkyldithiophosphates, "OOS triesters" = reaction products of dithiophosphoric acid with activated double bonds from olefins,

cyclopentadiene, norbornadiene, α -pinene, polybutene, acrylic esters, maleic esters, triphenyl phosphorothionate (TPPT); compounds having sulfur and nitrogen, for example zinc bis(amyldithiocarbamate) or methylenebis(di-n-butyl dithiocarbamate); sulfur compounds with elemental sulfur and H₂S sulfurized hydrocarbons (diisobutylene, terpene); sulfurized glycerides and fatty acid esters; overbased sulfonates; chlorine compounds or solids, such as graphite or molybdenum disulfide.

Friction modifiers used may include mechanically active compounds, for example molybdenum disulfide, graphite (including fluorinated graphite), poly(trifluoroethylene), polyamide, polyimide; compounds that form adsorption layers, for example long-chain carboxylic acids, fatty acid esters, ethers, alcohols, amines, amides, imides; compounds which form layers through tribochemical reactions, for example saturated fatty acids, phosphoric acid and thiophosphoric esters, xanthogenates, sulfurized fatty acids; compounds that form polymer-like layers, for example ethoxylated dicarboxylic partial esters, dialkyl phthalates, methacrylates, unsaturated fatty acids, sulfurized olefins or organometallic compounds, for example molybdenum compounds (molybdenum dithiophosphates and molybdenum dithiocarbamates MoDTCs) and combinations thereof with ZnDTPs, copper-containing organic compounds.

Some of the compounds listed above may fulfil multiple functions. ZnDTP, for example, is primarily an antiwear additive and extreme pressure additive, but also has the character of an antioxidant and corrosion inhibitor (here: metal passivator/deactivator).

The above-detailed additives are described in detail, inter alia, in T. Mang, W. Dresel (eds.): "Lubricants and Lubrication", Wiley-VCH, Weinheim 2001; R. M. Mortier, S. T. Orszulik (eds.): "Chemistry and Technology of Lubricants".

Dispersants (including borated dispersants) are preferably used in a concentration of 0% to 2% by weight, defoamers in a concentration of 10 to 2500 ppm, detergents in a concentration of 0.05% to 1% by weight, demulsifiers in a concentration of 0% to 0.1% by weight, antioxidants in a concentration of 0.5% to 1.5% by weight, antiwear and extreme pressure additives each in a concentration of 0.1% to 1% by weight, friction modifiers in a concentration of 0.05% to 2% by weight, anticorrosion additives in a concentration of 0.05% to 0.5% by weight, and dyes in a concentration of 0.01% to 1% by weight. The concentration is based in each case on the total weight of the lubricating oil composition.

Preferably, the total concentration of the one or more additives (C) in a lubricating oil composition is up to 5% by weight, more preferably 0.1% to 4% by weight, more preferably 0.5% to 3% by weight, based on the total weight of the lubricating oil composition.

A further fifth object of the present invention is directed to a lubricating composition, comprising:

- (A) 20 to 60% by weight of poly-ethylhexyl acrylate, having a weight-average molecular weight is in the range of 10,000 to 20,000 g/mol and being characterized by a residual monomer content of 0.1% or lower;
- (B) 40 to 80% by weight of a base oil selected from the group consisting of API Group II oils, API Group III oils, API Group IV oils, and mixtures thereof; and
- (C) 0 to 5% by weight of one or more additives.

The content of each component (A), (B) and (C) is based on the total weight of the lubricating composition. In a particular embodiment, the proportions of components (A), (B) and (C) add up to 100% by weight.

A sixth object of the present invention is directed to the use of the above-described lubricating oil composition as industrial gear oil.

- A further sixth object of the present invention is directed to a method of preparing a lubricating composition, the method comprising:
- combining 20 to 60% by weight of at least one polyalkyl acrylate, comprising:
- (a) 95 to 100% by weight of branched C₈₋₁₀-alkyl acrylates; and
- (b) 0 to 5% by weight of C₁₋₂₀-alkyl (meth)acrylates,
- characterized in that the weight-average molecular weight is in the range of 7,000 to 25,000 g/mol and the residual monomer content is 0.1% or lower, with
- 40 to 80% by weight of a base oil selected from the group consisting of API Group II oils, API Group III oils, API Group IV oils, and mixtures thereof, and
- 0 to 5% by weight of one or more additives.

- A further sixth object of the present invention is directed to a method of lubricating an industrial gear, comprising the steps of:
- (i) preparing a lubricating composition as described further above; and
- (ii) applying the lubricating composition prepared under (i) to an industrial gear.

The polyalkyl acrylates as described further above are prepared in a special feed process. Control over absolute molecular weight and molecular weight distribution is of highest importance for the application as high viscosity base fluid. This can be conventionally achieved by addition of chain transfer agents or high radical initiator concentrations (see e.g. US 2013/0229016). The process described herein works without addition of a chain transfer agent and with a comparably small amount of initiator, relative to the obtained molecular weight.

- A sixth object of the present invention is directed to a process for preparing the polyalkyl acrylates as described further above, the process comprising the steps of:
- (i) charging a reaction vessel with a base oil;
- (ii) heating the base oil of step (i) to a reaction temperature of 130°C to 170°C;

- (iii) constantly feeding a mixture of branched C₈₋₁₀-alkyl acrylates and 0.1 to 1.2% of an initiator, based on the amount of branched C₈₋₁₀-alkyl acrylates, to the reaction vessel over a time of 120 to 240 minutes;
- (iv) optionally stirring the reaction mixture obtained under step (iii) for another 50 to 90 minutes; and
- (vi) cooling the reaction mixture obtained under step (iv) to an ambient temperature and obtaining the desired polyalkyl acrylate.

The base oil to be used in step (i) can be selected from the group consisting of API Group II oils, API Group III, API Group IV oils and mixtures thereof.

