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(54) **THE USE OF ISOSTEARIC ACID ESTERS AS LUBRICANTS**

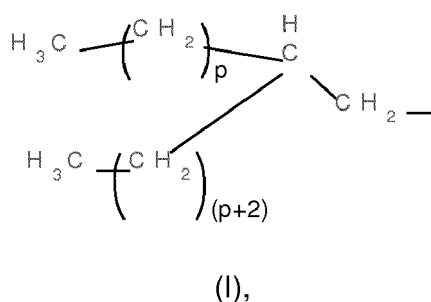
(57) The presently claimed invention is directed to the preparation of esters obtainable from reacting a mixture of acids comprising at least 70 weight-% of mono-branched or poly-branched, saturated C₁₆-C₂₂ fatty

acids with Guerbet alcohols, lubricant compositions thereof and the use of these esters obtained from Guerbet alcohols for improving seal compatibility of lubricants.

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[0013] The presently claimed invention is directed to a carboxylic acid ester obtainable by reacting a mixture comprising

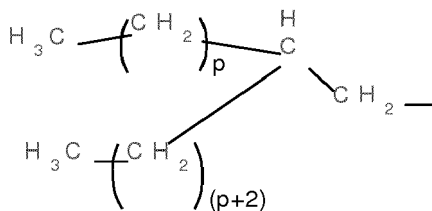
- a) a mixture of acids comprising at least 70 weight-% of mono-branched or poly-branched, saturated C₁₆-C₂₂ fatty acids, based on the total weight of fatty acids, , and
- b) a mixture of alcohols according to the formula R-OH, wherein R is a mixture of different radicals in which at least 65 weight-% of the radicals have the general formula (I).



wherein p is 0, 1, 2, 3 or 4, more preferably 0, 1 or 2 and even more preferably 2.

[0014] Preferably the mixture of acids comprises mono-branched or poly-branched, saturated C₁₆-C₂₂ fatty acids in the range of 70 weight-% to 95 weight-%, more preferably in the range of 73 weight-% to 90 weight-% and most preferably in the range of 77 weight-% to 85 weight-%, based on the total weight of fatty acids.

[0015] In another preferred embodiment of the presently claimed invention, the carboxylic acid ester is characterized in that at least 80 weight-% of the radicals have the general formula (I),



(1),

wherein p is 0, 1, 2, 3 or 4, more preferably 0, 1, 2, or even more preferably 2.

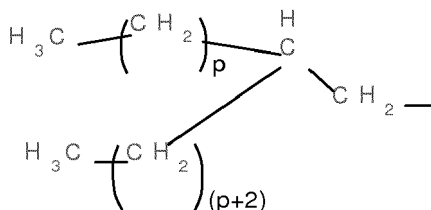
[0016] In another preferred embodiment of the presently claimed invention, the carboxylic acid ester is characterized in that the mixture of acids comprises mono-branched or poly-branched, saturated C₁₆-C₂₂ fatty acids in the range of 70 weight-% to 95 weight-%, more preferably in the range of 73 weight-% to 90 weight-% and most preferably in the range of 77 weight-% to 85 weight-% which are at least partially derived from a renewable source.

[0017] The mono-branched or poly-branched, saturated C₁₆-C₂₂ fatty acids comprise alkyl side branches which are directly attached to a carbon atom of the longest linear chain and have on average less than 3, more preferably less than 2.5, particularly in the range from 1.05 to 2, and especially 1.1 to 1.4 carbon atoms, i.e. the side branches are predominantly methyl groups. In a preferred embodiment of the presently claimed invention, greater than 50%, more preferably greater than 60%, particularly in the range from 70 to 97%, and especially 80 to 93% by number of the side-branched groups are methyl groups. In a further preferred embodiment, greater than 30%, more preferably greater than 40%, particularly in the range from 45 to 90%, and especially 50 to 80% by number of the mono-branched or poly-branched, saturated C₁₆-C₂₂ fatty acids contain single methyl side branches. The presently claimed invention is also directed to a lubricant composition comprising the carboxylic acid ester of the presently claimed invention.

[0018] In a preferred embodiment, the presently claimed invention is directed to a carboxylic acid ester obtainable by reacting a mixture comprising

a) a mixture of acids comprising mono-branched or poly-branched, saturated C₁₆-C₂₂ fatty acids in the range of 70 weight-% to 95 weight-%, and

b) a mixture of alcohols according to the formula R-OH, wherein R is a mixture of different radicals in which at least 80 weight-% of the radicals have the general formula (I),



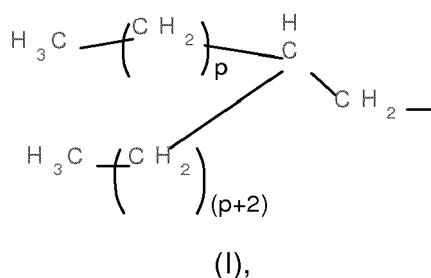
(1),

wherein p is 2.

[0019] In another preferred embodiment, the presently claimed invention is directed to a carboxylic acid ester obtainable by reacting a mixture comprising

a) a mixture of acids comprising mono-branched or poly-branched, saturated C₁₆-C₂₂ fatty acids in the range of 70 weight-% to 95 weight-%, and

b) a mixture of alcohols according to the formula R-OH, wherein R is a mixture of different radicals in which at least 80 weight-% of the radicals have the general formula (I),

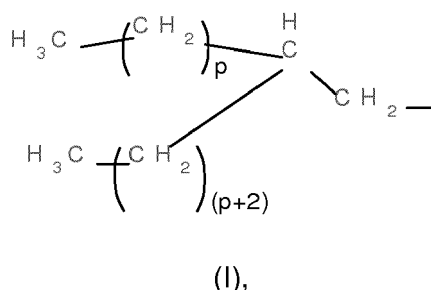


wherein p is 1.

[0020] In another preferred embodiment of the presently claimed invention, the lubricant composition is characterized in that it further includes a base oil component and at least one additive.

[0021] The presently claimed invention is also directed to a process for preparing the carboxylic acid ester of the presently claimed invention, comprising the steps of

- providing a mixture of acids comprising at least 70 weight-% of mono-branched or poly-branched, saturated C₁₆-C₂₂ fatty acids from a non-renewable source and/or a renewable source,
- preparing a mixture of the mixture of acids comprising at least 70 weight-% of mono-branched or poly-branched, saturated C₁₆-C₂₂ fatty acids and a mixture of alcohols R-OH, wherein in the mixture of alcohols R-OH, at least 65 weight-% of the radicals R have the general formula (I),



wherein p is 0, 1, 2, 3 or 4; more preferably 0, 1, or 2, even more preferably 2;

- carrying out esterification of the mixture of acids comprising at least 70 weight-% of mono-branched or poly-branched, saturated C₁₆-C₂₂ fatty acids and the mixture of alcohols R-OH.

[0022] The presently claimed invention is also directed to the use of the lubricant composition of the presently claimed invention in an automatic transmission fluid, a manual transmission fluid, a hydraulic fluid, a grease, a gear fluid, a metal-working fluid, a crankcase engine oil or shock absorber fluid.

[0023] Seal compatibility (elastomer compatibility) is a critical parameter for many lubrication specifications. Currently, the detailed chemistry of seal compatibility is relatively unknown, thus adjusting formulations for suitable seal compatibility is not straightforward and can lead to significant costs. In particular, nitrile-based elastomers tend to be very challenging materials for lubricant-elastomer compatibility. It is therefore valuable and essential to identify lubricant base stocks that are capable of improving seal compatibility. Modern internal combustion engines and transmissions include numerous gaskets and other seals formed of nitrile rubber materials. Lubricant sulfur has been found to contribute to the deterioration of materials. Before certifying a crankcase lubricant for use in their engines, engine manufacturers (oftentimes referred to as "original equipment manufacturers" or "OEMs") require passage of a number of performance tests, including tests for compatibility with engine seal materials. Therefore, it would be desirable to provide a method of improving the seal compatibility of lubricant compositions, particularly lubricant compositions having significant sulfur contents, and lubricant compositions having significant sulfur contents that provide improved seal-compatibility performance.

