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(19) **United States**(12) **Patent Application Publication****Täubert et al.**(10) **Pub. No.: US 2007/0130821 A1**(43) **Pub. Date: Jun. 14, 2007**(54) **ADDITIVE MIXTURE AS COMPONENT OF MINERAL OIL COMPOSITIONS**(76) Inventors: **Hiltrud Täubert**, Leissling (DE);
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An additive mixture as component of compositions of mineral oil as the main component and trace portions of an additive mixture contains the additive components

a) ethylene-vinylester copolymers with molecular mass weight averages from 3000 to 50000 and an ethylene proportion of 50 to 90 mass %, and

b) mixed esters of glycerine in which 50 to 80 mol % of the hydroxy groups are esterified with unsaturated C₁₂-C₄₀ monocarboxylic acids and 20 to 50 mol % of the hydroxy groups are esterified with partially imidated and/or partially esterified maleic anhydride copolymers,

and/or

c) partially and/or completely imidated copolymers consisting of maleic anhydride and α -methylstyrene with molecular mass number averages from 1500 to 15000 and at least one terminal group based on dimeric α -methylstyrene, and/or

d) wax compositions based on natural starting materials of type

d1) wax-like oligomeric esters based on glyceryl monostearate and dimeric acid and/or

d2) wax esters with vaseline-like consistency, based on at least two different straight-chain and/or branched C₁₄-C₃₆-alcohols and dimeric acid

whereby the content of the additive mixture in the mineral oil is 0.005 to 1 mass % and the mass proportion of the additive components a/b or a/c or a/d is in the range from 10:90 to 90:10, respectively.

The mineral oil compositions are suitable as flowable media to be transported at low temperatures and as mineral oil fuels with high lubricity and flowability.

ADDITIVE MIXTURE AS COMPONENT OF MINERAL OIL COMPOSITIONS

[0001] This invention relates to an additive mixture as component of compositions with mineral oil as the main component and trace portions of an additive mixture as well as a method for producing mineral oil compositions that contain the additive mixture.

[0002] Compositions of mineral oil as the main component and trace portions of additive mixtures of ethylene-vinylacetate copolymers, hydrocarbon polymers, esterified maleic anhydride-olefin copolymers, polar nitrogen compounds such as amine salts of multivalent carboxylic acids and esterified polyoxyalkylenes are known (WO 94/10 267 A1, WO 95/33 012 A1, EP 0 921 183 A1, WO 93/14 178 A1, EP 0 889 323 A1).

[0003] Disadvantages include insufficient flow properties and stability in storage of these compositions at low temperatures as well as limited lubricating ability of these formulations when the mineral oil component has a sulfur content below 0.005 mass %.

[0004] It is the object of this invention to provide an additive mixture as component for compositions of mineral oil as their main component and trace portions of an additive mixture that have improved flow properties and improved stability in storage at low temperatures and improved lubricity. The improved flow behavior is to result in energy savings at the pump sets through which these formulations are transported. These additive mixtures are to be developed taking into account that mineral oils with a very low sulfur content are to be used to make fuels with improved environmental compatibility as regards pollutant emissions.

[0005] The object of the invention was achieved by an additive mixture as component of compositions of mineral oil as main component and trace portions of an additive mixture comprising the following additive components according to the invention:

[0006] a) ethylene-vinylester copolymers with molecular mass weight averages from 3000 to 50000 and an ethylene portion of 50 to 90 mass %, and

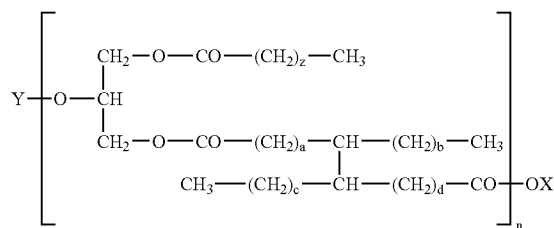
[0007] b) mixed esters of glycerine, in which 50 to 80 mol % of the hydroxy groups are esterified with unsaturated C_{12} - C_{40} monocarboxylic acids and 20 to 50 mol % of the hydroxy groups are esterified with partially imidated and/or partially esterified maleic anhydride copolymers, and/or

[0008] c) partially and/or completely imidated copolymers of maleic anhydride and α -methylstyrene with molecular mass weight averages from 1500 to 15000 and at least one terminal group based on dimeric α -methylstyrene,

[0009] and/or

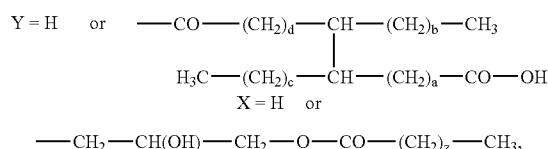
[0010] d) wax compositions based on natural starting materials of type

[0011] d1) wax-like oligomeric esters based on glyceryl monostearate and dimeric acid in which the conversion product corresponds to the



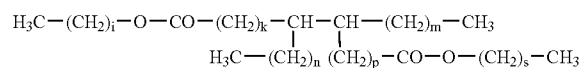
[0012] n structure by at least 90 mass %,

[0013] where $n=1$ to 20, the total of $a+b+c+d=30$, $z=12$ to 20



[0014] and/or

[0015] d2) wax esters with the vaseline-like consistency based on at least two different straight-chain and/or branched C_{14} - C_{36} -alcohols and dimeric acids in which the conversion product corresponds to the



[0016] structure by at least 80 mass %,

[0017] where $i=13$ to 35; $s=13$ to 35,

[0018] the total of $k+m+n+p$ is 30 to 34, and

[0019] $(\text{CH}_2)_i$ or $(\text{CH}_2)_s$ are straight-chain or straight-chain and branched,

[0020] whereby the content of the additive mixture in the mineral oil is 0.005 to 1 mass % and the mass proportion of the additive components a/b or a/c or a/d is in the range from 10:90 to 90:10, respectively.

[0021] Examples of vinyl ester components that may be contained as additive component a) in the ethylene-vinylester copolymers are vinyl acetate, vinyl propionate, 2-ethylhexyl vinylester, vinyl laurate, 2-hydroxyethyl vinylester, and 4-hydroxybutyl vinylester.

[0022] The ethylene-vinylester copolymers may contain 1 to 30 mass %, in relation to the vinyl ester, of other unsaturated ester components such as (meth)acrylic esters like methyl methacrylate, acrylic methyl ester, methacrylic ethyl ester, butyl acrylate, 2-ethylhexyl acrylate, dodecyl acrylate, ethyleneglycol dimethacrylate or hydroxyethyl methacrylate and/or vinyl ethers such as octylvinyl ether or hexanediol monovinyl ether.

[0023] Such ethylene-vinylester copolymers are preferred as additive component a) in the ethylene-vinylacetate copolymer additive mixture that has a vinyl acetate content of 12 to 50 mass %.

[0024] Another preferred variant of the ethylene-vinylester copolymers contained as additive component a) in the additive mixture is that the ethylene-vinylester copolymers are mixtures of 10 to 90 mass % of unmodified ethylene-vinylester copolymers and 90 to 10 mass % of ethylene-vinylester copolymers modified with polar groups.

[0025] The ethylene-vinylester copolymers are modified by polar groups in that specific terminal groups such as aldehyde terminal groups, preferably terminal groups from acetaldehyde, propionaldehyde, butyraldehyde, or isobutyraldehyde, carboxyalkylmercapto terminal groups, preferably terminal groups from mercaptoacetic acid or mercaptopropionic acid, or alkoxy terminal groups are incorporated into the copolymer, in that hydroxy and/or carboxy groups are incorporated into the copolymer by partial oxidation, saponification, or acetalation as well as by grafting polar, ethylenically unsaturated monomers onto the copolymer.

[0026] Preferred are the modified ethylene-vinylester copolymers oxidized ethylene-vinylester copolymers, partially saponified ethylene-vinylester copolymers, hemiacetals of partially saponified ethylene-vinylester copolymers and/or ethylene-vinylester copolymers grafted with polar unsaturated monomers of the vinyl ester, (meth)acryl ester, and/or vinyl ether type.

[0027] The oxidized ethylene-vinylester copolymers preferably are oxidized ethylene-vinylacetate copolymers with molecular mass number averages from 800 to 5000, acid numbers from 2 to 40 mg KOH/g and OH numbers from 20 to 150 mg KOH/g.