The concentration of the alkyl acrylates in the reaction mixture is 70 to 95% by weight, preferably 80 to 90% by weight. That means that the reaction mixture obtained under step (iii) contains 5 to 30% by weight, preferably 10 to 20% by weight of base oil and 70 to 95% by weight, preferably 80 to 90% by weight, of alkyl acrylates.

Usable initiators include azo initiators widely known in the technical field, such as AIBN and 1,1-azobiscyclohexanecarbonitrile, and also peroxy compounds such as methyl ethyl ketone peroxide, acetylacetone peroxide, dilauryl peroxide, tert-butyl per-2-ethylhexanoate, ketone peroxide, tert-butyl peroctoate, methyl isobutyl ketone peroxide, cyclohexanone peroxide, dibenzoyl peroxide, tert-butyl peroxybenzoate, tert-butyl peroxyisopropylcarbonate, 2,5-bis(2-ethylhexanoylperoxy)-2,5-dimethylhexane, tert-butyl peroxy-2-ethylhexanoate, tert-butyl peroxy-3,5,5-trimethylhexanoate, dicumyl peroxide, 1,1-bis(tert-butylperoxy)cyclohexane, 1,1-bis(tert-butylperoxy)-3,3,5-trimethylcyclohexane, cumyl hydroperoxide, tert-butyl hydroperoxide, bis(4-tert-butylcyclohexyl) peroxydicarbonate, mixtures of two or more of the aforementioned compounds with one another, and mixtures of the aforementioned compounds with unspecified compounds which can likewise form free radicals.

Preferred initiators are dicumylperoxide and tert-butyl peroxy-2-ethylhexanoate.

The invention has been further illustrated by the following non-limiting examples.

Experimental Part

Abbreviations

BV	bulk viscosity
BV40	bulk viscosity @40°C
BV100	bulk viscosity @100°C
C600R	Group II base oil from Chevron with a KV ₁₀₀ of 12 cSt
DDM	dodecyl mercaptane
EHA	ethylhexyl acrylate, commercially available from Aldrich
HA	hexyl acrylate

	Hitec® 307	DI Package commercially available from Afton
	IDA	<i>iso</i> -decyl acrylate, commercially available from Aldrich
	ITDA	<i>iso</i> -tridecyl acrylate, commercially available from Aldrich
	KV	kinematic viscosity measured according to ASTM D445
5	KV ₄₀	kinematic viscosity measured @40°C to ASTM D445
	KV ₁₀₀	kinematic viscosity measured @100°C to ASTM D445
	KV ₋₁₀	kinematic viscosity measured @-10°C to ASTM D445
	LA	lauryl acrylate, dodecyl acrylate, commercially available from Aldrich
	M _n	number-average molecular weight
10	M _w	weight-average molecular weight
	NB3080	Nexbase® 3080; Group III base oil from Neste with a KV ₁₀₀ of 7.9 cSt
	PAO6	polyalphaolefin base oil with a KV ₁₀₀ of 6 cSt
	PAO8	polyalphaolefin base oil with a KV ₁₀₀ of 8 cSt
	PDI	polydispersity index
15	PHA	propylheptyl acrylate, commercially available from Aldrich
	PP	pour point
	VI	viscosity index
	VPL 1-180	VISCOPLEX® 1-180, pour point depressant commercially available from Evonik
	VPL 14-520	VISCOPLEX® 14-520, defoamer commercially available from Evonik
20	Yubase 6	Group III base oil from SK Lubricants with a KV ₁₀₀ of 6 cSt

Test methods

The polyalkyl acrylates according to the present invention and the comparative examples were characterized with respect to their molecular weight, PDI and bulk viscosity at 40°C and 100°C (BV40 and BV100).

Molecular weights were determined by size exclusion chromatography (SEC) using commercially available polymethylmethacrylate (PMMA) standards. The determination is effected by gel permeation chromatography (GPC) to DIN 55672-1 with THF as eluent (flow rate: 1 mL/min; injected volume: 100 µl).

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The lubricating oil compositions including the polyalkyl acrylates according to the present invention and comparative examples were characterized with respect to kinematic viscosity at -10°C (KV₋₁₀), 40°C (KV₄₀) and 100°C (KV₁₀₀) to ASTM D445, their viscosity index (VI) to ASTM D2270, Brookfield viscosity to ASTM D-2983 and their pour point to ASTM D5950.

35 The lubricating compositions were formulated to ISO viscosity grade 220 or 320, within a range of ±10%. The International Standards Organization Viscosity Grade, ISO VG, is recommended for industrial applications.

The reference temperature of 40°C represents the operating temperature in machinery.

This ISO viscosity classification is consequently based on kinematic viscosity at 40°C (KV₄₀).

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ISO Viscosity Grade	Midpoint Viscosity @40°C [mm ² /s]	Kinematic viscosity limits @40°C [mm ² /s]	
220	220	198	242
320	320	288	352

Tapered roller bearing measurements to determine the shear loss were run (20 hours, 60°C, 5kN and 1450 rpm) to CEC L-45-A-99 and corresponding kinematic viscosities measured at 40°C (KV₄₀) and 100°C (KV₁₀₀) to ASTM D-445

- 5 In connection with the evaluation of gear oil formulations, foam tests to ASTM D892 were run, air release was determined to DIN ISO 9120.

Synthesis 1: General synthesis of polyalkyl acrylates using a CTA feed process

- A round-bottom flask equipped with a glass stir rod, nitrogen inlet, reflux condenser and thermometer was charged with 41.9 g NB3080. 200.0 g EHA, 6.0 g DDM, 0.5 g *tert*-butylper-2-ethylhexanoate and 4.5 g NB080 were added within 2 hours at 110°C under nitrogen bubbling. Afterwards, 0.4 g *tert*-butylper-2-ethylhexanoate and 3.6 g NB3080 were fed to the reaction mixture over 1 hour.