[0024] Thus, the presently claimed invention is also directed to the use of the carboxylic acid ester of the presently claimed invention in a lubricant composition for improving seal compatibility, in particular nitrile seal compatibility, wherein seal compatibility is determined according to VDA 675 301.

[0025] The carboxylic acid ester is preferably present in an amount sufficient for the lubricant compositions to exhibit improved seal compatibility, in particular improved nitrile seal compatibility, with a lubricant composition in an engine lubricated with the lubricant compositions, as compared to seal compatibility, in particular nitrile seal compatibility achieved using a lubricant composition containing other than the carboxylic acid ester of the presently claimed invention,

[0026] Commercially available mixtures of acids comprising at least 70 weight-%, preferably at least 80 weight-%, of mono-branched or poly-branched, saturated C₁₆-C₂₂ fatty acids are obtained as a by-product of the catalytic or thermal dimerization of unsaturated straight chain fatty acids. Isostearic acid is produced by heating oleic acid in the presence of a catalyst, generally clay, to produce dimer, trimer and higher oligomer acids. But instead of polymerizing a portion of the oleic acid rearranges to give a branched, monomeric fatty acid which can be isolated by distillation and hydrogenated. This saturated branched monomeric fatty acid is a mixture of various linear and mainly branched, both mono-branched and poly-branched, saturated C₁₆-C₂₂ fatty acids which is known as isostearic acid.

[0027] a mixture of acids comprising at least 70 weight-% of mono-branched or poly-branched, saturated C₁₆-C₂₂ fatty acids of renewable origin refers to a mixture of acids comprising at least 70 weight-% of mono-branched or poly-branched, saturated C₁₆-C₂₂ fatty acids acid that has been obtained from a vegetable source, preferably from agricultural production of a certain plant in which a mixture of acids comprising at least 70 weight-% of mono-branched or poly-branched, saturated C₁₆-C₂₂ fatty acids is formed during the normal growth cycle of this plant. The plant in which the mixture of acids comprising at least 70 weight-% of mono-branched or poly-branched, saturated C₁₆-C₂₂ fatty acids is formed can be a genetically modified (genetically engineered by recombinant DNA or RNA technology) plant, in a way that the mixture of acids comprising at least 70 weight-% of mono-branched or poly-branched, saturated C₁₆-C₂₂ fatty acids is a recombinant plant product of such genetically modified plant.

[0028] Alternatively, the mixture of acids comprising at least 70 weight-% of mono-branched or poly-branched, saturated C₁₆-C₂₂ fatty acids is isolated from the natural, wild-type plant which has not been modified by recombinant technology but in which the mixture of acids comprising at least 70 weight-% of mono-branched or poly-branched, saturated C₁₆-C₂₂ fatty acids is formed as a natural component of said plant.

[0029] When providing the mixture of acids comprising at least 70 weight-% of mono-branched or poly-branched, saturated C₁₆-C₂₂ fatty acids for obtaining the carboxylic acid ester according to the presently claimed invention, at least 40 mole percent of the mixture of acids comprising at least 70 weight-% of mono-branched or poly-branched, saturated C₁₆-C₂₂ fatty acids are from a renewable source or origin. Preferably, at least 50 mole percent, more preferably at least 65 mole percent, even more preferably at least 75 mole percent, and most preferably at least 85 mole percent of the mixture of acids comprising at least 70 weight-% of mono-branched or poly-branched, saturated C₁₆-C₂₂ fatty acids used for obtaining the carboxylic acid ester of the presently claimed invention can be derived from a renewable source.

[0030] However, in another very preferred embodiment of the presently claimed invention, the mixture of acids comprising at least 70 weight-% of mono-branched or poly-branched, saturated C₁₆-C₂₂ fatty acids comprises isostearic acid which is fully of renewable origin, i.e. the carboxylic acid ester of the presently claimed invention consists of at least 90 mole percent, at least 95 mole percent, or even 100 mole percent of material from a renewable source.

[0031] In addition, a mixture of acids comprising at least 70 weight-% of mono-branched or poly-branched, saturated C₁₆-C₂₂ fatty acids as used in the presently claimed invention has very low level of unsaturated components. The content of unsaturated components is normally less than 5 weight-%, preferably less than 3 weight-%, more preferably less than 1 weight-%, even more preferably less than 0.5 weight-%, and most preferably less than 0.1 weight-%, based on the total weight of the mixture of acids comprising at least 70 weight-% of mono-branched or poly-branched, saturated C₁₆-C₂₂ fatty acids.

[0032] C₁₆-C₂₂ fatty acids that can be used according to the presently claimed invention can be obtained from palm oil, rape seed oil, palm kernel oil, coconut oil, soybean oil, castor oil, sunflower oil, olive oil, linseed oil, cottonseed oil, safflower oil, tallow, whale or fish oils, grease, lard and mixtures thereof.

[0033] One preferred alcohol R-OH, or mixture of alcohols R-OH, which is used in the presently claimed invention for preparing the carboxylic acid ester according to the presently claimed invention, is a so-called "Guerbet alcohol".

[0034] The term "Guerbet alcohol" is known to those skilled in the art. Reference is made by way of example to "Alcohols, Aliphatic", page 5 and page 10 respectively in Ullmann's Encyclopedia of Industrial Chemistry, Seventh Edt., Electronic Release, 2008, Wiley-VCH, Weinheim, N.Y., and the literature cited there.

[0035] The term "Guerbet alcohol" as used in the presently claimed invention relates to alcohols, or a mixture of alcohols, which is obtained by the so-called Guerbet reaction. Accordingly, the mixture of alcohols as used in the presently claimed invention for obtaining the carboxylic acid ester of the presently claimed invention is a mixture of alcohols obtained from the Guerbet reaction, particularly as defined in the above references.

[0036] In the course of the Guerbet reaction, primary alcohols are ultimately dimerized to α -branched primary alcohols in the presence of suitable catalysts. According to the literature, the primary products formed from the alcohols are aldehydes which subsequently dimerize to saturated alcohols by aldol condensation with elimination of water and subsequent hydrogenation. As well as the main product, different by-products can also form, for example unsaturated α -

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(continued)

	Lubricant type A	Lubricant type B	Lubricant type C
Additives	10.0 to 30.0; or 15.0 to 25.0;	5.0 to 25.0; or 10.0 to 20.0;	5.0 to 15.0; or 8.0 to 13.0;

[0045] The following lubricant compositions are especially preferred (all numbers in weight-%); the second range ("or") given is an even more preferred range, respectively:

	Lubricant type A'	Lubricant type B'	Lubricant type C'
Base oil	37.0 to 85.0; or 45.0 to 70.0;	25.0 to 75.0; or 32.0 to 60.0;	0 to 45.0; or 20.0 to 30.0;
Carboxylic acid ester of the presently claimed invention	5.0 to 18.0; or 10.0 to 15.0;	20.0 to 50.0; or 30.0 to 40.0;	50.0 to 85.0; or 65.0 to 80.0;
Additives (without VI improvers)	5.0 to 15.0; or 8.0 to 12.0;	0 to 10.0; or 5.0 to 8.0;	0.0 to 5.0; or 2.0 to 4.0;
Additives (VI improvers only)	5.0 to 30.0; or 10.0 to 20.0;	5.0 to 15.0; or 8.0 to 12.0;	5.0 to 10.0; or 6.0 to 8.0;

[0046] Viscosity index (VI) improvers are one possible class of additives that can optionally be used in the lubricant compositions of the presently claimed invention. Examples of viscosity index improvers are disclosed below where the additives are listed in more detail (see point 5).

[0047] The lubricant compositions according to the presently claimed invention may further optionally include base oils or co-solvents.

[0048] Preferred base oils contemplated for optional use in the lubricating oil compositions according to the presently claimed invention include mineral oils, poly-alpha-olefin synthetic oils and mixtures thereof.

[0049] Suitable base oils also include base stocks obtained by isomerization of synthetic wax and slack wax, as well as base stocks produced by hydrocracking (rather than solvent extracting) the aromatic and polar components of the crude. In general, both the mineral and synthetic base oils will each have a kinematic viscosity ranging from about 1 to about 40 cSt at 100°C, although typical applications will require each oil to have a viscosity ranging from about 1 to about 10 cSt at 100°C.