[0028] The partially saponified ethylene-vinylester copolymers preferably are ethylene-vinylacetate copolymers with molecular mass number averages from 800 to 5000, 5 to 30 mass % of whose vinyl acetate units are saponified.

[0029] In another preferred variant, the modified ethylene-vinylester copolymers are hemiacetals of ethylene-vinylester-vinylalcohol copolymers with butyraldehyde. Examples of hemiacetals of ethylene-vinylester-vinylalcohol copolymers with butyraldehyde are hemiacetals of ethylene-vinylacetate-vinylalcohol copolymers that were reacted in heterogenic phase with butyraldehyde as described in DD 295 507 A7.

[0030] Grafted ethylene-vinylester copolymers can be produced by reacting the unsaturated monomers in an extruder (DD 282 462 B5) or stirred tank reactor (DD 293 125 B5) in the presence of thermally decomposing radical formers. It is also possible to perform the modification during the production of the copolymer according to the high-pressure process by adding the monomer dose to the polymer melt in a low-pressure separator or in a discharging extruder.

[0031] In particular, the grafted ethylene-vinylester copolymers as additive component a) are ethylene-vinylacetate copolymers grafted with vinylacetate and having molecular mass number averages from 800 to 5000 and a total vinylacetate content of 20 to 60 mass %, the vinylac-

etate content of the copolymer backbone chain being from 10 to 40 mass %, and the portion of the grafted vinylacetate branches making up 10 to 20 mass %.

[0032] The ethylene-vinylester copolymers in the additive compositions may contain up to 35 mass % of poly-C₆-C₃₆-alkyl (meth)acrylate.

[0033] Examples of maleic anhydride copolymers that may be present partially imidated or partially esterified as acid component in the mixed esters of glycerine as additive component b) the additive mixture are copolymers of maleic anhydride and the comonomer components C₂-C₂₀-olefins, C₈-C₂₀-vinyl aromatics, C₄-C₂₁-acrylic esters, C₅-C₂₂-methacrylic esters, C₅-C₁₄-vinylsilane, C₆-C₁₅ acrylate silanes, acrylic acid, methacrylic acid, acrylnitrile, vinyl pyridine, vinyl oxazoline, isopropenyl oxazoline, vinyl pyrrolidone, amino-C₁-C₈-alkyl-(meth)acrylate, C₃-C₂₀-vinylester, C₃-C₂₀-vinylether and/or hydroxy-C₁-C₈-alkyl-(meth)acrylate. Particularly preferred comonomer components are isobutylene, diisobutylene, vinylacetate, styrene and α -methylstyrene.

[0034] The maleic anhydride copolymers preferably have a molar ratio of maleic anhydride to comonomer from 1:1 to 1:9 and molecular mass weight averages from 5000 to 500000. Partial imidation can be performed using ammonia, C₁-C₂₄-monoalkyl amines, C₆-C₁₈-aromatic monoamines, C₂-C₁₈-monoaminoalcohols, monoaminated poly(C₂-C₄-alkylene) oxides with a molar weight of 400 to 3000 and/or monoetherified poly(C₂-C₄-alkylene) oxides with a molar weight of 100 to 10000, the molar ratio of anhydride groups copolymer/ammonia, C₁-C₂₄-monoalkylamine, C₆-C₁₈-aromatic monoamines, C₂-C₁₈-monoaminoalcohols or monoaminated poly-(C₂-C₄-alkylene) oxide, respectively, being in the range from 1:1 to 20:1.

[0035] Examples of suitable amines with which maleic anhydride copolymers are partially imidated are C₁₂-C₂₄-monoalkyl amines such as oleylamine, dodecylamine, hexadecylamine, octadecylamine, or eicosylamine, monosubstituted diamines such as N-dodecyl-1,3-diaminopropane, N-octadecyl-1,3-diaminopropane, or N-octadecyl propylene triamine, or aminoalcohols such as aminodecane-10-ol or aminohexadecane-16-ol.

[0036] Examples of suitable alcohols with which the maleic anhydride copolymers are partially esterified as acid components in the mixed esters of glycerine as additive component b) of the additive mixture are C₁-C₁₈-alcohols such as methanol, ethanol, ethyl hexanol, or stearyl alcohol.

[0037] Examples of the unsaturated C₁₂-C₄₀-monocarboxylic acids contained as esterifying component in the mixed esters of glycerine of the additive mixture are oleic acid, elaidinic acid, ricinoleic acid, eleostearic acid, linolic acid, linolenic acid, and erucaic acid, or dimeric acids based on oleic acid or linolenic acid.

[0038] Examples of suitable methods for producing the mixed esters of glycerine in which 50 to 80 mol % of the hydroxy groups are esterified with unsaturated C₁₂-C₄₀-monocarboxylic acids and 20 to 50 mol % of the hydroxy groups are esterified with partially imidated and/or partially esterified maleic anhydride copolymers are partial reaction of glycerine with unsaturated C₁₂-C₄₀-monocarboxylic acids and subsequently with partially imidated and/or partially esterified maleic anhydride copolymers or partial reaction of

glycerine with partially imidated and/or partially esterified maleic anhydride copolymers and subsequently with unsaturated C_{12} - C_{40} -monocarboxylic acids. The reaction can be performed in the melt, preferably in continuous kneaders at temperatures from 50 to 135° C. under vacuum degassing or as a solvent process preferably in aromatic solvents at 85 to 140° C.

[0039] In the mixed esters of glycerine of the additive mixture, the C_{12} - C_{40} -monocarboxylic acids contained as esterifying component preferably consist of 45 to 52 mass % C_{22} -monocarboxylic acids in relation to the overall weight of the C_{12} - C_{40} -monocarboxylic acids.

[0040] The partially imidated maleic anhydride copolymers contained as esterifying components in the mixed esters of glycerine as additive component b) of the additive mixture preferably are maleic anhydride- α -methylstyrene copolymers partially imidated with C_6 - C_{24} -monoalkylamines in which the mole ratio of anhydride groups in the copolymer/bound C_6 - C_{24} -monoalkylamine in the copolymer is in the range from 8:1 to 2:1.

[0041] Examples of partially imidated copolymers of maleic anhydride and α -methylstyrene as additive component c) are copolymers with an approximately equimolar ratio of both monomers in which the partial and/or complete imidation was performed with ammonia, C_1 - C_{24} -monoalkylamines, C_6 - C_{18} -aromatic monoamines, C_2 - C_{18} -monoaminoalcohols, monoaminated poly- $(C_2$ - C_4 -alkylene) oxides, and/or monoetherified poly- $(C_2$ - C_4 -alkylene) oxides whereas the mole ratio of anhydride groups copolymer/ammonia, amino group C_1 - C_{24} monoalkylamines, C_6 - C_{18} -aromatic monoamines, C_2 - C_{18} monoaminoalcohols and monoaminated poly- $(C_2$ - C_4 -alkylene) oxide, respectively is 1:1 to 20:1.

[0042] The partially imidated copolymers consisting of maleic anhydride and α -methylstyrene as additive component c) preferably are maleic anhydride- α -methylstyrene copolymers partially imidated with C_6 - C_{24} -monoalkylamines in which the mole ratio of anhydride groups in the copolymer to bound C_6 - C_{24} -monoalkylamine in the copolymer is 8:1 to 1.3:1.

[0043] Examples of C_{12} - C_{24} -monoalkylamines with which the partially imidated maleic anhydride- α -methylstyrene copolymers contained in the additive mixture can be imidated are dodecylamine, tetradecylamine, hexadecylamine, octadecylamine, oleylamine, or eicosylamine.

[0044] The wax-like oligomeric esters on the basis of glyceryl monostearate and dimeric acid as additive component d1) are the oligomeric esters described in EP 0 934 921 A1. The glyceryl monostearate component can be produced by enzymatically cleaving rape-seed oil, isolating the glycerine monooleate that forms, and subsequent hydration. A suitable method for producing the dimeric acid component is the splitting of vegetable oils and subsequent dimerization of the unsaturated fatty acids that form. The oligomeric esters are produced by solvent-free oligocondensation with acid catalysis.

[0045] Preferred as additive components d1) are wax-like oligomeric esters that have a degree of oligomerization from 2 to 8.

[0046] The wax esters with the vaseline-like consistency d2) are the wax esters described in EP 0 970 988 A1.