15 Synthesis 2: General synthesis of polyalkyl acrylates using ATRP

- 1.88 g of pentamethyldiethylenetriamine, 0.78 g CuBr and 100.0 g of EHA were purged with nitrogen for 30 minutes and heated to 65°C. After addition of 2.12 g of ethylene bis(2-bromoisobutyrate) the reaction mixture was heated to 95°C. After 4 hours 1.10 g DDM were added. The mixture was stirred for 2 h, cooled to room temperature and purified by pressure filtration. After filtration, a clear and slightly yellow colored highly viscous liquid was obtained which was applied without further purification.

Synthesis 3: General synthesis of polyalkyl acrylates using the novel acrylate process

- 0.85 g (0.5% by weight, based on the amount of EHA) of dicumylperoxide dissolved in 170.0 g of EHA was fed to 26.77 g of NB3080 under nitrogen at 150°C over 3 hours. Optionally, after this time, the temperature of the mixture was lowered to 110°C and 0.17 g of *tert*-butylper-2-ethylhexanoate (0.1% by weight, based on the amount of EHA) dissolved in 3.23 g of NB3080 was added. After stirring for another hour, the resulting clear polymer solution was cooled down and used in subsequent experiments without further purification.

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Synthesis 4: General synthesis of polyalkyl methacrylates

- A round-bottom flask equipped with a glass stir rod, nitrogen inlet, reflux condenser and thermometer was charged with 284.4 g EHMA and 8.9 g DDM. 0.75 g *tert*-butylper-2-ethylhexanoate and 15.0 g EHMA were added within 3 hours at 110°C under nitrogen bubbling. After holding the temperature for 1 hour, 0.6 g *tert*-butylper-2-ethylhexanoate were added. After waiting for another hour, a final shot of 0.6 g *tert*-butylper-2-ethylhexanoate was added and the

solution as stirred at 110°C for one hour. The resulting clear and highly viscous liquid was used without further purification.

Table 1: Initiators used in the different syntheses.

Initiator	Name
A	<i>tert</i> -butylper-2-ethylhexanoate
B	dicumylperoxide
C	dicetyl peroxydicarbonate
D	<i>tert</i> -butylperbenzoate
E	1,1-di- <i>tert</i> -butylperoxy-3,3,5-trimethyl cyclohexane

5

All initiators are commercially available. Diacetyl peroxydicarbonate is commercially available from AkzoNobel.

The compositions of reaction mixtures used to prepare the working examples and comparative examples are shown in the following Table 2. The amounts of monomer and base oil do always add up to 100%. The amounts of initiator and DDM are given relative to the total amount of monomer.

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Table 2: Compositions of reaction mixtures used to prepare the working examples and comparative examples.

Example #	Monomer	Base Oil	Initiator					DDM [%]
			A [%]	B [%]	C [%]	D [%]	E [%]	
1	EHA	NB3080	0.25	--	--	--	--	3.00
2	EHA	NB3080	0.25	--	--	--	--	1.90
3	EHA	NB3080	0.50	--	--	--	--	1.90
4	EHA	NB3080	--	--	--	--	--	--
5	EHA	NB3080	1.00	--	--	--	--	--
6	EHA	NB3080	--	1.25	--	--	--	--
7	EHA	NB3080	--	--	2.64	--	--	--
8	EHA	NB3080	--	0.90	--	--	--	--
9	EHA	NB3080	--	0.90	--	--	--	--
10	EHA	NB3080	--	0.90	--	--	--	--
11	EHA	NB3080	--	0.90	--	--	--	--
12	EHA	NB3080	--	0.90	--	--	--	--
13	EHA	NB3080	--	0.90	--	--	--	--
14	EHA	NB3080	--	0.50	--	--	--	--
15	EHA	NB3080	--	0.90	--	--	--	--
16	EHA	NB3080	--	0.90	--	--	--	--
17	EHA	NB3080	--	0.50	--	--	--	--
18	EHA	NB3080	--	0.30	--	--	--	--
19	EHA	NB3080	--	0.20	--	--	--	--
20	EHA	NB3080	--	0.05	--	--	--	--
21	EHA	NB3080	--	0.50	--	--	--	--
22	HA	NB3080	--	0.50	--	--	--	--
23	IDA	NB3080	--	0.50	--	--	--	--
24	LA	NB3080	--	0.50	--	--	--	--
25	HA	NB3080	--	0.50	--	--	--	--
26	ITDA	NB3080	--	0.50	--	--	--	--
27	EHA	C600R	--	0.50	--	--	--	--
28	EHA	C600R	--	0.50	--	--	--	--
29	EHA	C600R	--	0.50	--	--	--	--
30	EHA	C600R	--	0.10	--	--	--	--
31	EHA	C600R	--	0.20	--	--	--	--
32	EHA	C600R	--	0.30	--	--	--	--
33	EHA	C600R	--	0.40	--	--	--	--
34	EHA	Yubase 6	--	0.50	--	--	--	--
35	EHA	PAO 8	--	0.50	--	--	--	--
36	EHA	PAO 8	--	0.50	--	--	--	--
37	PHA	PAO 8	--	0.50	--	--	--	--
38	PHA	PAO 8	--	0.50	--	--	--	--
39	PHA	PAO 8	--	0.20	--	--	--	--
40	PHA	PAO 8	--	0.10	--	--	--	--
41	EHA	PAO 8	--	0.50	--	--	--	--
42	EHA	PAO 8	--	0.90	--	--	--	--
43	EHA	PAO 8	--	1.30	--	--	--	--
44	EHA	PAO 8	--	--	--	0.50	--	--
45	EHA	PAO 8	--	--	--	--	0.50	--
46	EHMA	--	0.25	--	--	--	--	2.95

Conclusions:

- 5 Examples 1 to 4 were prepared according to known processes. Although temperature control and economics were poor, the targeted polymers could be prepared. Examples 1 to 4 are encompassed by claim 1 of the present invention and show good performance as base oils in

lubricant compositions (see results presented further down in Table 5). Aside from this, Examples 1 to 3 contain a substantial amount of sulphur which is considered to be detrimental to the compatibility with certain metals and rubber seals. Examples 1 to 3 do further contain high residual monomer contents (see Table 4 further down).