[0050] The mineral oils useful as optional components in the lubricant compositions according to the presently claimed invention include all common mineral oil base stocks. This includes oils that are naphthenic, paraffinic or aromatic in chemical structure.

[0051] Naphthenic oils are made up of methylene groups arranged in ring formation with paraffinic side chains attached to the rings. The pour point is generally lower than the pour point for paraffinic oils.

[0052] Paraffinic oils comprise saturated, straight chain or branched hydrocarbons.

[0053] The straight chain paraffins of high molecular weight raise the pour point of oils and are often removed by dewaxing.

[0054] Aromatic oils are hydrocarbons of closed carbon rings of a semi-unsaturated character and may have attached side chains. This oil is more easily degraded than paraffinic and naphthalenic oils leading to corrosive by-products.

[0055] In reality, a base stock will normally contain a chemical composition which contains some proportion of all three oils (paraffinic, naphthenic and aromatic). For a discussion of types of base stocks, see Motor Oils and Engine Lubrication by A. Schilling, Scientific Publications, 1968, section 2.2 through 2.5.

[0056] Further optional base oils include gas to liquid oils (GTL). Gaseous sources include a wide variety of materials such as natural gas, methane, C1-C3 alkanes, landfill gases, and the like. Such gases may be converted to liquid hydrocarbon products suitable for use as lubricant base oils by a gas to liquid (GTL) process, such as the process described in U.S. patent 6,497,812, of which the disclosure is incorporated herein by reference.

[0057] Base oils derived from a gaseous source, hereinafter referred to as "GTL base oils", typically have a viscosity index of greater than about 130, a sulfur content of less than about 0.3 weight-%, contain greater than about 90 weight-% saturated hydrocarbons (isoparaffins), typically from about 95 to about 100 weight-% branched aliphatic hydrocarbons, have a pour point of below -15 to -20°C.

[0058] The GTL base oils may be mixed with more conventional base oils such as Groups I to V as specified by API. For example, the base oil component of the lubricant compositions of the presently claimed invention may include 1 to

100 weight-% of GTL base oil.

[0059] Thus, the lubricating oil composition of the presently claimed invention may optionally be at least partially derived from a gaseous source.

[0060] Oils may be refined by conventional methodology using acid, alkali, and clay or other agents such as aluminum chloride, or they may be extracted oils produced, for example, by solvent extraction with solvents such as phenol, sulfur dioxide, furfural, dichlorodiethyl ether, etc.

[0061] They may be hydro-treated or hydro-refined, dewaxed by chilling or catalytic dewaxing processes, or hydro-cracked. The mineral oil may be produced from natural crude sources or be composed of isomerized wax materials or residues of other refining processes. The preferred synthetic oils are oligomers of α -olefins, particularly oligomers of 1-decene, also known as polyalphaolefins or PAO's.

[0062] The base oils may be derived from refined, re-refined oils, or mixtures thereof. Unrefined oils are obtained directly from a natural source or synthetic source (e.g., coal, shale, or tar sands bitumen) without further purification or treatment. Examples of unrefined oils include a shale oil obtained directly from a retorting operation, petroleum oil obtained directly from distillation, or ester oil obtained directly from an esterification process, each of which is then used without further treatment. Refined oils are similar to the unrefined oils except that refined oils have been treated in one or more purification steps to improve one or more properties. Suitable purification techniques include distillation, hydro-treating, dewaxing, solvent extraction, acid or base extraction, filtration, and percolation, all of which are known to those skilled in the art. Re-refined oils are obtained by treating used oils in processes similar to those used to obtain the refined oils. These re-refined oils are also known as reclaimed or reprocessed oils and are often additionally processed by techniques for removal of spent additives and oils breakdown products.

[0063] In the lubricant compositions according to the presently claimed invention comprising the carboxylic acid esters of the presently claimed invention, it is optional to include other esters being capable of reducing friction between moving surfaces.

[0064] For instance, the lubricant compositions of the presently claimed invention can further comprise other monocarboxylic acid esters or dicarboxylic acid esters. Both additional types of optional esters are suitable for reducing friction and can be added together or individually to the lubricant compositions of the presently claimed invention.

[0065] The monocarboxylic and dicarboxylic acid esters that can be optionally used are present in the lubricant compositions either individually, or in the form of mixtures comprising at least one monocarboxylic acid ester and at least one dicarboxylic acid ester.

[0066] Such monocarboxylic and dicarboxylic acid esters are obtained from known procedures, preferably by esterification of the corresponding monocarboxylic and/or dicarboxylic acid with the corresponding alcohol or mixture of alcohols.

[0067] Representative monocarboxylic acids include n-butanoic acid, n-pentanoic acid, n-hexanoic acid, n-heptanoic acid, n-octanoic acid, n-nonanoic acid, n-decanoic acid, isobutanoic acid, isopentanoic acid, isohexanoic acid, isohexanoic acid, isooctanoic acid, 2-ethylhexanoic acid, isononanoic acid, 3,5,5-trimethylhexanoic acid, and isodecanoic acid.

[0068] Representative dicarboxylic acid esters can be obtained from aliphatic dicarboxylic acids. In preferred modes of the presently claimed invention, the optional dicarboxylic acid esters can be obtained from dicarboxylic acids selected from the group consisting of glutaric acid, diglycolic acid, succinic acid, azelaic acid, sebacic acid, 1,4-cyclohexanedicarboxylic acid, adipic acid, 2,6-decahydronaphthalene dicarboxylic acid, 1,3-cyclohexanedicarboxylic acid, and 2,5-norbornanedicarboxylic acid. A very preferred aliphatic dicarboxylic acid is adipic acid. Instead of the acids, their anhydrides can also be used.

[0069] Representative alcohols to be used for obtaining other optional monocarboxylic acid esters and/or dicarboxylic acid esters include 2-propylheptanol, 2-propyl-4-methyl-hexanol, 2-propyl-5-methyl-hexanol, 2-isopropyl-4-methyl-hexanol, 2-isopropyl-5-methyl-hexanol, 2-propyl-4,4-dimethylpentanol, 2-ethyl-2,4-dimethylhexanol, 2-ethyl-2-methyl-heptanol, 2-ethyl-2,5-dimethylhexanol and 2-isopropyl-heptanol.

[0070] Preferably the alcohol mixture comprises 80 to 95 weight-% of 2-n-propyl-heptanol, 1.0 to 10 weight-% of 2-propyl-4-methyl-hexanol, 1.0 to 10 weight-% of 2-propyl-5-methyl-hexanol and 0.1 to 2.0 weight-% of 2-isopropyl-heptanol, whereby the weight of each component is related to the total weight of the monoalcohols.

[0071] More preferably the mixture comprises 91.0 to 95.0 weight-% of 2-n-propyl-heptanol, 2.0 to 5.0 weight-% of 2-propyl-4-methyl-hexanol, 3.0 to 5.0 weight-% of 2-propyl-5-methyl-hexanol and 0.1 to 0.8 weight-% of 2-isopropyl-heptanol, whereby the weight of each component is related to the total weight of the monoalcohols.

[0072] In another embodiment, an additional optional carboxylic acid ester is obtained by reacting a mixture comprising adipic acid, 2-propyl-heptanol, 2-propyl-4-methyl-hexanol and 2-propyl-5-methyl-hexanol.

[0073] In another embodiment, an additional optional carboxylic acid ester to be present in the lubricant compositions of the presently claimed invention is obtained by reacting a mixture comprising adipic acid and 80 to 95 weight-% of 2-n-propyl-heptanol, 1.0 to 10 weight-% of 2-propyl-4-methyl-hexanol, 1.0 to 10 weight-% of 2-propyl-5-methyl-hexanol, and 0.1 to 2.0 weight-% of 2-isopropyl-heptanol, whereby the weight of each component is related to the total weight of the monoalcohols.

[0074] The addition of at least one additive, like an additional customary oil additive, to the lubricating oil compositions of the presently claimed invention is possible but not mandatory in every case. The mentioned lubricant compositions, e.g. greases, gear fluids, metal-working fluids and hydraulic fluids, may additionally comprise further additives that are added in order to improve their basic properties still further.