[0047] Preferred as wax esters with the vaseline-like consistency d2) contained in the additive mixture are wax esters based on Guerbet alcohols of the 2-hexyldecane-1-ol, 2-octyldecane-1-ol or 2-octyldecane-1-ol type and dimeric acids obtained by splitting vegetable oils with a high oleic acid content and subsequent catalytic dimerization. The wax esters can be produced from the Guerbet alcohols and the dimeric acid by catalytic esterification in the presence of acidic catalysts at temperatures from 100 to 160° C. in stirred tank reactors by applying a vacuum of -0.5 to -1.5 bar.

[0048] Examples of mineral oils that form the main component in the mineral oil compositions are crude oils and petroleum distillates with a distillation range from 100 to 500° C. such as lubricating oils, kerosine, diesel oil, heating oil, heavy fuel oils, petroleum, tractor fuel, and cracked gasoline. The mineral oils may also contain up to 30 mass % of synthesized hydrocarbons from the Fischer-Tropsch process, up to 20 mass % of modified vegetable oils based on sunflower oil, soybean oil, rape-seed oil, or animal oils, biodiesel and/or up to 10 mass % of alcohols such as methanol or ethanol.

[0049] Preferred are mineral oils crude oils, or fuel oils from a middle distillate with a sulfur content of under 0.05 mass %, particularly fuel oils, gas oils, or diesel oils.

[0050] The compositions of mineral oil may contain a total of up to 200 mass % in relation to the additive components a+b, a+c, a+d, a+b+c, a+b+c+d, or a+c+d, other additive components of the type of fatty acid mixtures, polar nitrogen compounds, preferably polyamines, etheramines, aminoalcohols, amine salts, amides or imides of multivalent carboxylic acids; modified copolymers of ethylenically unsaturated C_4 - C_{20} -dicarboxylic anhydrides, non-modified ethylene-vinylester copolymers, C_7 - C_{30} -alcohols, polyalkylene glycols, esters or ethers of polyoxyalkylene compounds, C_2 - C_6 -oxyalkyl-bridged C_{12} - C_{40} -monocarboxylic acids, preferably C_3 - C_4 -oxyalkyl-bridged unsaturated C_{16} - C_{24} monocarboxylic acids with a content of C_{22} -monocarboxylic acids in relation to the overall weight of the C_{16} - C_{24} monocarboxylic acids of 45 to 52 mass %, hydrocarbon polymers, alkylphenol-aldehyde copolymers, aromatic compounds with C_8 - C_{100} -alkyl substituents, carboxylated polyamines, detergents, corrosion inhibitors, demulsifiers, metal deactivators, cetane number improvers, defoaming agents and/or cosolvents.

[0051] Examples of the fatty acid mixtures contained as other additive components in the mineral oil compositions are mixtures of saturated and/or unsaturated C_6 - C_{40} -carboxylic acids such as lauric acid, palmitic acid, oleic acid, linolenic acid, dimeric fatty acids, and alkenyl succinic acids.

[0052] Examples of the polar nitrogen compounds of the polyamine type contained as other additive components in the mineral oil compositions are N-hexadecyl-1,3-diaminopropane, N-octadecyl dipropylenetriamine, N-dodecyl-1,3-diaminopropane, N,N'-didodecyl-1,3-diaminopropane, and N,N'-dioctadecyl-dipropylenetriamine.

[0053] Examples of the polar nitrogen compounds of the etheramine type contained as other additive components in the mineral oil compositions are 3-methoxypropylamine, 3-N-octyloxypropyl-1,3-diaminopropane, and 3-N-(2,4,6-trimethyldecyloxypropyl)-1,3-diaminopropane.

[0054] Examples of the polar nitrogen compounds of the amino-alcohol type contained as other additive components in the mineral oil compositions are aminopentane-5-ol, aminoundecane-11-ol, and 2-amino-2-methylpropanol.

[0055] Examples of the amines on which polar nitrogen compounds of the amine salt, amide, or imide type of multivalent carboxylic acids are based are C_8 - C_{40} -amines such as hydrated tallamine, tetradecylamine, eicosylamine, di-octadecylamine, methyl behenylamine, N-oleyl-1,3-diaminopropane, N-stearyl-1-methyl-1,3-diaminopropane or N-oleyldipropylenetriamine.

[0056] Examples of the multivalent carboxylic acids on which polar nitrogen compounds of the amine salt or amide of multivalent carboxylic acids types are based are phthalic acid, isophthalic acid, terephthalic acid, naphthalene dicarboxylic acid, ethylene diamine tetraacetic acid, and cyclohexane dicarboxylic acid.

[0057] Special examples of the polar nitrogen compounds of the amine salt type contained as other additive components in the mineral oil compositions are N-methyl triethanol ammonium distearyl ester chloride and N-methyl triethanol ammonium distearyl ester methosulfate.

[0058] Examples of ethylenically unsaturated C_4 - C_{20} -dicarboxylic anhydrides that may be contained as the monomeric component in the modified copolymers of ethylenically unsaturated C_4 - C_{20} -dicarboxylic anhydrides as another additive component are allylsuccinic anhydride, bicycloheptene dicarboxylic anhydride, bicyclooctene dicarboxylic anhydride, carbomethoxymaleic anhydride, citraconic anhydride, cyclohexene dicarboxylic anhydride, dodecencyl succinic anhydride, glutaconic anhydride, itaconic anhydride, maleic anhydride, mesaconic anhydride, methyl bicycloheptene dicarboxylic anhydride and/or methyl cyclohexene dicarboxylic anhydride, of which maleic anhydride and/or itaconic anhydride are preferred.

[0059] Examples of suitable comonomers for ethylenically unsaturated C_4 - C_{20} -dicarboxylic anhydrides that may be contained as the monomeric component in the modified copolymers of ethylenically unsaturated C_4 - C_{20} -dicarboxylic anhydrides as another additive component are ethylenically unsaturated monomers such as C_2 - C_{20} -olefins, C_8 - C_{20} -vinylaromatics, C_4 - C_{21} -acrylic esters, C_5 - C_{22} -methacrylic esters, C_5 - C_{14} -vinylsilanes, C_6 - C_{15} -acrylate silanes, acrylic acid, methacrylic acid, acrylonitrile, vinyl pyridine, vinyl oxazoline, isopropenyl oxazoline, vinyl pyrrolidone, amino- C_1 - C_8 -alkyl-(meth)acrylate, C_3 - C_{20} -vinylester, C_3 - C_{20} -vinylether and/or hydroxy- C_1 - C_8 -alkyl-(meth)acrylate. Particularly preferred ethylenically unsaturated monomers are isobutylene, diisobutylene, vinylacetate, styrene and α -methylstyrene.

[0060] Particularly preferred as modified copolymers are copolymers of C_4 - C_{20} -ethylenically unsaturated acid anhydrides and ethylenically unsaturated monomers with a mole ratio from 1:1 to 1:9 and molecular mass weight averages from 5000 to 500000 that were reacted with ammonia, C_1 - C_{24} -monoalkyl amines, C_6 - C_{18} -aromatic monoamines, C_2 - C_{18} -monoaminoalcohols, monoaminated poly(C_2 - C_4 -alkylene) oxides with a molar weight of 400 to 3000 and/or monoetherified poly(C_2 - C_4 -alkylene) oxides with a molar weight of 100 to 10000, the molar ratio of anhydride groups copolymer/ammonia, C_1 - C_{24} -monoalkylamine, C_6 - C_{18} -aro-

matic monoamines, C_2 - C_{18} -monoaminoalcohols or monoaminated poly(C_2 - C_4 -alkylene) oxide amino groups, respectively, being in the range from 1:1 to 20:1.

[0061] Particularly suited as partially or completely imidated copolymers from ethylenically unsaturated C_4 - C_{20} -dicarboxylic anhydrides are maleic anhydride copolymers imidated with C_{12} - C_{24} -monoalkyl amines such as oleylamine, dodecylamine, hexadecylamine, octadecylamine, or eicosylamine, monosubstituted diamines such as N-dodecyl-1,3-diaminopropane, N-octadecyl-1,3-diaminopropane, or N-octadecyl propylene triamine, or aminoalcohols such as aminodecane-10-ol or aminohexadecane-16-ol.