- 5 Example 4 is produced by ATRP which is very challenging in commercial production as lubricants require a product free of contaminants. Removal of the process chemicals from the highly viscous product has proven to be very time-consuming, even on lab-scale.

- 10 To obtain control over temperature, a monomer feed process was used. Attempts to adjust the molecular weight of the polymers to the targeted range below 25,000 g/mol using sulfur-containing chain transfer agents yielded no satisfying residual monomer levels.

- 15 Aside from this, the required amounts of chain transfer agent to be used in this process was quite significant, leading to unwanted high sulfur levels in the product (Examples 1 to 3; 1.90 and 3.00% of DDM are used, respectively). Despite their positive effects on oxidation and wear performance, sulfur components are known to cause problems with yellow metals and rubber sealings (see L. R. Rudnick, Lubricant Additives: Chemistry and Applications, 3rd Edition, 2017, p.197ff).

- 20 Examples 5, 7, 20, 22, 30, 44 and 45 are comparative examples as the molecular weight M_w is outside the claimed range of 7000 to 25,000 g/mol.

Examples 6, 8-19, 21, 23, 27-29 and 31-43 are in accordance with the present invention.

- 25 Examples 22, 24-26 and 46 are comparative examples as they are prepared from monomers that are not encompassed by claim 1.

The following Table 3 provides details regarding the preparation method used to synthesize working examples and comparative examples.

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Table 3: Process details.

Example #	Process	Feed Time [h]	Temperature [°C]	Concentration [%]
1	Synthesis 1	2	110	80
2	Synthesis 1	5	110	60
3	Synthesis 1	5	110	60
4	Synthesis 2	--	--	50
5*)	Synthesis 3	4	110	60
6	Synthesis 3	4	160	60
7*)	Synthesis 3	4	84	60
8	Synthesis 3	4	160	60
9	Synthesis 3	4	160	80
10	Synthesis 3	4	160	85
11	Synthesis 3	3	160	85
12	Synthesis 3	3	150	85
13	Synthesis 3	3	150	85
14	Synthesis 3	3	150	90
15	Synthesis 3	3	150	90
16	Synthesis 3	3	150	85
17	Synthesis 3	2	150	85
18	Synthesis 3	3	150	85
19	Synthesis 3	3	150	85
20*)	Synthesis 3	3	150	85
21	Synthesis 3	3	150	85
22*)	Synthesis 3	3	150	85
23	Synthesis 3	3	150	75
24*)	Synthesis 3	3	150	70
25*)	Synthesis 3	3	150	50
26*)	Synthesis 3	3	150	75
27	Synthesis 3	3	150	85
28	Synthesis 3	3	150	80
29	Synthesis 3	3	150	90
30*)	Synthesis 3	3	150	80
31	Synthesis 3	3	150	90
32	Synthesis 3	3	150	90
33	Synthesis 3	3	150	90
34	Synthesis 3	3	150	85
35	Synthesis 3	3	150	85
36	Synthesis 3	3	150	85
37	Synthesis 3	3	150	85
38	Synthesis 3	3	150	80
39	Synthesis 3	3	150	90
40	Synthesis 3	3	150	90
41	Synthesis 3	3	150	80
42	Synthesis 3	3	150	85
43	Synthesis 3	3	150	85
44*)	Synthesis 3	3	140	85
45*)	Synthesis 3	3	125	85
46*)	Synthesis 4	3	110	100

*) comparative example

First attempts to prepare the targeted polyacrylates in a batch process similar to poly(EHMA)

5 (Synthesis 4, Example 46) failed due to poor temperature control. Good results were obtained by

using the ATRP process (Synthesis 2, Example 4), but due to the poor economics a new process had to be developed.

5 A novel feed process without chain transfer agent was developed which provided polymers with very low residual monomer content (Synthesis 3). Low molecular weights are accessible with good conversion and narrow molecular weight distributions. The process works well, especially at elevated temperatures which are beneficial for reaching high temperatures and good conversions (see e.g. Examples 5, 6, 7, 41, 44 and 45).

10 Aside from temperature that needs to be adjusted to the respective initiator system, the molecular weight can be controlled by several measures. Surprisingly low is the influence of the amount of initiator. Very small amounts of initiator result in an increase of the molecular weight, but around 0.5 wt.% variations of the initiator content result in insignificant changes in the molecular weight (Examples 16-20, 29, 31, 32, 33, 42 and 43).

15 Feed times have also just minor influence in a reasonable window of 2-4 hours (see Examples 10, 11, 17 and 21).

The molecular weight can be also influenced by the amount of base oil in the heel at the beginning of the reaction (see Examples 8-10, 22, 25 and 27-29).

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The characteristics of the polyalkyl acrylates prepared in the course of the present invention are disclosed in the following Table 4.

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Table 4: Characteristics of the polyalkyl acrylates prepared according to the present invention.