[0075] Such additives include: further antioxidants or oxidation inhibitors, corrosion inhibitors, friction modifiers, metal passivators, rust inhibitors, anti-foamants, viscosity index enhancers, additional pour-point depressants, dispersants, detergents, further extreme-pressure agents and/or anti-wear agents.

[0076] Such additives are present in the amounts customary for each of them, which range in each case from 0.01 to 30.0 weight-%, preferably from 0.05 to 20.0 weight-%, more preferably from 0.1 to 10.0 weight-%, and even more preferably 0.2 to 5.0 weight-%, based on the total weight of the lubricating oil composition. Examples of further additives are given below:

1. Examples of phenolic antioxidants:

1.1. Alkylated monophenols: 2,6-di-tert-butyl-4-methylphenol, 2-butyl-4,6-dimethylphenol, 2,6-di-tert-butyl-4-ethylphenol, 2,6-di-tert-butyl-4-n-butylphenol, 2,6-di-tert-butyl-4-isobutylphenol, 2,6-dicyclopentyl-4-methylphenol, 2-(alpha-methylcyclohexyl)-4,6-dimethylphenol, 2,6-dioctadecyl-4-methylphenol, 2,4,6-tricyclohexylphenol, 2,6-di-tert-butyl-4-methoxymethylphenol, linear nonylphenols or nonylphenols branched in the side chain, such as, for example, 2,6-dinonyl-4-methylphenol, 2,4-dimethyl-6-(1'-methylundec-1'-yl)-phenol, 2,4-dimethyl-6-(1'-methylheptadec-1'-yl)-phenol, 2,4-dimethyl-6-(1'-methyltridec-1'-yl)-phenol and mixtures thereof;

1.2. Alkylthiomethylphenols: 2,4-dioctylthiomethyl-6-tert-butylphenol, 2,4-dioctylthiomethyl-6-methylphenol, 2,4-dioctylthiomethyl-6-ethylphenol, 2,6-didodecylthiomethyl-4-nonylphenol;

1.3. Hydroquinones and alkylated hydroquinones: 2,6-di-tert-butyl-4-methoxyphenol, 2,5-di-tert-butylhydroquinone, 2,5-di-tert-amylhydroquinone, 2,6-diphenyl-4-octadecyloxyphenol, 2,6-di-tert-butylhydroquinone, 2,5-di-tert-butyl-4-hydroxyanisole, 3,5-di-tert-butyl-4-hydroxyanisole, 3,5-di-tert-butyl-4-hydroxyphenyl stearate, bis(3,5-di-tert-butyl-4-hydroxyphenyl) adipate;

1.4. Tocopherols: alpha-, beta-, gamma- or delta-tocopherol and mixtures thereof (vitamin E);

1.5. Hydroxylated thiodiphenyl ethers: 2,2'-thio-bis(6-tert-butyl-4-methylphenol), 2,2'-thio-bis(4-octylphenol), 4,4'-thio-bis(6-tert-butyl-3-methylphenol), 4,4'-thio-bis(6-tert-butyl-2-methylphenol), 4,4'-thio-bis(3,6-di-sec-amylphenol), 4,4'-bis(2,6-dimethyl-4-hydroxy-phenyl)disulfide;

1.6. Alkylidene bisphenols: 2,2'-methylene-bis(6-tert-butyl-4-methylphenol), 2,2'-methylene-bis(6-tert-butyl-4-ethylphenol), 2,2'-methylene-bis[4-methyl-6-(alpha-methylcyclohexyl)phenol], 2,2'-methylene-bis(4-methyl-6-cyclohexylphenol), 2,2'-methylene-bis(6-nonyl-4-methylphenol), 2,2'-methylene-bis(4,6-di-tert-butylphenol), 2,2'-ethylidene-bis(4,6-di-tert-butylphenol), 2,2'-ethylidene-bis(6-tert-butyl-4-isobutylphenol), 2,2'-methylene-bis[6-(alpha-methylbenzyl)-4-nonylphenol], 2,2'-methylene-bis[6-(alpha, alpha-dimethyl-benzyl)-4-nonylphenol], 4,4'-methylene-bis(2,6-di-tert-butylphenol), 4,4'-methylene-bis(6-tert-butyl-2-methylphenol), 1,1-bis(5-tert-butyl-4-hydroxy-2-methylphenyl)butane, 2,6-bis(3-tert-butyl-5-methyl-2-hydroxybenzyl)-4-methylphenol, 1,1,3-tris(5-tert-butyl-4-hydroxy-2-methylphenyl)butane, 1,1-bis(5-tert-butyl-4-hydroxy-2-methylphenyl)-3-n-dodecylmercaptobutane, ethylene glycol bis[3,3-bis(3'-tert-butyl-4'-hydroxyphenyl)-butyrate], bis(3-tert-butyl-4-hydroxy-5-methylphenyl)dicyclopentadiene, bis[2-(3'-tert-butyl-2'-hydroxy-5'-methylbenzyl)-6-tert-butyl-4-methylphenyl]terephthalate, 1,1-bis(3,5-dimethyl-2-hydroxyphenyl)butane, 2,2-bis(3,5-di-tert-butyl-4-hydroxyphenyl)-propane, 2,2-bis(5-tert-butyl-4-hydroxy-2-methylphenyl)-4-n-dodecylmercaptobutane, 1,1,5,5-tetra(5-tert-butyl-4-hydroxy-2-methylphenyl)pentane;

1.7. O-, N- and S-benzyl compounds: 3,5,3',5'-tetra-tert-butyl-4,4'-dihydroxydibenzyl ether, octadecyl-4-hydroxy-3,5-dimethylbenzyl-mercaptoacetate, tridecyl-4-hydroxy-3,5-di-tert-butylbenzyl-mercaptoacetate, tris(3,5-di-tert-butyl-4-hydroxybenzyl)amine, bis(4-tert-butyl-3-hydroxy-2,6-dimethylbenzyl)dithioterephthalate, bis(3,5-di-tert-butyl-4-hydroxybenzyl)sulfide, isooctyl-3,5-di-tert-butyl-4-hydroxybenzyl-mercaptoacetate;

1.8. Hydroxybenzylated malonates: dioctadecyl-2,2-bis(3,5-di-tert-butyl-2-hydroxybenzyl)malonate, dioctadecyl-2-(3-tert-butyl-4-hydroxy-5-methylbenzyl)malonate, didodecyl-mercaptoethyl-2,2-bis(3,5-di-tert-butyl-4-hydroxybenzyl) malonate, di[4-(1,1,3,3-tetramethylbutyl)-phenyl]-2,2-bis(3,5-di-tert-butyl-4-hydroxyben-

zyl)malonate;

1.9. Hydroxybenzyl aromatic compounds: 1,3,5-tris(3,5-di-tert-butyl-4-hydroxybenzyl)-2,4,6-trimethylbenzene, 1,4-bis(3,5-di-tert-butyl-4-hydroxybenzyl)-2,3,5,6-tetramethylbenzene, 2,4,6-tris(3,5-di-tert-butyl-4-hydroxybenzyl)phenol;

1.10. Triazine compounds: 2,4-bis-octylmercapto-6-(3,5-di-tert-butyl-4-hydroxyanilino)-1,3,5-triazine, 2-octylmercapto-4,6-bis(3,5-di-tert-butyl-4-hydroxyanilino)-1,3,5-triazine, 2-octylmercapto-4,6-bis(3,5-di-tert-butyl-4-hydroxyphenoxy)-1,3,5-triazine, 2,4,6-tris(3,5-di-tert-butyl-4-hydroxyphenoxy)-1,2,3-triazine, 1,3,5-tris(3,5-di-tert-butyl-4-hydroxybenzyl)isocyanurate, 1,3,5-tris(4-tert-butyl-3-hydroxy-2,6-dimethylbenzyl)isocyanurate, 2,4,6-tris(3,5-di-tert-butyl-4-hydroxyphenylethyl)-1,3,5-triazine, 1,3,5-tris(3,5-di-tert-butyl-4-hydroxyphenylpropionyl)hexahydro-1,3,5-triazine, 1,3,5-tris(3,5-dicyclohexyl-4-hydroxybenzyl)isocyanurate;