[0062] Examples of C_7 - C_{30} -alcohols that can be contained as other additive components in the mineral oil compositions are dodecanol, stearyl alcohol, and ceryl alcohol.

[0063] Examples of polyalkylene glycols that can be contained as other additive components in the mineral oil compositions are polyethylene glycols, polypropylene glycols, and ethylene oxide-propylene oxide copolymers with molar weights from 500 to 5000.

[0064] Examples of esters of polyoxyalkylene compounds that can be contained as other additive components in the mineral oil compositions are C_{10} - C_{24} -monoalkyl esters or dialkyl esters of polyalkylene glycols such as polyethylene glycol monostearyl ester or polypropylene glycol dioleate.

[0065] Examples of ethers of polyoxyalkylene compounds that can be contained as other additive components in the mineral oil compositions are C_1 - C_4 -monoalkyl ethers or dialkyl ethers of polyalkylene glycols such as polyethylene glycol monomethyl ether or polypropylene glycol dibutyl ether.

[0066] The C_2 - C_6 -oxyalkyl-bridged C_{12} - C_{40} -monocarboxylic acids that can be contained as other additive components in the mineral oil compositions consist of a C_2 - C_6 -polyalcohol component and a C_{12} - C_{40} -monocarboxylic acid component.

[0067] Examples of polyalcohols that can be contained as alcohol component in the C_2 - C_6 -oxyalkyl-bridged C_{12} - C_{40} -monocarboxylic acids that may form another additive component are ethylene glycol, polyalkylene glycols, glycerine, 1,1,1-tris-(hydroxymethyl) propane, pentaerythritol, and sorbitol.

[0068] Examples of C_{12} - C_{40} -monocarboxylic acids that may be contained as carboxylic acid component in the C_2 - C_6 -oxyalkyl-bridged C_{12} - C_{40} -monocarboxylic acid that may form another additive component are lauric acid, palmitic acid, stearic acid, oleic acid, elaidic acid, ricinoleic acid, eleostearic acid, linolic acid, linolenic acid, and erucic acid or dimeric acids based on oleic acid or linolenic acid.

[0069] Also preferred as C_2 - C_6 -oxyalkyl-bridged C_{12} - C_{40} -monocarboxylic acids are mixed esters of polyalcohols in which the polyalcohols are esterified by mixtures of C_{12} - C_{40} -monocarboxylic acids. Special examples of C_2 - C_6 -oxyalkyl-bridged C_{12} - C_{40} -monocarboxylic acids are the monoester of ethylene glycol with dilinolenic acid, a C_{36} -dimeric acid, the diester of propylene glycol with oleic acid, and the triester of pentaerythritol with stearic acid.

[0070] Particularly preferred as C_2 - C_6 -oxyalkyl-bridged C_{12} - C_{40} -monocarboxylic acids are esters of unsaturated

C₁₆-C₂₄-monocarboxylic acids with C₃-C₄-polyalcohols, the C₂₂-monocarboxylic acid content in relation to the overall weight of the C₁₆-C₂₄-monocarboxylic acids being 45 to 52 mass %.

[0071] Examples of unsaturated C₁₆-C₂₄-monocarboxylic acids that may be contained in the preferred esters of unsaturated C₁₆-C₂₄-monocarboxylic acids with C₃-C₄-polyalcohols are oleic acid, linolic acid, linolenic acid, and erucic acid.

[0072] Examples of hydrocarbon polymers that may be contained as other additive components in the mineral oil compositions are copolymers of ethylene and C_3-C_{20} - α -olefins such as ethylene-propylene copolymers or ethylene-dodecene copolymers or hydrated polymers of multiply unsaturated monomers of the hydrated diene copolymer type such as hydrated polybutadiene or hydrated polyisoprene with molecular mass number averages up to 30000.

[0073] Examples of alkyl phenol-aldehyde copolymers that may be contained as other additive components in the mineral oil compositions are copolymers that can be produced by reacting alkylated phenols such as phenol-propylene oligomer adducts with paraformaldehyde.

[0074] Examples of aromatic compounds with C₈-C₁₀₀-alkyl substituents that may be contained as other additive components in the mineral oil compositions are compounds that can be produced by means of Friedel-Crafts condensation of halogenated hydrocarbons such as halogenated polyethylene wax with aromatic hydrocarbons like benzene or naphthalene.

[0075] Examples of detergents that may be contained as other additive components in the mineral oil compositions are aliphatic sulfonic acids such as C₈-C₃₀-alkane sulfonates or aromatic-aliphatic alkane sulfonates, especially nonylbenzene sulfonic acid, dodecylbenzene sulfonic acid, didodecylbenzene sulfonic acid, and nonylnaphthalene sulfonic acid.

[0076] Examples of demulsifiers that may be contained as other additive components in the mineral oil compositions are oxalkylated phenol-formaldehyde condensates, polyalkylene glycol-modified diglycid ethers, polyesteramines or alkoxylated fatty acids.

[0077] Examples of cetane number improvers that may be contained as other additive components in the mineral oil compositions are organic nitric esters such as ethylhexyl nitrate, cyclohexyl nitrate, or ethoxyethyl nitrate, or soluble organic peroxides, hydroperoxides, or peresters.

[0078] Preferred defoaming agents that may be contained as other additive components in the mineral oil compositions are polyalkylene oxide-siloxane block copolymers and carboxylated polyamines.

[0079] Examples of polyalkylene oxide-siloxane block copolymers are block copolymers that contain a combination of trifunctional siloxane blocks such as monomethyl siloxane groups, difunctional siloxane groups such as dimethyl siloxane groups, and monofunctional siloxane groups such as trimethyl siloxane groups; a preferred length of the siloxane blocks is from 5 to 20 monomeric units. The preferred block length for the polyalkylene oxide blocks is 2 to 40 monomeric units, preferred are polyoxyalkylene blocks consisting of ethylene oxide and/or propylene oxide units.

[0080] Examples of carboxylated polyamines as defoaming agents are reaction products of C_8 - C_{24} -fatty acids and amines such as ethylene diamine, butylene diamine, diethylene triamine, and pentaethylene hexamine-1,2-diaminobutanol.

[0081] Examples of cosolvents that may be contained as other additive components in the mineral oil compositions are gasoline fractions, toluene, xylene, ethyl benzene, isononanol, ethyl hexanol, dodecyl phenol, epoxidized rape-seed oil, and epoxidized soybean oil.

[0082] The compositions of mineral oil as the main component and trace portions of an additive mixture are produced using a method in which, according to the invention, mineral oil compositions that comprise the additive components

[0083] a) ethylene-vinylester copolymers with molar mass averages from 3000 to 50000 and an ethylene portion of 50 to 90 mass %, and

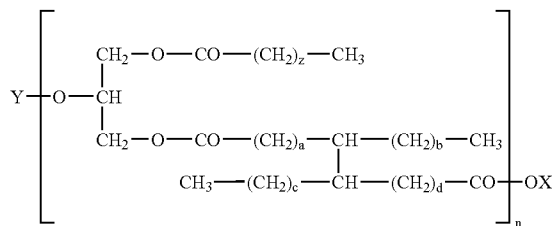
[0084] b) mixed esters of glycerine wherein 50 to 80 mol % of the hydroxy groups are esterified with unsaturated C₁₂-C₄₀ monocarboxylic acids and 20 to 50 mol % of the hydroxy groups are esterified with partially imidated and/or partially esterified maleic anhydride copolymers, and/or

[0085] c) partially and/or completely imidated copolymers of maleic anhydride and α -methylstyrene with molecular mass weight averages from 1500 to 15000 and at least one terminal group based on dimeric α -methylstyrene.