Example #	M _w [g/mol]	M _n [g/mol]	PDI	ReMo [%]	BV40 [mm ² /s]	BV100 [mm ² /s]	VI
1 ^{*)}	13,000	7,060	1.84	0.24	1141	104.4	185
2 ^{*)}	16,500	8,440	1.95	0.54	499	54.4	175
3 ^{*)}	15,600	8,010	1.95	0.49	480	52.4	173
4 ^{*)}	14,400	8,460	1.70	0.01	323	38.3	165
5 ^{*)}	34,400	11,300	3.04	0.05	1076	108.1	197
6	7,590	4,730	1.60	0.04	294	31.9	149
7 ^{*)}	52,200	15,700	3.32	0.18	1472	148.6	214
8	7,130	4,650	1.53	0.03	287	30.8	147
9	10,500	5,560	1.89	0.01	983	85.4	170
10	12,600	5,960	2.11	0.01	1577	126.3	180
11	11,600	5,750	2.02	0.02	1329	108.6	175
12	16,700	7,060	2.37	0.01	2191	172.1	194
13	13,900	6,430	2.16	<0.01	1798	144.5	187
14	18,600	7,400	2.51	<0.01	3457	252.7	208
15	18,700	7,270	2.57	0.09	3348	244.9	206
16	15,100	6,720	2.25	0.01	1936	153.7	189
17	15,200	7,030	2.16	<0.01	2078	162.0	190
18	16,100	7,240	2.22	0.01	2155	170.0	194
19	17,200	7,500	2.29	0.03	2311	183.0	198
20 ^{*)}	30,900	10,300	3.00	0.03	4360	339.2	231
21	15,200	7,190	2.11	0.06	2131	168.6	194
22 ^{*)}	53,600	11,800	4.54	0.10	3446	318.3	247
23	15,400	7,490	2.06	--	975	82.9	166
24 ^{*)}	15,600	8,530	1.83	--	314	43.0	192
25 ^{*)}	14,800	7,570	1.96	--	61	9.6	138
26 ^{*)}	14,700	7,270	2.02	--	1320	95.9	157
27	16,300	7,470	2.18	0.02	2723	203.8	198
28	13,700	6,930	1.98	0.06	1872	138.2	176
29	18,800	7,670	2.45	0.05	4441	305.1	212
30 ^{*)}	25,100	9,830	2.55	--	6444	434.1	231
31	23,300	9,320	2.50	--	--	--	--
32	20,600	8,640	2.38	--	--	--	--
33	20,800	8,900	2.34	--	--	--	--
34	16,100	7,270	2.21	0.02	2165	172.0	195
35	18,600	8,380	2.22	<0.01	2771	216.1	206
36	17,300	8,060	2.15	0.04	2537	200.4	203
37	14,100	7,270	1.94	<0.01	1671	145.8	197
38	11,500	6,560	1.75	0.09	1016	90.6	175
39	15,400	7,770	1.98	0.05	2556	201.0	203
40	17,800	8,800	2.02	--	--	--	--
41	14,900	7,600	1.96	0.04	1645	138.0	190
42	20,200	8,530	2.37	--	--	229.0	--
43	20,200	8,190	2.47	--	2704	221.8	213
44	30,900	10,200	3.03	<0.01	4587	345.7	229
45 ^{*)}	96,700	16,400	5.90	<0.01	13648	993.3	290
46 ^{*)}	14,800	7,990	1.85	--	--	--	--

^{*)} comparative example

It can be seen that all polymers prepared by Synthesis 3 have residual monomer contents of 0.1% or even well below. All working examples which are in accordance with the present invention have bulk viscosities (BV40) well above 320 mm²/s, i.e. can be easily formulated to ISO viscosity grade 320.

- 5 It is further visible that polymers having a weight-average molecular weight of around 7,000 g/mol show borderline bulk viscosities at 40°C (see Examples 6 and 8), i.e. they can only be formulated to an ISO viscosity grade of 220 or below.

- 10 Different acrylate monomers were used to generate homopolymers for the evaluation as high viscosity base fluids. Hexyl acrylate has proven to be completely unsuitable as the bulk viscosity of the synthesized polymers was too low to be of any use (Example 25). Even with a massive boost in molecular weight, high treat rate and the expected lack of shear stability are so poor that no further investigation was done (Example 22).

15 **Lubricating Compositions**

- To proof the performance of the acrylate polymers prepared in accordance with the present invention, lubricating compositions were prepared by using the acrylate polymers as a base fluid and mixing them together with other base oil(s) to reach ISO viscosity grades of 220 and 320. The results for typical formulation parameters like KV100, VI, PP and Brookfield viscosity are
20 presented in the following Tables 5 to 9.

- While acrylates and methacrylates are often regarded interchangeable in the field of VI improvers, the results presented in the present invention clearly show a difference when using them as high viscosity base stocks. While the EHMA homopolymer (Example 46) showed very poor miscibility
25 with Nexbase 3080 (an API Group III oil), and phase separation was observed, no such issues were found for EHA homopolymers in any of the used solvents and concentrations.

- Poly(lauryl acrylate, LA) (Example 24) showed poor performance in treat rate and low temperature properties in a fully formulated ISO 320 formulation. Poly(isodecylacrylate) (Example 23) and
30 poly(isotridecylacrylate) (Example 26) both showed insufficient performance at low temperatures compared to poly(EHA).

- Improved low temperature performance was observed for poly(propylheptylacrylate) (Examples 37-40) at the cost of a slightly increased treat rate compared to poly(EHA).
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- Due to the high conversion of the monomers and as no other volatile components are used in the process such as chain transfer agents, the flashpoints of the acrylate polymers are very high. Data are given for Example 27 and the measured flashpoint (COC method ASTM D92) was the same as specified for the dilution oil Chevron 600R used in the process (Example 27).
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For the use of Example 30, precipitation was observed in an ISO 220 formulation in API Group III base oil. As this was not observed for other samples at lower molecular weight, it can be concluded that the in all other experiments observed perfect oil compatibility even in extremely poor solvency base oils is limited to molecular weights below 25,000 g/mol for EHA homopolymers.