1.11. Acylaminophenols: 4-hydroxylauric acid anilide, 4-hydroxystearic acid anilide, N-(3,5-di-tert-butyl-4-hydroxyphenyl)-carbamic acid octyl ester;

1.12. Esters of beta-(5-tert-butyl-4-hydroxy-3-methylphenyl) propionic acid: with polyhydric alcohols, e.g. with 1,6-hexanediol, 1,9-nonanediol, ethylene glycol, 1,2-propanediol, neopentyl glycol, thiodiethylene glycol, diethylene glycol, triethylene glycol, pentaerythritol, tris(hydroxyethyl)isocyanurate, N,N'-bis(hydroxyethyl) oxalic acid diamide, 3-thiaundecanol, 3-thiapentadecanol, trimethylhexanediol, trimethylolpropane, 4-hydroxymethyl-1-phospha-2,6,7-trioxabicyclo[2.2.2]octane;

1.13. Esters of beta-(3,5-di-tert-butyl-4-hydroxyphenyl) propionic acid, gamma-(3,5-dicyclohexyl-4-hydroxyphenyl) propionic acid, 3,5-di-tert-butyl-4-hydroxyphenylacetic acid: with mono- or polyhydric alcohols, e.g. with methanol, ethanol, n-octanol, isooctanol, octadecanol, 1,6-hexanediol, 1,9-nonanediol, ethylene glycol, 1,2-propanediol, neopentyl glycol, thiodiethylene glycol, diethylene glycol, triethylene glycol, pentaerythritol, tris(hydroxyethyl)isocyanurate, N,N'-bis-hydroxyethyl oxalic acid diamide, 3-thiaundecanol, 3-thiapentadecanol, trimethylhexanediol, trimethylolpropane, 4-hydroxymethyl-1-phospha-2,6,7-trioxabicyclo[2.2.2]octane;

1.14. Amides of beta-(3,5-di-tert-butyl-4-hydroxyphenyl) propionic acid: N,N'-bis(3,5-di-tert-butyl-4-hydroxyphenylpropionyl)hexamethylenediamine, N,N'-bis(3,5-di-tert-butyl-4-hydroxyphenylpropionyl)trimethylenediamine, N,N'-bis(3,5-di-tert-butyl-4-hydroxyphenylpropionyl)hydrazine;

1.15. Ascorbic acid (vitamin C);

1.16. Aminic antioxidants: N,N'-diisopropyl-p-phenylenediamine, N,N'-di-sec-butyl-p-phenylenediamine, N,N'-bis(1,4-dimethylpentyl)-p-phenylenediamine, N,N'-bis(1-ethyl-3-methylpentyl)-p-phenylenediamine, N,N'-bis(1-methylheptyl)-p-phenylenediamine, N,N'-dicyclohexyl-p-phenylenediamine, N,N'-diphenyl-p-phenylenediamine, N,N'-di(naphth-2-yl)-p-phenylenediamine, N-isopropyl-N'-phenyl-p-phenylenediamine, N-(1,3-dimethylbutyl)-N'-phenyl-p-phenylenediamine, N-(1-methylheptyl)-N'-phenyl-p-phenylenediamine, N-cyclohexyl-N'-phenyl-p-phenylenediamine, 4-(p-toluenesulfonamido)-diphenylamine, N,N'-dimethyl-N,N'-di-sec-butyl-p-phenylenediamine, diphenylamine, N-allyldiphenylamine, 4-isopropoxydiphenylamine, 4-n-butylaminophenol, 4-butyrylaminophenol, 4-nonanoylaminophenol, 4-dodecanoylaminophenol, 4-octadecanoylaminophenol, di(4-methoxyphenyl)amine, 2,6-di-tert-butyl-4-dimethylaminomethyl phenol, 2,4'-diaminodiphenylmethane, 4,4'-diaminodiphenylmethane, N,N,N',N'-tetramethyl-4,4'-diaminodiphenylmethane, 1,2-di[(2-methylphenyl)amino]-ethane, 1,2-di(phenylamino)propane, (o-tolyl)biguanide, di[4-(1',3'-dimethylbutyl)phenyl]amine, tert-octylated N-phenyl-1-naphthylamine, mixture of mono- and di-alkylated tert-butyl/tert-octyl-diphenylamines, mixture of mono- and di-alkylated nonylidiphenylamines, mixture of mono- and di-alkylated dodecyldiphenylamines, mixture of mono- and di-alkylated isopropyl/isohexyl-diphenylamines, mixtures of mono- and di-alkylated tert-butylidiphenylamines, 2,3-dihydro-3,3-dimethyl-4H-1,4-benzothiazine, phenothiazine, mixture of mono- and di-alkylated tert-butyl/tert-octylphenothiazines, mixtures of mono- and di-alkylated tert-octylphenothiazines, N-allylphenothiazine, N,N,N',N'-tetraphenyl-1,4-diaminobut-2-ene, N,N-bis(2,2,6,6-tetramethylpiperidin-4-yl)hexamethylenediamine, bis(2,2,6,6-tetramethylpiperidin-4-yl)sebacate, 2,2,6,6-tetramethylpiperidin-4-one, 2,2,6,6-tetramethylpiperidin-4-ol.

2. Examples of further antioxidants: aliphatic or aromatic phosphites, esters of thiodipropionic acid or thiodiacetic acid or salts of dithiocarbamic acid, 2,2,12,12-tetramethyl-5,9-dihydroxy-3,7,11-trithiamidecane and 2,2,15,15-tetramethyl-5,12-dihydroxy-3,7, 10,14-tetrathiahexadecane.

3. Examples of metal deactivators, e.g. for copper:

3.1. Benzotriazoles and derivatives thereof: 2-mercaptobenzotriazole, 2,5-dimercaptobenzotriazole, 4- or 5-alkylbenzotriazoles (e.g. tolutriazole) and derivatives thereof, 4,5,6,7-tetrahydrobenzotriazole, 5,5'-methylene-bis-benzotriazole; Mannich bases of benzotriazole or tolutriazole, such as 1-[di(2-ethylhexyl)aminomethyl]tolutriazole and 1-[di(2-ethylhexyl)aminomethyl]benzotriazole; alkoxyalkylbenzotriazoles, such as 1-(nonyloxy-methyl)benzotriazole, 1-(1-butoxyethyl)-benzotriazole and 1-(1-cyclohexyloxybutyl)-tolutriazole;

3.2. 1,2,4-Triazoles and derivatives thereof: 3-alkyl-(or -aryl-) 1,2,4-triazoles, Mannich bases of 1,2,4-triazoles, such as 1-[di(2-ethylhexyl)aminomethyl]-1,2,4-triazole; alkoxyalkyl-1,2,4-triazoles, such as 1-(1-butoxyethyl)-1,2,4-triazole; acylated 3-amino-1,2,4-triazoles;

3.3. Imidazole derivatives: 4,4'-methylene-bis(2-undecyl-5-methyl) imidazole and bis[(N-methyl)imidazol-2-yl]carbinol-octyl ether;

3.4. Sulfur-containing heterocyclic compounds: 2-mercaptobenzothiazole, 2,5-dimercapto-1,3,4-thiadiazole, 2,5-dimercaptobenzothiadiazole and derivatives thereof; 3,5-bis[di(2-ethylhexyl)aminomethyl]-1,3,4-thiadiazolin-2-one;

3.5. Amino compounds: salicylidene-propylenediamine, salicylaminoguanidine and salts thereof.

4. Examples of rust inhibitors:

4.1. Organic acids, their esters, metal salts, amine salts and anhydrides: alkyl- and alkenylsuccinic acids and their partial esters with alcohols, diols or hydroxycarboxylic acids, partial amides of alkyl- and alkenylsuccinic acids, 4-nonylphenoxyacetic acid, alkoxy- and alkoxyethoxy-carboxylic acids, such as dodecyloxyacetic acid, dodecyloxy (ethoxy)acetic acid and amine salts thereof, and also N-oleoyl-sarcosine, sorbitan monooleate, lead naphthenate, alkenylsuccinic acid anhydrides, e.g. dodecenylsuccinic acid anhydride, 2-(2-carboxyethyl)-1-dodecyl-3-methylglycerol and salts thereof, especially sodium and triethanolamine salts thereof.