[0086] and/or

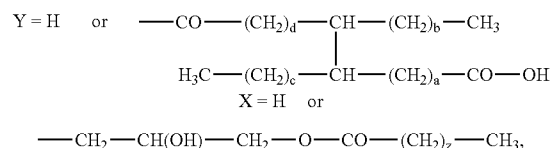
[0087] d) wax compositions based on natural starting materials of type

[0088] d1) wax-like oligomeric esters based on glyceryl monostearate and dimeric acid in which the conversion product corresponds to the



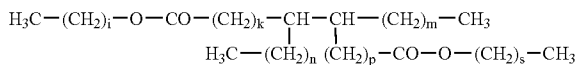
[0089] structure by at least 90 mass %,

[0090] where n=1 to 20, the total of a+b+c+d=30, z=12 to 20



[0091] and/or

[0092] d2) wax esters with vaseline-like consistency based on at least two different straight-chain and/or branched C_{14} - C_{36} alcohols and dimeric acids in which the conversion product corresponds to the



[0093] structure by at least 80 mass %,

[0094] where $i=13$ to 35 ; $s=13$ to 35 ,

[0095] the total of $k+m+n+p$ is 30 to 34 , and

[0096] $(\text{CH}_2)_i$ or $(\text{CH}_2)_s$ are straight-chain or straight-chain and branched,

[0097] whereby the content of the additive mixture in the mineral oil is 0.005 to 1 mass % and the mass proportion of the additive components a/b or a/c or a/d is in the range from $10:90$ to $90:10$, respectively,

are produced in a prehomogenization process in which

[0098] solutions containing 1 to 60 mass % of additive components in mineral oil middle distillates are produced at 20 to 90°C . in a first process step, and

[0099] the solutions containing the additive components are homogenized with the mineral oil as the main component in a second process step,

while other additive components of a total of 0 to 200 mass % in relation to the additive components a+b, a+c, a+d, a+b+c, a+b+c+d, or a+c+d are added to the mineral oil in the first and/or second process step.

[0100] The compositions of mineral oil as the main component and trace portions of an additive mixture are especially suitable as flowable media to be transported at low temperatures and as mineral oil with high lubricity and flowability.

[0101] Examples of the flowable media to be transported at low temperatures are the transport of crude oil formulations from the extraction site of the crude oil through pipelines to loading and storage and the transport of diesel or heating oil formulations in pipelines.

[0102] The invention is explained in greater detail by the examples below.

EXAMPLES

[0103] The characteristic numbers were determined in accordance with the following test methods:

Cloud point (CP): DIN EN 23 015

Cold filter plugging point (CFPP): EN 116

Distillation analysis: EN ISO 3405, ASTM D 86

Acid number: DIN 53402

Saponification number: DIN 53401

Kinematic viscosity: DIN 51562

Solidification point: DIN ISO 2207

Penetration: DIN 51580

Vinyl acetate content: modified method according to ISO 8995, DIN 16778 Part 2

[0104] 2 g of sample are weighed in with 0.001 g precision and dissolved in a 300 ml Erlenmeyer flask with 70 ml distilled xylene and 2 boiling beads under refluxing for ca. 15 minutes. Then ca. 30 ml of ethanol are slowly added via the reflux cooler, the Erlenmeyer flask is taken off the heating plate, 30 ml of ethanol, 0.5 n KOH from the burette and 2 boiling beads are added, and the sample is refluxed for 1 hour. The sample is taken off the reflux again, mixed with 30 ml of methanolic-aqueous 0.5 n HCl and 2 boiling beads, and refluxed for another 15 minutes. After adding 2 to 3 drops of phenolphthaleine solution (1 mass % in ethanol), the sample is titrated drop by drop under shaking with ethanolic 0.5 n KOH until its color changes to red. A blank value has to be determined at the same time.

$$\text{Vinyl acetate content in mass \%} = \frac{(V - BV) \times F \times 43}{10 \times E}$$

E=original sample weight in g

F=factor of the ethanolic 0.5 n KOH

V=consumption in ml of 0.5 n ethanolic KOH for the sample

B=consumption in ml of 0.5 n ethanolic KOH for the blank value

Lubricating ability: Lubricity test (adjusted "wear scar diameter" at 60°C .)

according to ISO 12156-1

Short-Time Sedimentation Test:

[0105] To test the sedimentation tendency of recrystallized paraffins in mineral oil, a 500 ml sample is stored in a graduated cylinder for 16 hours, then the top 80 volume percent of the sample are drawn off and discarded. The remaining 20 vol % of the sample (100 ml) are homogenized at 40°C ., then the cloud point (CP) is determined according to DIN EN 23 015.

SEDAB Filtration Test:

[0106] A 500 ml mineral oil sample is shaken vertically 20 times, kept at 10°C . for 16 hours, shaken vertically 10 times, and the entire sample is filtered all at once through a filter of cellulose nitrate (50 mm in diameter, 0.8 μm pore size) that sits on a suction cap with a vacuum of approx. 200 hPa. The time in which the sample runs through the filter is measured. The SEDAB filtration test is deemed passed if the sample passes through the filter in a period <120 s.

Example 1

1.1 Parent Products

1.1.1 Diesel without Additives

Batch: 16080601 test DF 1

Characterization:

Cloud point (CP): $+6^\circ\text{C}$;

Cold filter plugging point (CFPP): $+2^\circ\text{C}$.

Lubricity test: 563 μm

[0107] Distillation analysis:

Distilled quantity (vol. %)/temperature (° C.)										
IBP	10	20	30	40	50	60	70	80	90	FBP
189	243	259	271	281	292	303	317	334	357	385

1.1.2 Additive Component a)

[0108] Ethylene-vinylacetate copolymer wax (manufactured by LEUNA Polymer GmbH, vinyl acetate content 28.3 mass %, molecular mass weight average 3150 g/mol).

1.1.3 Additive Component b)

[0109] The mixed ester of glycerine was produced in a melt esterification process.

[0110] A maleic anhydride-octadecene copolymer partially esterified with dodecyl alcohol (mole ratio 1:2.2, acid number 40, molecular mass number average 2400) is dosed at 3.8 kg/h into the feed screw of a Werner&Pfleiderer ZSK 30 twin-screw extruder, L/D ratio 48, with a side stream dosing unit for liquid media and two vacuum degassing zones and a belt weigher continuous scale for dosing and melted at 90° C. Glycerine dierucic ester from a storage tank heated to 90° C. is added to the melt via the side stream dosing unit at 2.0 kg/h, reacted in the first reaction zone (dwell time 4.5 min) at 110° C., degassed, reacted in the second reaction zone at 130° C. (dwell time 3.5 min), degassed, delivered at 85° C. into a self-cleaning melt filter

CP value of the short-time sedimentation test is +7° C. The SEDAB filtration test is deemed passed (500 ml in 84 s).

[0115] If a mineral oil formulation that only contains the copolymer wax as an additive is produced under the same conditions, the CFPP value is -3° C. and the “wear scar diameter” is 520 µm. The CP value of the short-time sedimentation test is +10° C. The SEDAB filtration test is deemed failed (468 ml in >120 s).

Example 2

2.1 Parent Products

2.1.1 Diesel without Additives

Batch: 030210 test DF 2

Characterization:

Cloud point (CP): +7° C.

Cold filter plugging point (CFPP): +2° C.

Lubricity test: 556 µm

[0116] Distillation Analysis:

Distilled quantity (vol. %)/temperature (° C.)										
IBP	10	20	30	40	50	60	70	80	90	FBP
235	266	279	291	301	310	320	337	342	357	374

using a melt gear pump (extrex SP, Maag pump systems) and molded into pastilles in a briquetting press with cooling conveyor.

[0111] The resulting mixed ester of glycerine has an acid number of 8.5 and a melting range from 52 to 59° C.

1.2 Production of Solutions Containing the Additive Components in Mineral Oil Middle Distillates

[0112] 20 kg of the additive component b) are mixed in a stirred tank reactor with 60 kg of a 50% solution of additive component a) in an aromatic hydrocarbon mixture (Solvesso) at 65° C. for 120 minutes and the mixture is transferred into a storage tank.

1.3 Production and Testing of the Mineral Oil Compositions

[0113] The additive solution according to 1.2 is injected at 0.48 kg/min into a product stream of diesel without additives, batch 16080601, flowing at 800 kg/min and the mixture is transferred into a storage tank.

[0114] Testing the mineral oil formulation for low-temperature resistance revealed a CFPP value of -10° C. The lubricity test shows a “wear scar diameter” of 405 µm. The

2.1.2 Additive Component a)

[0117] 10 mass % of a partially saponified ethylene-vinylacetate copolymer wax (molecular mass weight average 1850 g/mol, vinyl acetate content of the unsaponified ethylene-vinylacetate copolymer wax 32.5 mass %, degree of saponification 15 mole %) and 90 mass % of an unsaponified ethylene-vinylacetate copolymer wax (manufactured by LEUNA Polymer GmbH, vinylacetate content 31 mass %, molecular mass weight average 2800 g/mole) are intermixed.