Table 5: Formulation data of compositions **A** formulated to ISO 320 ($KV_{40} = 320 \pm 10\%$)

Composition	A-1	A-2	A-3	A-4	A-5	A-6	A-7	A-8	A-9
Example 1 [%]	65.70	--	--	--	--	--	--	--	--
Example 2 [%]	--	80.90	--	--	--	--	--	--	--
Example 3 [%]	--	--	81.80	--	--	--	--	--	--
Example 4 [%]	--	--	--	46.9	--	--	--	--	--
Example 9 [%]	--	--	--	--	69.00	--	--	--	--
Example 10 [%]	--	--	--	--	--	63.00	--	--	--
Example 12 [%]	--	--	--	--	--	--	58.00	--	--
Example 13 [%]	--	--	--	--	--	--	--	60.20	--
Example 21 [%]									58.00
Viscoplex 1-180 [%]	0.70	0.70	0.70	0.70	0.70	0.70	0.70	0.70	0.70
Hitec 307 [%]	2.65	2.65	2.65	2.65	2.65	2.65	2.65	2.65	2.65
NB3080 [%]	30.95	15.75	14.85	49.75	27.65	33.65	38.65	36.45	38.65
Blend Total [%]	100.0	100.0	100.00	100.00	100.00	100.00	100.00	100.00	100.00
Polymer content [%]	52.6	48.5	49.1	46.9	55.2	53.55	49.3	51.8	49.3
KV_{40} [mm ² /s]	326.1	322.9	319.4	317.8	321.2	322.2	322.0	320.9	317.1

Composition	A-1	A-2	A-3	A-4	A-5	A-6	A-7	A-8	A-9
KV ₁₀₀ [mm ² /s]	37.45	37.71	37.03	36.73	35.27	35.71	36.65	36.07	36.21
VI	164	167	165	164	156	157	162	159	162
KV ₁₀ [mm ² /s]	14,020	14,270	14,618		14,828	14,913	14,661	14,713	
Brookfield (Air)	184,000	510,000	244,000		140,000	152,000	216,000	160,000	
[mPas]	188,000	498,000	240,000		140,000	152,000	200,000	152,000	
PP	-33	-36	-30		-39	-33	-36	-33	
[°C]									
KRL @20 hours									
KV ₄₀ [mm ² /s]	320.5	314.7							317.5
KV ₁₀₀ [mm ² /s]	36.78	36.74							35.93
shear loss @100°C [%]	1.8	2.6							0.8
RL 209 reference oil value [%]	9.9	9.9							10.2

Table 6: Formulation data of compositions **A** formulated to ISO 320 ($KV_{40} = 320 \pm 10\%$)

Composition	A-10	A-11	A-12	A-13	A-14	A-15	A-16	A-17
Example 23 [%]	67.50	--	--	--	--	--	--	--
Example 24 [%]	--	96.65	--	--	--	--	--	--
Example 26 [%]	--	--	62.00	--	--	--	--	--
Example 35 [%]	--	--	--	54.70	--	--	--	--
Example 36 [%]	--	--	--	--	56.00	--	--	--
Example 37 [%]	--	--	--	--	--	62.40	--	--
Example 41 [%]	--	--	--	--	--	--	61.20	--
Example 46 [%]								30.55
Viscoplex 1-180 [%]	0.70	0.70	0.70	--	--	--	--	0.70
Hitec 307 [%]	2.65	2.65	2.65	2.65	2.65	2.65	2.65	2.65
NB3080 [%]	29.15	--	34.65	--	--	--	--	66.10
PAO 8 [%]	--	--	--	42.65	41.35	34.95	36.15	--
Blend Total [%]	100.0	100.00	100.00	100.00	100.00	100.00	100.00	100.00
Polymer content [%]	50.63	67.66	46.50	46.50	47.60	53.04	48.96	30.55
KV₄₀ [mm ² /s]	314.5	315.5	313.6	325.3	325.1	328.1	323.2	309.8
KV₁₀₀ [mm ² /s]	35.20	42.94	33.06	38.02	37.86	38.13	37.09	31.54

Composition	A-10	A-11	A-12	A-13	A-14	A-15	A-16	A-17
VI	158	193	147	167	166	166	163	141
KV ₋₁₀ [mm ² /s]	15,695	solid	16,180					solid
Brookfield (Air) [mPas]	220,000	solid	200,000	108,000	94,000	82,000	110,000	solid
	216,000	solid	212,000	112,000	96,000	81,000	106,000	solid
PP [°C]	-39	-6	-36	-36	-39	-45	-36	???
KRL @20 hours								
KV ₄₀ [mm ² /s]				315.3	317.0	324.5	311.0	
KV ₁₀₀ [mm ² /s]				36.86	36.79	37.69	35.76	
shear loss @100°C [%]				3.1	2.8	1.2	3.6	
RL 209 reference oil value [%]				9.7	9.7	9.7	8.3	

Table 7: Formulation data of compositions **A** formulated to ISO 320 ($KV_{40} = 320 \pm 10\%$)

Composition	A-18	A-19	A-20	A-21	A-22	A-23	A-24	A-25	A-26	A-27
Example 34 [%]	57.80	61.00	62.70	--	--	--	--	--	--	--
Example 27 [%]	--	--	--	42.0	--	--	--	--	--	--
Example 35 [%]	--	--	--	--	54.70	--	--	--	--	--
Example 36 [%]	--	--	--	--	--	56.00	--	--	--	--
Example 37 [%]	--	--	--	--	--	--	62.40	--	--	--
Example 39 [%]	--	--	--	--	--	--	--	57.60	--	--
Example 40 [%]	--	--	--	--	--	--	--	--	54.70	--
Example 41 [%]	--	--	--	--	--	--	--	--	--	61.20
Viscomplex 1-180 [%]	0.70	0.70	--	0.80	--	--	--	--	--	--
Hitec 307 [%]	2.65	2.65	2.65	2.65	2.65	2.65	2.65	2.65	2.65	2.65
Chevron 600R [%]	--	--	--	54.50	--	--	--	--	--	--
NB3080 [%]	38.85	--	--	--	--	--	--	--	--	--
Yubase 6 [%]	--	35.65	--	--	--	--	--	--	--	--
PAO 6 [%]	--	--	34.65	--	--	--	--	--	--	--
PAO 8 [%]	--	--	--	--	42.65	41.35	34.95	39.75	42.65	36.15
Blend Total [%]	100.0	100.0	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00