4.2. Nitrogen-containing compounds:

4.2.1. Tertiary aliphatic or cycloaliphatic amines and amine salts of organic and inorganic acids, e.g. oil-soluble alkylammonium carboxylates, and 1-[N,N-bis(2-hydroxyethyl)amino]-3-(4-nonylphenoxy)propan-2-ol;

4.2.2. Heterocyclic compounds: substituted imidazolines and oxazolines, e.g. 2-heptadecenyl-1-(2-hydroxyethyl)-imidazoline;

4.2.3. Sulfur-containing compounds: barium dinonylnaphthalene sulfonates, calcium petroleum sulfonates, alkylthio-substituted aliphatic carboxylic acids, esters of aliphatic 2-sulfocarboxylic acids and salts thereof.

5. Examples of additional viscosity index enhancers: polyacrylates, polymethacrylates, nitrogen containing polymethylmethacrylates, vinylpyrrolidone/methacrylate copolymers, polyvinylpyrrolidones, polybutenes, polyisobutylenes, olefin copolymers such as ethylenepropylene copolymers, styrene-isoprene copolymers, hydrated styrene-isoprene copolymers, styrene/acrylate copolymers and polyethers. Multifunctional viscosity improvers, which also have dispersant and/or antioxidancy properties are known and may optionally be used in addition to the products of this invention.

6. Examples of pour-point depressants: polymethacrylates, ethylene/vinyl acetate copolymers, alkyl polystyrenes, fumarate copolymers, alkylated naphthalene derivatives.

7. Examples of dispersants/surfactants: polybutenylsuccinic acid amides or imides, polybutenylphosphonic acid derivatives, basic magnesium, calcium and barium sulfonates and phenolates.

8. Examples of extreme-pressure and anti-wear additives: sulfur- and halogen-containing compounds, e.g. chlorinated paraffins, sulfurized olefins or vegetable oils (soybean oil, rape oil), alkyl- or aryl-di- or -tri-sulfides, benzotriazoles or derivatives thereof, such as bis(2-ethylhexyl)aminomethyl tolutriazoles, dithiocarbamates, such as methylene-

bis-dibutylidithiocarbamate, derivatives of 2-mercaptobenzothiazole, such as 1-[N,N-bis(2-ethylhexyl)aminomethyl]-2-mercapto-1H-1,3-benzothiazole, derivatives of 2,5-dimercapto-1,3,4-thiadiazole, such as 2,5-bis(tert-nonyldithio)-1,3,4-thiadiazole.

9. Examples of coefficient of friction reducers: lard oil, oleic acid, tallow, rape oil, sulfurized fats, amides, amines. Further examples are given in EP-A-0 565 487.

10. Examples of special additives for use in water/oil metal-working fluids and hydraulic fluids: Emulsifiers: petroleum sulfonates, amines, such as polyoxyethylated fatty amines, non-ionic surface-active substances; buffers: such as alkanolamines; biocides: triazines, thiazolinones, tris-nitromethane, morpholine, sodium pyridenethiol; processing speed improvers: calcium and barium sulfonates.

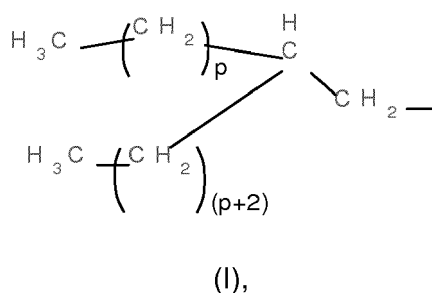
[0077] Depending on the end use applications, small quantities of additives such as anti-misting agents may be also optionally added in an amount ranging from 0.05 to 5.0% by vol. in one embodiment, and less than 1 wt. %, in other embodiments.

[0078] For certain applications, a small amount of foam inhibitors in the prior art can also be added to the composition in an amount ranging from 0.02 to 15.0 wt. %.

[0079] The compositions may further comprise oil soluble metal deactivators in an amount of 0.01 to 0.5 vol. % (based on the final oil volume).

[0080] The carboxylic acid esters of the presently claimed invention can be prepared in a preferred manner by initially providing a mixture of acids comprising at least 70 weight-% of mono-branched or poly-branched, saturated C₁₆-C₂₂ fatty acids from a non-renewable and/or renewable source as defined above.

[0081] Then, in a next step, a mixture is prepared of the mixture of acids comprising at least 70 weight-% of mono-branched or poly-branched, saturated C₁₆-C₂₂ fatty acids with the mixture of alcohols, preferably the Guerbet alcohols of the formula R-OH, obtainable from the Guerbet reaction, wherein the preferred R radical is a mixture of different radicals in which at least 65 weight-%, preferably at least 80 weight-%, of the radicals have the general formula I,



wherein p is 0, 1, 2, 3, or 4; while p is preferably 0, 1 or 2, or more preferably p is 2;

[0082] More preferably, the radical R denotes a branched or linear, substituted or unsubstituted aliphatic hydrocarbon moiety having from 7 to 20 carbon atoms.

[0083] Even more preferably, the radical R denotes a branched or linear, substituted or unsubstituted aliphatic hydrocarbon moiety having from 10 to 18 carbon atoms.

[0084] Most preferably, the radical R denotes a moiety selected from the group consisting of decyl, isodecyl, undecyl, dodecyl, tridecyl, tetradecyl, pentadecyl, hexadecyl, heptadecyl, octadecyl, 2-propylheptyl, 2-butyloctyl, 2-pentylonyl and 2-hexyldeacyl as well as mixtures thereof.

[0085] In the subsequent process stage or step, the esterification of the mixture of acids comprising at least 70 weight-% of mono-branched or poly-branched, saturated C₁₆-C₂₂ fatty acids is carried out with the mixture of alcohols R-OH as defined above. This esterification reaction for the mixture of acids comprising at least 70 weight-% of mono-branched or poly-branched, saturated C₁₆-C₂₂ fatty acids preferably includes the following steps.

[0086] The mixture obtained in the previous step(s) is heated to a temperature in the range of 80°C to 160°C, followed by adding a basic aqueous solution, and followed in a third step by removing the remaining alcohol.

[0087] Optionally, the carboxylic acid ester which was thus obtained can be further purified by drying and filtering.

[0088] The reaction between the mixture of acids comprising at least 70 weight-% of mono-branched or poly-branched, saturated C₁₆-C₂₂ fatty acids and the mixture of alcohols can be preferably carried out using stoichiometric amounts of the mixture of acids comprising at least 70 weight-% of mono-branched or poly-branched, saturated C₁₆-C₂₂ fatty acids and the alcohol, particularly when entrainers are used. However, preference is given to using a stoichiometric excess of the alcohol component of from 0.05 to 1.0 mole per mole of the mixture of acids comprising at least 70 weight-% of

mono-branched or poly-branched, saturated C_{16} - C_{22} fatty acids in order to achieve a complete conversion of isostearic acid.

[0089] In another preferred manner, the esterification reaction between the mixture of acids comprising at least 70 weight-% of mono-branched or poly-branched, saturated C_{16} - C_{22} fatty acids and the mixture of alcohols is carried out in two stages, wherein already in the first stage substantial amounts of the desired carboxylic acid ester are formed without the addition of a catalyst, preferably tin carboxylates such as tin octoate, tin oleate, tin acetate, tin butyrate and tin stearate and titanium compounds such as tetramethyl titanate, tetraethyl titanate, tetraallyl titanate, tetrapropyl titanate, tetraisopropyl titanate, tetrabutyl titanate, tetraisobutyl titanate, tetraamyl titanate, tetracyclopentyl titanate, tetrahexyl titanate, tetracyclohexyl titanate, tetrabenzyl titanate, tetraoctyl titanate, tetraethylhexyl titanate, tetranonyl titanate, tetradecyl titanate, and tetraoleyl titanate. The temperatures to be employed in this first stage depend largely on the starting materials. Satisfactory reaction rates are achieved above 100°C, and preferably above 120°C. It is possible to already complete the carboxylic ester formation at these temperatures.