2.1.3 Additive Component b)

[0118] The mixed ester of glycerine was produced in a melt esterification process.

[0119] An α -methylstyrene maleic anhydride-octadecene copolymer partially imidated with C₁₆-C₁₈-fatty amine (mole ratio 1.3:1.0, acid number 42, melting point 70° C.) is dosed at 3.6 kg/h via a belt weigher continuous scale into the feed screw of a Werner&Pfleiderer ZSK 30 twin-screw extruder, L/D ratio 48, with side stream dosing unit for liquid media and two vacuum degassing zones and dissolved by heat at 110° C. Glycerine dioleil ester is added to the melt

from a storage tank heated to 90° C. via the side stream dosing unit at 1.14 kg/h, the melt is reacted in the first reaction zone (dwell time 4.5 min) at 115° C., degassed, reacted in the second reaction zone at 130° C. (dwell time 3.5 min), degassed, delivered at 85° C into a self-cleaning melt filter using a melt gear pump (extrex SP, Maag pump systems) and molded into pastilles in a briqueting press with cooling conveyor.

[0120] The resulting mixed ester of glycerine has an acid number of 4.5 and a melting range from 55 to 66° C.

2.1.4 Other Additive Components

[0121] Dodecylacrylate-ethylacrylate copolymer (mole ratio 2:1, molecular mass number average 13500)

2.2 Production of Solutions Containing the Additive Components in Mineral Oil Middle Distillates

[0122] 20 kg of additive component b), 40 kg of a 60% solution of additive component a) in C₈-C₉-diesel aromatic fraction, and 20 kg of a 10% solution of the other additive component, dodecylacrylate-ethylacrylate copolymer in toluene are stirred for 120 minutes in a stirred tank reactor at 65° C. and the mixture is transferred into a storage tank.

2.3 Production and Testing of the Mineral Oil Compositions

[0123] The additive solution according to 2.2 is injected at 0.12 kg/min into a product stream of diesel without additives, batch 030210 DGO, flowing at 800 kg/min and the mixture is transferred into a storage tank.

[0124] Testing the mineral oil formulation for low-temperature resistance revealed a CFPP value of -11° C. The lubricity test shows a "wear scar diameter" of 402 µm.

[0125] The CP value of the short-time sedimentation test is +9° C. The SEDAB filtration test is deemed passed (500 ml in 96 s).

[0126] If a mineral oil formulation that only contains the unsaponified copolymer wax as an additive is produced under the same conditions, the CFPP value is -5° C. and the "wear scar diameter" is 528 µm. The CP value of the short-time sedimentation test is +12° C. The SEDAB filtration test is deemed failed (468 ml in >120 s).

Example 3

3.1 Starting Materials

3.1.1 Heating Oil without Additives

Batch: 030225 test HEL type 1

Characterization:

Cloud point (CP): +1° C.

Cold filter plugging point (CFPP): -1° C.

[0127] Distillation Analysis:

3.1.2 Additive Component a)

[0128] 15 mass % of an oxidized ethylene-vinylacetate copolymer wax (molecular mass weight average 950 g/mol, acid number 18 mg KOH/g, OH number 70 mg KOH/g) and 85 mass % of an unoxidized ethylene-vinylacetate copolymer wax (manufactured by LEUNA Polymer GmbH, vinyl acetate content 32 mass %, molecular mass weight average 2300 g/mol) are intermixed.

3.1.3 Additive Component b)

[0129] The mixed ester of glycerine was produced in a melt esterification process.

[0130] An octadecene maleic anhydride-octadecene copolymer partially imidated with C₁₆-C₁₈-fatty amine (mole ratio 1.4:1.0, acid number 57, melting point 55° C.) is dosed at 4.2 kg/h via a belt weigher continuous scale into the feed screw of a Werner&Pfleiderer ZSK 30 twin-screw extruder, L/D ratio 48, with a side stream dosing unit for liquid media and two vacuum degassing zones, and dissolved by heat at 115° C. Glycerine and an acid mixture of erucic acid and oleic acid are added to the melt from a storage tank heated to 90° C. via the side stream dosing unit at 2.72 kg/h, the melt is reacted in the first reaction zone (dwell time 4.5 min) at 120° C., degassed, reacted in the second reaction zone at 130° C. (dwell time 3.5 min), degassed, delivered at 95° C. into a self-cleaning melt filter using a melt gear pump (extrex SP, Maag pump systems) and molded into pastilles in a briqueting press with cooling conveyor.

[0131] The resulting mixed ester of glycerine has an acid number of 3.5 and a melting range from 55 to 64° C.

3.2 Production of Solutions Containing the Additive Components in Mineral Oil Middle Distillates

[0132] 25 kg of the additive component b) are mixed with 50 kg of a 60% solution of additive component a) in a C₈-C₉-diesel aromatic fraction at 65° C. in a stirred tank reactor for 120 minutes and the mixture is transferred into a storage tank.

3.3 Production and Testing of the Mineral Oil Compositions

[0133] The additive solution according to 3.2 is injected at 0.24 kg/min into a product stream of heating oil without additives, batch 030225, flowing at 800 kg/min, and the mixture is transferred into a storage tank.

[0134] Testing the mineral oil formulation for low-temperature resistance revealed a CFPP value of -15° C.

[0135] If a mineral oil formulation containing only the copolymer wax as an additive is produced under the same conditions, the CFPP value is -12° C.

Distilled quantity (vol. %)/temperature (° C.)

IBP	10	20	30	40	50	60	70	80	90	FBP
165	196	213	230	249	269	290	310	327	344	363

Example 4

4.1 Starting Materials

4.1.1 Heating Oil without Additives

Batch: 030218 test HEL 2

Characterization:

Cloud point (CP): +2° C.

Cold filter plugging point (CFPP): -1° C.

[0136] Distillation Analysis:

Distilled quantity (vol. %)/temperature (° C.)										
IBP	10	20	30	40	50	60	70	80	90	FBP
173	194	207	225	247	273	299	320	337	355	379

4.1.2 Additive Component a)

[0137] 10 mass % of an ethylene-vinylacetate copolymer wax grafted with vinyl acetate (produced according to DD 293 125 A5, total vinyl acetate content 38 mass %, molecular mass weight average 3400 g/mol, vinyl acetate content of the ungrafted ethylene-vinylacetate copolymer wax 32.5 mass %, degree of saponification 32 mole %) and 90 mass % of an ungrafted ethylene-vinylacetate copolymer wax (manufactured by LEUNA Polymer GmbH, vinylacetate content 32.5 mass %, molecular mass weight average 2400 g/mol) are intermixed.

4.1.3 Additive Component b)

[0138] The mixed ester of glycerine was produced in a melt esterification process.

[0139] An α -methylstyrene maleic anhydride copolymer partially esterified with octadecyl alcohol (mole ratio 1.1:1.0, acid number 55, melting point 64° C.) is dosed at 4.0 kg/h via a belt weigher continuous scale into the feed screw of a Werner&Pfleiderer ZSK 30 twin-screw extruder, L/D ratio 48, with a side stream dosing unit for liquid media and two vacuum degassing zones, and dissolved by heat at 90° C. An ester of glycerine and an acid mixture of erucic acid/oleic acid/linolenic acid (mole ratio 6:1:1:1) are added to the melt from a storage tank heated to 110° C. via the side stream dosing unit at 2.4 kg/h, the melt is reacted in the first reaction zone (dwell time 4.5 min) at 125° C., degassed, reacted in the second reaction zone at 135° C. (dwell time 3.5 min), degassed, delivered at 95° C. into a self-cleaning melt filter using a melt gear pump (extrex SP, Maag pump systems) and molded into pastilles in a briquetting press with cooling conveyor.

[0140] The resulting mixed ester of glycerine has an acid number of 5.5 and a melting range from 53 to 63° C.

4.1.4 Other Additive Components

[0141] Polyethylene glycol monomethyl ether, molecular mass number average 1500 2-ethylhexylacrylate-ethylacrylate copolymer (mole ratio 2:1)

4.2 Production of Solutions Containing the Additive Components in Mineral Oil Middle Distillates

[0142] 20 kg of additive component b), 20 kg of a 60% solution of additive component a) in C₈-C₉-diesel aromatic fraction, and 1 kg of the other additive component, polyethylene glycol monomethyl ether, molecular mass number average 1500, and 8 kg of a 10% solution of the other additive component, ethylhexylacrylate-ethylacrylate copolymer (mole ratio 2:1) in toluene are introduced into a stirred tank reactor, stirred for 120 minutes at 65° C., and the mixture is transferred into a storage tank.