Composition	A-18	A-19	A-20	A-21	A-22	A-23	A-24	A-25	A-26	A-27
Polymer content [%]	49.13	51.85	53.30	35.70	46.50	47.60	53.04	51.84	49.23	48.96
top treat Viscoplex 14-520 [ppm]	2000	2000	2000	--	--	--	--	--	--	--
KV ₄₀ [mm ² /s]	324.7	324.6	322.7	319.2	325.3	325.1	328.1	323.7	317.0	323.2
KV ₁₀₀ [mm ² /s]	37.37	37.89	38.31	32.37	38.02	37.86	38.13	38.06	38.05	37.09
VI	164	167	169	142	167	166	166	168	170	163
Brookfield (Air) [mPas]		128,000	95,000	143,970	108,000	94,000	82,000	80,000	74,000	110,000
		130,000	96,000		112,000	96,000	81,000	80,000	72,000	106,000
PP [°C]	-36	-36	-39	-33	-36	-39	-45	-48	-45	-36
KRL @20 hours										
KV ₄₀ [mm ² /s]	310.8	309.6	313.3	309.3	315.3	317.0	324.5			311.0
KV ₁₀₀ [mm ² /s]	35.69	36.13	37.21	31.69	36.86	36.79	37.69			35.76
shear loss @100°C [%]	4.5	4.6	2.9	2.1	3.1	2.8	1.2			3.6
RL 209 reference oil value [%]	10.1	10.1	10.1		9.7	9.7	9.7			8.3
water content Karl Fischer [%]	0.02	0.02	0.02							
flash point [°C]	238	232	234							

For ISO 320 formulations, the data disclosed in Tables 5 to 6 show that for EHA and PHA polymers the required polymer content is 40 to 60% by weight. The polymers in accordance with the present invention show good solubility in the used base oils (i.e. Group III and IV oils as well as mixtures thereof) at all temperatures down to the PP (pour point) of the formulation.

- 5 The polymers of the present invention further show good low temperature behavior (see KV₋₁₀ and BF₋₂₆ values) and pour points what is remarkable for polymers having such high polarities. The formulations comprising the polymers of the present invention have high VIs of around 160. This means that the KV₁₀₀ of the formulations is higher than the KV₁₀₀ of a regular mineral oil-based ISO 460 formulation. This allows the combination of high protection of the equipment and good flow
- 10 properties at low temperatures.

- Formulation A17 provides the surprising result that the EHMA polymer is different to the EHA polymers; the EHMA polymer is not compatible with the base oils at low temperatures even though the treat rate is substantially lower. Such a difference between acrylates and methacrylates has not
- 15 been reported before as oil soluble VI improvers are not pushed that hard to the solubility limits. The combination of high treat rates and a rather thick apolar base oil with poor solvency is a special case not covered by the state of the art so far.

- When comparing different acrylate homopolymers, poly-LA (A-11) is obviously unsuitable as the
- 20 formulation becomes solid at temperatures above -10°C. While poly-IDA performs only slightly inferior in terms of VI and low-temperature properties compared to EHA and PHA polymers the gap is larger for poly-ITDA. Also, the polarity of poly-ITDA is lower which does not make it a promising candidate compared to the other options.

25 Table 8: Foam test

Composition		A-18	A-19	A-20
sequence I	Foam after Blowing Period @24°C [mL]	0	0	0
sequence I	Foam after 10 min @24°C [mL]	0	0	0
sequence I	Collapse time @24°C [s]	0	0	0
sequence II	Foam after Blowing Period @94°C [mL]	210	40	50
sequence II	Foam after 10 min @94°C [mL]	0	0	0
sequence II	Collapse time @94°C [s]	334	129	134
sequence III	Foam after Blowing Period @24°C [mL]	0	0	0
sequence III	Foam after 10 min @24°C [mL]	0	0	0
sequence III	Collapse time @24°C [s]	0	0	0

Due to the high polarity of some of the polymer blocks an impact on performance tests involving interfaces was expected. For the air release and foam tests no strong effect was observed. Filtration of the fluid is no problem at all which confirms the visual observation that the polymer and the additives are completely dissolved in the oil phase.

Table 9: Formulation data of compositions **B** formulated to ISO 220 ($KV_{40} = 220 \pm 10\%$)

Composition	B-1	B-2	B-3	B-4	B-5	B-6
Example 28 [%]	35.00	--	--	--	--	--
Example 29 [%]	--	28.00	--	--	--	--
Example 30 [%]	--	--	25.00	--	--	--
Example 32 [%]	--	--	--	27.10	--	--
Example 33 [%]	--	--	--	--	27.10	--
Example 31 [%]	--	--	--	--	--	--
Hitec 307 [%]	2.65	2.65	2.65	2.65	2.65	2.65
Chevron 600R [%]	62.35	69.35	72.35	70.25	70.25	--
Blend Total [%]	100.0	100.0	100.00	100.00	100.00	100.00
Polymer content [%]	28.00	25.20	20.00	24.39	24.39	--
KV₄₀ [mm ² /s]	218.7	217.9	219.8	220.9	219.8	--
KV₁₀₀ [mm ² /s]	23.51	23.67	24.14	24.00	23.93	--
VI	133	134	137	135	136	--
KRL @20 hours						
KV₄₀ [mm ² /s]	216.5	209.2				
KV₁₀₀ [mm ² /s]	23.23	22.80				
shear loss @100°C [%]	1.2	3.7				
RL 209 shear loss @100°C [%]	10.1	10.1				

- 10 For ISO 220 formulations, the data disclosed in Table 9 show that the required minimum polymer content is about 20% by weight. The polymers in accordance with the present invention show good solubility in the used base oils (i.e. Group III and IV oils as well as mixtures thereof) at all temperatures down to the pour point of the formulation. The resulting formulations have high VIs of around 130.