[0090] However, it is more advantageous to increase the temperature continuously up to 160 °C. When using the mixture of acids comprising at least 70 weight-% of mono-branched or poly-branched, saturated C_{16} - C_{22} fatty acids (rather than the corresponding carboxylic anhydride thereof) as the esterification component, the water formed is removed from the reaction system as an azeotrope with the alcohol, as long as the reaction temperature is above the boiling point of the azeotrope (i.e. in a range from 90°C to 100°C under atmospheric pressure). The course and completion of the esterification can in this case be observed via the formation of water. The use of subatmospheric or superatmospheric pressure is not ruled out, but is rather restricted to special cases. To suppress the occurrence of concentration differences, it is advisable to stir the reactor contents or to mix them from time to time, e.g. by passing an inert gas through the reaction mixture.

[0091] It is further optional to work up the formed carboxylic acid ester by filtration, optionally followed by distillation.

[0092] In the second stage, the esterification of the mixture of acids comprising at least 70 weight-% of mono-branched or poly-branched, saturated C_{16} - C_{22} fatty acids is completed. The second stage is carried out in the presence of catalysts at temperatures which are above those employed in the first stage and go up to 250°C. Water formed during the reaction is removed as an azeotrope, with the alcohol acting as an entrainer.

[0093] After completion of the reaction, the reaction mixture comprises not only the desired reaction product, but it may still contain a mixture of acids comprising at least 70 weight-% of mono-branched or poly-branched, saturated C_{16} - C_{22} fatty acids together with excess alcohol and the catalyst.

[0094] To work up the crude carboxylic acid ester, the product from the reactor is first neutralized with alkali metal hydroxide or alkaline earth metal hydroxide. The alkaline reagent is employed as an aqueous solution containing from 5 to 20 weight-%, preferably from 10 to 15 weight-%, of the hydroxide, based on the overall weight of the solution.

[0095] The amount of neutralizing agent to be used depends on the proportion of acid components, free acid and carboxylic acid ester in the crude product. The use of the selected hydroxides, among which sodium hydroxide has been found to be particularly useful, as aqueous solution having a particular concentration and in a defined excess ensures that the acidic constituents of the reaction mixture are precipitated in a crystalline, very readily filterable form.

[0096] At the same time, the catalyst is largely decomposed to form likewise easily filterable products. The alkaline treatment of the crude carboxylic acid ester is not tied to the maintenance of particular temperatures. It is advantageously carried out immediately after the esterification step without prior cooling of the reaction mixture.

[0097] Subsequently any free alcohol is separated from the reaction mixture. Steam distillation has been found to be useful for this step and can be carried out in simple form by passing steam into the crude product.

[0098] The removal of the free alcohol is typically followed by the drying of the carboxylic acid ester. In a particularly simple and effective embodiment of this step, drying is achieved by passing an inert gas through the product. The crude carboxylic acid ester is then filtered to free it of solids. The filtration is carried out in conventional filtration equipment at room temperature or at temperatures up to 150°C. The filtration can also be facilitated by customary filter aids such as cellulose or silica gel.

[0099] The carboxylic acid ester according to the presently claimed invention as well as the lubricant compositions according to the presently claimed invention comprising the inventive carboxylic acid ester can be favourably used for various applications.

[0100] One preferred application are as components in engine oils. Such general applications includes all sorts of engine oils, including light, medium and heavy duty engine oils, industrial engine oils, marine engine oils, crankshaft oils, compressor oils, refrigerator oils, hydrocarbon compressor oils, very low-temperature lubricating oils and fats, high temperature lubricating oils and fats, wire rope lubricants, textile machine oils, refrigerator oils, aviation and aerospace lubricants, aviation turbine oils, transmission oils, gas turbine oils, spindle oils, spin oils, traction fluids, transmission oils, plastic transmission oils, passenger car transmission oils, truck transmission oils, industrial transmission oils, industrial gear oils, insulating oils, instrument oils, brake fluids, transmission liquids, shock absorber oils, heat distribution medium oils, transformer oils, fats, chain oils, metalworking operations in general, particularly as minimum quantity lubricants for metalworking operations, oil to the warm and cold working, oil for water-based metalworking liquids, oil for neat oil

metalworking fluids, oil for semi-synthetic metalworking fluids, oil for synthetic metalworking fluids, drilling detergents for the soil exploration, hydraulic oils, in biodegradable lubricants or lubricating greases or waxes, chain saw oils, release agents, moulding fluids, gun, pistol and rifle lubricants or watch lubricants and food grade approved lubricants.

[0101] In preferred embodiments, the carboxylic acid esters of the presently claimed invention as well as the lubricant compositions comprising the carboxylic acid ester are used as co-solvents or base oils in lubricant compositions, in particular the carboxylic acid esters are used in lubricant compositions in automatic transmission fluids, manual transmission fluids, hydraulic fluids, grease, gear fluids, crankcase engine oils, shock absorber fluids, industrial oils, metalworking fluids, transformer oils, biodegradable lubricants and seal plasticizing agents.

[0102] The presently claimed invention is also directed to the use of a mixture of acids comprising at least 70 weight-% of mono-branched or poly-branched, saturated C₁₆-C₂₂ fatty acids, in one special embodiment, isostearic acid, which is at least partially obtained from a renewable source, for preparing a carboxylic acid ester to be used in a lubricant composition.

[0103] At least 40 mole percent of the mixture of acids comprising at least 70 weight-% of mono-branched or poly-branched, saturated C₁₆-C₂₂ fatty acids, preferably at least 50 mole percent, more preferably at least 65 mole percent, even more preferably at least 75 mole percent, and most preferably at least 85 mole percent of the isostearic acid, and sometimes even at least 90 mole percent, or at least 95 mole percent or even 100 mole percent are hereby from a renewable source.

[0104] In a preferred use, the carboxylic acid ester is obtained by esterification of the mixture of acids comprising at least 70 weight-% of mono-branched or poly-branched, saturated C₁₆-C₂₂ fatty acids, preferably of the mixture of acids comprising at least 70 weight-% of mono-branched or poly-branched, saturated C₁₆-C₂₂ fatty acids of at least partial renewable origin, with the mixture of Guerbet alcohols as defined herein, which is a mixture that was obtained from the Guerbet reaction.

[0105] The carboxylic acid esters obtained from esterification of the mixture of acids comprising at least 70 weight-% of mono-branched or poly-branched, saturated C₁₆-C₂₂ fatty acids and the mixture of Guerbet alcohols as described herein allow the preparation of lubricant compositions with attractive viscosity profiles and very good seal compatibility.

[0106] The lubricant compositions of the presently claimed invention due to the presence of the carboxylic acid ester of the presently claimed invention have better seal performance than other lubricants that are based on different carboxylic acid esters. Similarly, the overall seal performance of known lubricant compositions can be improved by the addition of the carboxylic acid ester of the presently claimed invention.

[0107] One important problem of lubricant compositions is that they can compromise seal materials. Those negative effects include physical deterioration of seals by swelling or shrinking of the seal due to the prolonged contact with lubricants, and/or chemical damage by affecting elasticity of the seal leading to softening or hardening of the seal. Ultimately, oil leakage and engine damage can be the result illustrating the critical importance of optimized seal compatibility of lubricants.

[0108] The carboxylic acid ester of the presently claimed invention has basically no aromaticity due to being derived from an aliphatic carboxylic acid and a mixture of aliphatic alcohols. Therefore, the carboxylic acid ester according to the presently claimed invention has the advantage of being able to increase the aniline point of a lubricant composition when added thereto.

[0109] The carboxylic acid esters of the presently claimed invention have an aniline point in the range of from 20°C to 80°C, preferably 30 to 70°C, more preferably from 40°C to 60°C and most preferably from 50 to 55°C determined based on ASTM D 611.

[0110] One important technical consequence of such favourable aniline point is that the solubility of additional additives in the lubricant compositions, particularly non-aromatic additives can be improved due to the presence of the carboxylic acid ester of the presently claimed invention. Accordingly, higher relative amounts of such additives can be used in lubricant compositions due to better solubility.