4.3 Production and Testing of the Mineral Oil Compositions

[0143] Additive solution according to 4.2 is injected at 0.28 kg/min into a product stream of heating oil without additives, batch 030225, flowing at 800 kg/min, and the mixture is transferred into a storage tank.

[0144] Testing the mineral oil formulation for low-temperature resistance revealed a CFPP value of -14° C.

[0145] If a mineral oil formulation containing only the copolymer wax as an additive is produced under the same conditions, the CFPP value is -1° C.

Example 5

5.1 Starting Materials

5.1.1 Diesel without Additives

Batch: 16080601 test DF 1

Characterization:

Cloud point (CP): +6° C.;

Cold filter plugging point (CFPP): +2° C.

[0146] Distillation Analysis:

Distilled quantity (vol. %)/temperature (° C.)										
IBP	10%	20%	30%	40%	50%	60%	70%	80%	90%	FBP
189	243	259	271	281	292	303	317	334	357	385

5.1.2 Additive Component a)

[0147] Ethylene-vinylacetate copolymer wax (manufactured by LEUNA Polymer GmbH, vinyl acetate content 32 mass %, molecular mass weight average 2300 g/mol).

5.1.3 Additive Component c)

[0148] α -Methylstyrene-maleic anhydride copolymer, partially imidated with C₁₆-C₁₈-fatty amine, molecular mass number average 12800 g/mol, acid number 35

Production of Additive Component C)

[0149] 81 l of α -methylstyrene, 7 l of α -methylstyrene-dimer, and 20 liters of acetone are placed in a 500 l stirred tank reactor, and the stirred tank reactor is heated to 59° C. A solution of 52 kg maleic anhydride and 2.4 kg of azoisobutyric acid dinitrile in 150 l of acetone is evenly dosed into a stirred tank reactor over 6 hours and the reaction mixture is stirred for 6 more hours at 70 to 73° C.

[0150] An analysis sample of the copolymer (MCP5) has an acid number of 445 mg KOH per gram of copolymer. NMR examinations result in 1.3 α -methylstyrene-dimer terminal groups per mole.

[0151] The polymer solution that is still at 54 to 56° C. is now continuously fed into a twin-drum vacuum drier and split into a powdered copolymer with a residual content of 1.1 mass % of volatile ingredients and acetone.

[0152] 382 kg of a C₈-C₉-diesel aromatic fraction boiling above 160° C. and 122 kg of C₁₆-C₁₈-fatty amine are placed in a 500 l stirred tank reactor and heated to 130° C. for partial imidation of the copolymer. 135.5 kg of the copolymer are continuously added to this solution over 4 hours. This raises the temperature inside the stirred tank reactor to 180 to 185° C., and water is formed that is distilled off azeotropically with an approximately equal quantity of C₈-C₉-diesel aromatic fraction. After a total reaction time of 6 hours at 160 to 190° C., 8.5 kg of water and 10.2 kg of solvent are distilled off. A 40% solution of the partially imidated copolymer with an acid number of 35 and a molecular mass number average of 12800 g/mole is obtained.

5.2 Production of Solutions Containing the Additive Components in Mineral Oil Middle Distillates

[0155] 25 kg of a 40% solution of additive component c) in C₈-C₉-diesel aromatic fraction, 50 kg of a 50% solution of additive component a) in an aromatic hydrocarbon mixture (Solvesso), 20 kg of a mixture of C₃-oxyalkyl-bridged unsaturated C₁₈-C₂₄-carboxylic acids as other additive component and 19 kg of a 20% solution of another additive component, ethylacrylate-ethylhexylacrylate copolymer in toluene are intermixed in a stirred tank reactor for 90 minutes at 65° C., and the mixture is transferred into a storage tank.

5.3 Production and Testing of the Mineral Oil Formulation

[0156] Additive solution according to 5.2 is injected at 0.48 kg/min into a product stream of diesel without additives, batch 16080601, flowing at 800 kg/min and the mixture is transferred into a storage tank.

[0157] Testing the mineral oil formulation for low-temperature resistance revealed a CFPP value of -16° C. The CP value of the short-time sedimentation test is +5° C. The SEDAB filtration test is deemed passed (500 ml in 76 s).

[0158] If a mineral oil formulation containing only the copolymer wax as an additive is produced under the same conditions, the CFPP value is -3° C. The CP value of the short-time sedimentation test is +10° C. The SEDAB filtration test is deemed failed (468 ml in >120 s).

Example 6

6.1 Starting Materials

6.1.1 Diesel without Additives

Batch: 030210 test DF 2

Characterization:

Cloud point (CP): +7° C.

Cold filter plugging point (CFPP): +2° C.

[0159] Distillation Analysis:

Distilled quantity (vol. %)/temperature (° C.)										
IBP	10%	20%	30%	40%	50%	60%	70%	80%	90%	FBP
235	266	279	291	301	310	320	337	342	357	374

5.1.4 Other Additive Components

[0153] Mixture of C₃-oxyalkyl-bridged unsaturated C₁₈-C₂₄-carboxylic acids, degree of esterification 92 mol %, content of C₁₈-unsaturated fatty acids 32 mass %, content of C₂₂-unsaturated fatty acids 48 mass %, iodine number 96

[0154] Ethylacrylate-ethylhexylacrylate copolymer (mole ratio 3:2, molecular mass number average 13500)

6.1.2 Additive Component a)

[0160] 10 mass % of a partially saponified ethylene-vinylacetate copolymer wax (molecular mass weight average 1600 g/mol, vinyl acetate content of the unsaponified ethylene-vinylacetate copolymer wax 32 mass %, degree of saponification 15 mole %) and 90 mass % of an ethylene-vinylacetate copolymer wax (manufactured by LEUNA Polymer GmbH, vinylacetate content 32 mass %, molecular mass weight average 2300 g/mol) are intermixed.

6.1.3 Additive Component c)

[0161] α -Methylstyrene-maleic anhydride copolymer, partially imidated with dodecylamine, molecular mass number average 14200 g/mol, acid number 56

Production of Additive Component c)

[0162] 83 l of α -methylstyrene, 5.1 of α -methylstyrene-dimer, and 62 kg of maleic anhydride, and 110 l of 2-butanone are placed in a 500 l stirred tank reactor, and the stirred tank reactor is heated to 70° C. A solution of 1.9 kg of dibenzoyl peroxide and 52 l of 2-butanone is evenly dosed into a stirred tank reactor over 2 hours and the reaction mixture is stirred for 10 more hours at 72 to 73° C.

[0163] An analysis sample of the copolymer has an acid number of 452 mg KOH per gram of copolymer. NMR examinations result in 1.1 α -methylstyrene-dimer terminal groups per mole. The polymer solution that is still at a temperature of 70° C. is now continuously dosed into a 500 l stirred tank reactor containing 280 l of 2-ethyl hexanol and

[0169] If a mineral oil formulation containing only the copolymer wax as an additive is produced under the same conditions, the CFPP value is -5° C. The CP value of the short-time sedimentation test is +12° C. The SEDAB filtration test is deemed failed (468 ml in >120 s).

Example 7

7.1 Starting Materials

7.1.1 Heating Oil without Additives

Batch: 030225 test HEL 1

Characterization:

Cloud point (CP): +1° C.;

Cold filter plugging point (CFPP): -1° C.

[0170] Distillation analysis:

Distilled quantity (vol. %)/temperature (° C.)										
IBP	10%	20%	30%	40%	50%	60%	70%	80%	90%	FBP
165	196	213	230	249	269	290	310	327	344	363

heated to 150° C. while 2-butanone-2 is removed by distillation. 104 kg of a C₁₆-C₁₈-fatty amine are added over 4 hours while the temperature is raised to 165 to 185° C. to remove the water together with a small quantity of 2-ethyl hexanol by distillation.

[0164] A 40% solution of the partially imidated copolymer c) with an acid number of 56 and a molecular mass number average of 14200 g/mole is obtained.