15

Different to the previously described formulations, the ISO220 formulations in Table 9 are more focused on formulation cost optimization rather than performance. For this reason, the treat rate of the acrylate polymers was minimized by choosing the lower viscosity grade and a Group II base fluid. The Group II base fluid does not only offer an economic advantage due to the simpler refinery process, it also has a higher viscosity than Group III and IV base fluids used in the previous examples which allows the reduction of the polymer treat rate below 30% by weight while maintaining excellent shear stability.

At such low treat rates, the positive influence on the VI is less pronounced, but still quite substantial. Not visible in the provided data, but apparent during formulation and investigation of the formulations is that the function of the inventive polymers as compatibilizer between additives and apolar base oils is in no way impaired at the reduced treat rates. Taking into account that an addition of 10% by weight of a polar low viscosity base stock with strong dissolving power is not uncommon in industrial gear oils based on apolar base stocks, this is an excellent result for the polyacrylates.

Claims

1. Use of polyalkyl acrylates, comprising:
 - (a) 95 to 100% by weight of branched C₈₋₁₀-alkyl acrylates; and
 - (b) 0 to 5% by weight of C₁₋₂₀-alkyl (meth)acrylates,characterized in that the weight-average molecular weight is in the range of 7,000 to 25,000 g/mol and the residual monomer content is 0.1% or lower,
as base oils in lubricant formulations, especially in industrial gear oil formulations.
2. The use according to claim 1, characterized in that the polyalkyl acrylates consist of 100% by weight of branched C₈₋₁₀-alkyl acrylates.
3. The use according to claim 1 or 2, characterized in that the C₈₋₁₀-alkyl acrylate is selected from the group consisting of 2-ethylhexyl acrylate and 2-propylheptyl acrylate.
4. Base oil composition, comprising:
 - (A) 70 to 95% by weight of at least one polyalkyl acrylate, comprising:
 - (a) 95 to 100% by weight of branched C₈₋₁₀-alkyl acrylates; and
 - (b) 0 to 5% by weight of C₁₋₂₀-alkyl (meth)acrylates,characterized in that the weight-average molecular weight is in the range of 7,000 to 25,000 g/mol and the residual monomer content is 0.1% or lower; and
 - (B) 5 to 30% by weight of a base oil selected from the group consisting of API Group II oils, API Group III oils, API Group IV oils, and mixtures thereof,based on the total weight of the base oil composition.
5. Base oil composition according to claim 4, characterized in that the polyalkyl acrylate (A) consists of 100% by weight of branched C₈₋₁₀-alkyl acrylates.
6. Base oil composition according to claim 4 or 5, characterized in that the C₈₋₁₀-alkyl acrylate is selected from the group consisting of 2-ethylhexyl acrylate and 2-propylheptyl acrylate.
7. Base oil composition according to claim 4 or 5, characterized in that the C₈₋₁₀-alkyl acrylate is ethylhexyl acrylate.
8. Use of a base oil composition according to any one of the preceding claims as industrial gear oil.
9. Polyalkyl acrylates, comprising:
 - (a) 95 to 100% by weight of branched C₈₋₁₀-alkyl acrylates; and
 - (b) 0 to 5% by weight of C₁₋₂₀-alkyl (meth)acrylates,

characterized in that the weight-average molecular weight is in the range of 7,000 to 25,000 g/mol and the residual monomer content is 0.1% by weight or lower.

10. Polyalkyl acrylates according to claim 9, consisting of 100% by weight of branched
5 C₈₋₁₀-alkyl acrylates.
11. Polyalkyl acrylates according to claim 9 or 10, characterized in that the C₈₋₁₀-alkyl acrylate is selected from the group consisting of 2-ethylhexyl acrylate and 2-propylheptyl acrylate.
- 10 12. Polyalkyl acrylates according to claim 9 or 10, characterized in that the C₈₋₁₀-alkyl acrylate is ethylhexyl acrylate.
13. Lubricating composition, comprising:
(A) 20 to 60% by weight of at least one polyalkyl acrylate, comprising:
15 (a) 95 to 100% by weight of branched C₈₋₁₀-alkyl acrylates; and
(b) 0 to 5% by weight of C₁₋₂₀-alkyl (meth)acrylates,
based on the total weight of the polyalkyl acrylate,
characterized in that the weight-average molecular weight is in the range of 7,000
to 25,000 g/mol and the residual monomer content is 0.1% by weight or lower;
20 (B) 40 to 80% by weight of a base oil selected from the group consisting of API Group
II oils, API Group III oils, API Group IV oils, and mixtures thereof; and
(C) 0 to 5% by weight of one or more additives,
based on the total weight of the lubricating composition.
- 25 14. Lubricating composition according to claim 8, characterized in that the one or more further
additives (C) are selected from the group consisting of pour point depressants, dispersants,
defoamers, detergents, demulsifiers, antioxidants, antiwear additives, extreme pressure additives,
friction modifiers, anticorrosion additives, dyes and mixtures thereof.
- 30 15. Process for preparing polyalkyl acrylates, comprising:
(a) 95 to 100% by weight of branched C₈₋₁₀-alkyl acrylates; and
(b) 0 to 5% by weight of C₁₋₂₀-alkyl (meth)acrylates,
characterized in that the weight-average molecular weight is in the range of 7,000
to 25,000 g/mol and the residual monomer content is 0.1% by weight or lower, the
35 process comprising the steps of:
(i) charging a reaction vessel with a base oil;
(ii) heating the base oil of step (i) to a reaction temperature of 130°C to 170°C;
(iii) constantly feeding a mixture of branched C₈₋₁₀-alkyl acrylates and 0.1 to 1.2% of an
initiator, based on the amount of branched C₈₋₁₀-alkyl acrylates, to the reaction
40 vessel over a time of 120 to 240 minutes;

- (iv) optionally stirring the reaction mixture obtained under step (iii) for another 50 to 90 minutes; and
- (vi) cooling the reaction mixture obtained under step (iv) to an ambient temperature and obtaining the desired polyalkyl acrylate.