[0111] The carboxylic acid esters according to the presently claimed invention have kinematic viscosity at 40°C as determined by ASTM D 445 in the range of from 8.0 to 20.0 mm²/s, preferably 10.0 to 18.0 mm²/s, and more preferably 12.0 to 15.0 mm²/s. Most preferred are values in the range of from 13.0 to 14.0 mm²/s.

[0112] The carboxylic acid esters according to the presently claimed invention have kinematic viscosity at 100°C as determined by ASTM D 445 in the range of from 2.0 to 4.5 mm²/s, preferably 2.5 to 4.0 mm²/s, and more preferably 3.0 to 3.8 mm²/s. Most preferred are values in the range of from 3.3 to 3.7 mm²/s.

[0113] The carboxylic acid esters of the presently claimed invention have viscosity index as determined by ASTM D 2270 in the range of from 125 to 150, preferably 130 to 145, and more preferably from 135 to 140.

[0114] The pour point of the carboxylic acid ester of the presently claimed invention is in the range of from -55°C to -30°C, preferably from -50°C to -35°C and more preferably from -45°C to -40°C.

[0115] The Noack volatility determined according to ASTM D 5800-B of the carboxylic acid ester of the presently claimed invention is in the range of from 8 to 20%, preferably 10 to 18%, and more preferably from 12 to 15%.

[0116] The flash point of the carboxylic acid esters of the presently claimed invention is in the range of from 215 to

240°C, preferably from 220 to 235°C, and more preferably from 225 to 230°C.

[0117] The cold cranking viscosity (CCS) of the carboxylic acid ester of the presently claimed invention at -30°C determined according to ASTM D 5293 is in the range of from 760 to 810 mPas, preferably 775 to 805 mPas, and more preferably from 785 to 795 mPas.

[0118] The density of the carboxylic acid ester of the presently claimed invention at 20°C as determined based on ASTM D 7042 is 0.866 g/mole, varying in the range of from 0.840 to 0.880 g/mole, preferably from 0.850 to 0.870 g/mole, and more preferably from 0.860 to 0.868 g/mole.

[0119] The carboxylic acid ester of the presently claimed invention also has very good oxidation stability as determined by the rotating pressure vessel oxidation test (RPVOT).

[0120] The following examples illustrate the invention without being intended to limit the invention thereto.

Examples

Preparation of 2-propylheptyl isostearate

[0121] Propylheptanol is commercially available from BASF SE, Ludwigshafen, Germany [93.0 % by weight 2-propylheptanol; 2.9 % by weight 2-propyl-4-methyl-hexanol; 3.9 % by weight 2-propyl-5-methylhexanol and 0.2 Gew.-% 2-isopropylheptanol]

[0122] Isostearic acid is commercially available as prisorine® 3503 from Croda, Gouda, The Netherlands [83 % by weight branched, saturated C₁₆-C₂₂ fatty acids]

[0123] Propylheptanol (1122g, 7.10 mole) and isostearic acid (1679 g, 5.91 mole) were reacted at 180°C until water distillation slowed down. The mixture was further reacted in the presence of tin octoate catalyst (2.8 g) at 230°C under vacuum (< 5 mbar) until an acid value of < 0.5 mg/KOH/g was reached.

[0124] The obtained ester product was then neutralized with 10 % NaOH aqueous solution at 95°C. Afterwards, the organic phase and aqueous phase were separated. The organic phase was then further washed twice with water. The ester was then dried under vacuum and filtered using diatomaceous earth as filter aid.

[0125] The resulting ester product had a density of 0.866 g/mole at 20°C, measured according to ASTM D 7042.

Characterization of 2-propylheptyl isostearate

[0126]

Table 1.

	Units	Methods	Result
Kinematic viscosity at 40°C	mm ² /s	ASTM D 445	13.4
Kinematic viscosity at 100°C	mm ² /s	ASTM D 445	3.5
Viscosity index		ASTM D 2270	139
Flash point	°C	ASTM D 92	228
Pour point	°C	ISO 3016	-42
Aniline point	°C	ASTM D 611	54
CCS at -30°C	mPa.s	ASTM D 5293	790
Seal Compatibility NBR1 - Volume change	%	VDA 675 301	8,6
Seal Compatibility NBR1 - Shore A hardness change	Points	VDA 675 301	-11

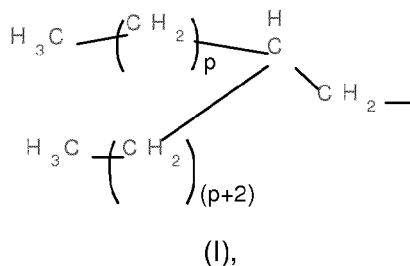
[0127] The improved seal compatibility of the inventively claimed esters were determined according to the VDA 675 301 test.

[0128] The low temperature viscosity requirements were determined by ASTM D 5293, Method of Test for Apparent Viscosity of Motor Oils at Low Temperature Using the Cold Cranking Simulator (CCS), and the results are reported in mPa.s. CCS is to measure the viscometric properties of lubricating base oils under low temperature and low shear. The esters of the presently claimed invention are able to meet low temperature requirements implying a cold cranking viscosity of not more than 3250 mPa.s at -30 °C.

Claims

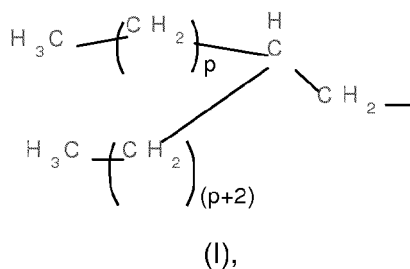
1. A carboxylic acid ester obtainable by reacting a mixture comprising

- a) a mixture of acids comprising at least 70 weight-% of mono-branched or poly-branched, saturated C₁₆-C₂₂ fatty acids, and
 b) a mixture of alcohols according to the formula R-OH, wherein R is a mixture of different radicals in which at least 65 weight-% of the radicals have the general formula (I),



wherein p is 0, 1, 2, 3 or 4.

2. The carboxylic acid ester according to claim 1, **characterized in that** at least 80 weight-% of the radicals have the general formula (I),



wherein p is 0, 1, 2, 3 or 4.

3. The carboxylic acid ester according to claim 1 or 2, **characterized in that** p is 0, 1 or 2.

4. The carboxylic acid ester according to any one of claims 1 to 3, **characterized in that** p is 2.

5. The carboxylic acid ester according to any one of claims 1 to 4, **characterized in that** the mixture of alcohols according to the formula R-OH comprises 80 to 95 weight-% of 2-n-propyl-heptanol, 1.0 to 10 weight-% of 2-propyl-4-methyl-hexanol, 1.0 to 10 weight-% of 2-propyl-5-methyl-hexanol and 0.1 to 2.0 weight-% of 2-isopropyl-heptanol, whereby the weight of each component is related to the total weight of the alcohols.

6. The carboxylic acid ester according to any one of claims 1 to 5, **characterized in that** the mixture of acids comprises mono-branched or poly-branched, saturated C₁₆-C₂₂ fatty acids in the range of 70 weight-% to 95 weight-%.

7. The carboxylic acid ester according to any one of claims 1 to 6, **characterized in that** the mixture of acids is derived from a renewable source.

8. A lubricant composition comprising the carboxylic acid ester according to any one of claims 1 to 7.

9. The lubricant composition according to claim 8, further including a base oil component and at least one additive.

10. A process for preparing the carboxylic acid ester according to any one of claims 1 to 7, comprising the steps of

- $$\begin{array}{c}
 \text{H}_3\text{C}-\left(\text{CH}_2\right)_p-\text{C}\begin{matrix} \nearrow \text{H} \\ \searrow \text{CH}_2- \end{matrix} \\
 | \\
 \text{H}_3\text{C}-\left(\text{CH}_2\right)_{(p+2)}
 \end{array}
 \quad (\text{I}),$$

- carrying out esterification of the mixture of acids and the mixture of alcohols R-OH.

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The present search report has been drawn up for all claims			TECHNICAL FIELDS SEARCHED (IPC)
Place of search Munich		Date of completion of the search 22 March 2016	Examiner Kaluza, Nora
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Place of search Munich		Date of completion of the search 22 March 2016	Examiner Kaluza, Nora
CATEGORY OF CITED DOCUMENTS X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document			

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