6.1.4 Other Additive Components

[0165] Triesters of pentaerythrite with oleic acid Diethylene glycol monolauryl ester

6.2 Production of Solutions Containing the Additive Components in Mineral Oil Middle Distillates

[0166] 25 kg of a 40% solution of additive component c) in 2-ethyl hexanol, 50 kg of a 60% solution of additive component a) in C₈-C₉-diesel aromatic fraction, 20 kg of triester of pentaerythrite with oleic acid as other additive component, and 1 kg of another additive component, diethylene glycol monolauryl ester are introduced into a stirred tank reactor, stirred for 90 minutes at 65° C., and the mixture is transferred into a storage tank.

6.3 Production and Testing of the Mineral Oil Formulation

[0167] The additive solution according to 6.2 is injected at 0.24 kg/min into a product stream of diesel without additives, batch 030210, flowing at 800 kg/min and the mixture is transferred into a storage tank.

[0168] Testing the mineral oil formulation for low-temperature resistance revealed a CFPP value of -7° C. The CP value of the short-time sedimentation test is +7° C. The SEDAB filtration test is deemed passed (500 ml in 82 s).

7.1.2 Additive Component a)

[0171] 15 mass % of an oxidized ethylene-vinylacetate copolymer wax (molecular mass weight average 950 g/mol, acid number

[0172] 18 mg KOH/g, OH number 70 mg KOH/g) and 85 mass % of an unoxidized ethylene-vinylacetate copolymer wax (manufactured by LEUNA Polymer GmbH, vinyl acetate content 32 mass %, molecular mass weight average 2300 g/mol) are intermixed.

7.1.3 Additive Component c)

[0173] α -Methylstyrene-maleic anhydride copolymer, partially imidated with C₁₂-C₁₄-fatty amine, molecular mass number average 7000 g/mol, acid number 25

Production of Additive Component c)

[0174] 83 l of α -methylstyrene, 12 l of α -methylstyrene-dimer, and 62 kg of maleic anhydride, and 140 l of 1,2-dichloroethane are placed in a 500 l stirred autoclave, and the stirred autoclave is heated to 90° C. A solution of 2.5 kg of tert.-butylperoxy-2-ethyl hexanoate and 55 l of 1,2-dichloroethane is evenly dosed into a stirred autoclave over 2 hours and the reaction mixture is stirred for 10 more hours at 90 to 93° C.

[0175] An analysis sample of the copolymer has an acid number of 430 mg KOH per gram of copolymer. NMR examinations result in 1,4 α -methylstyrene-dimer terminal groups per mole.

[0176] The polymer solution that is still at ca. 90° C. is now continuously fed into a 500 l stirred tank reactor containing 280 l of a C₈-C₉-diesel aromatic fraction and 122 kg of a C₁₂-C₁₄-fatty amine mixture and was heated up to

160° C. while 1,2-dichloroethane and the reaction water from the imidation were removed by distillation.

[0177] A 40% solution of the partially imidated copolymer c) in a C₈-C₉-diesel aromatic fraction with an acid number of 25 and a molecular mass number average of 7000 g/mol is obtained.

7.1.4 Other Additive Components

[0178] Diesters of ethylene glycol with erucic acid N-(2-hydroxyethyl)oleylamine

7.2 Production of Solutions Containing the Additive Components in Mineral Oil Middle Distillates

[0179] 50 kg of a 60% solution of additive component a) in C₈-C₉-diesel aromatic fraction, 20 kg of diester of ethylene glycol with erucic acid as other additive component, and 3 kg of another additive component, N-(2-hydroxyethyl)oleylamine, are added to a stirred tank reactor containing 25 kg of a 40% solution of additive component c) in C₈-C₉-diesel aromatic fraction at 65° C., stirred for 90 minutes at 65° C., and the mixture is transferred into a storage tank.

7.3 Production and Testing of the Mineral Oil Formulation

[0180] Additive solution according to 7.2 is injected at 0.24 kg/min into a product stream of heating oil without additives, batch 030225, flowing at 800 kg/min, and the mix is transferred into a storage tank.

[0181] Testing the mineral oil formulation for low-temperature resistance revealed a CFPP value of -15° C.

[0182] If a mineral oil formulation containing only the copolymer wax as an additive is produced under the same conditions, the CFPP value is -13° C.

Example 8

8.1 Starting Materials

8.1.1 Diesel without Additives

Batch: 16080601 test DF 1

Characterization:

Cloud point (CP): +6° C.;

Cold filter plugging point (CFPP): +2° C.

[0183] Distillation analysis:

Distilled quantity (vol. %)/temperature (° C.)										
IBP	10%	20%	30%	40%	50%	60%	70%	80%	90%	FBP
189	243	259	271	281	292	303	317	334	357	385

8.1.2 Additive Component a)

[0184] Ethylene-vinylacetate copolymer wax (manufactured by LEUNA Polymer GmbH, vinyl acetate content 32 mass %, molecular mass weight average 2300 g/mol).

8.1.3 Additive Component c)

[0185] α -Methylstyrene-maleic anhydride copolymer, partially imidated with stearyl amine, molecular mass weight average 13750 g/mol, acid number 51

Production of Additive Component c)

[0186] 81 l of α -methylstyrene, 7 l of α -methylstyrene-dimer, and 20 liters of acetone are placed in a 500 l stirred tank reactor, and the stirred tank reactor is heated to 59° C. A solution of 52 kg maleic anhydride and 2.4 kg of azoisobutyric acid dinitrile in 150 l of acetone is evenly dosed into a stirred tank reactor over 6 hours and the reaction mixture is stirred for 6 more hours at 70 to 73° C.

[0187] An analysis sample of the copolymer has an acid number of 445 mg KOH per gram of copolymer. NMR examinations result in 1.3 α -methylstyrene-dimer terminal groups per mole.

[0188] The polymer solution that is still at 54 to 56° C. is now continuously fed into a twin-drum vacuum drier and split into a powdered copolymer with a residual content of 1.1% of volatile ingredients and acetone.

[0189] 382 kg of a C₈-C₉-diesel aromatic fraction boiling above 160° C. and 135 kg of stearyl amine are placed in a 500 l stirred tank reactor and heated to 130° C. for partial imidation of the copolymer. 135.5 kg of the copolymer are continuously added to this solution over 4 hours. This raises the temperature inside the stirred tank reactor to 180 to 185° C., and water is formed that is distilled off azeotropically with an approximately equal quantity of C₈-C₉-diesel aromatic fraction. After a total reaction time of 6 hours at 160 to 190° C., 8.5 kg of water and 10.2 kg of solvent are distilled off.

[0190] A 40% solution of the copolymer partially imidated with stearyl amine with an acid number of 51 and an molecular mass weight average of 13750 g/mole is obtained.

8.1.4 Other Additive Components

[0191] Mixture of C₃-oxyalkyl-bridged unsaturated C₁₈-C₂₄-carboxylic acids, degree of esterification 92 mol %, content of C₁₈-unsaturated fatty acids 32 mass %, content of C₂₂-unsaturated fatty acids 48 mass %, iodine number 96

[0192] Ethylacrylate-octadecylacrylate copolymer (mole ratio 4:1, molecular mass number average 8400)

8.2 Production of Solutions Containing the Additive Components in Mineral Oil Middle Distillates

[0193] 25 kg of a 40% solution of additive component c) in C₈-C₉-diesel aromatic fraction, 50 kg of a 50% solution of additive component a) in an aromatic hydrocarbon mixture (Solvesso), 20 kg of a mixture of C₃-oxyalkyl-bridged

unsaturated C₁₈-C₂₄-carboxylic acids as other additive component and 19 kg of a 20% solution of another additive component, ethylacrylate-octadecylacrylate copolymer in toluene are intermixed in a stirred tank reactor for 90 minutes at 65° C., and the mixture is transferred into a storage tank.

8.3 Production and Testing of the Mineral Oil Formulation

[0194] The additive solution according to 8.2 is injected at 0.48 kg/min into a product stream of diesel without addi-

tives, batch 16080601, flowing at 800 kg/min and the mixture is transferred into a storage tank.

[0195] Testing the mineral oil formulation for low-temperature resistance revealed a CFPP value of -17°C .

[0196] If a mineral oil formulation containing only the copolymer wax as an additive is produced under the same conditions, the CFPP value is -3°C .

Example 9

9.1 Starting Materials

9.1.1 Diesel without Additives

Batch: 16080601 test DF 1

Characterization:

Cloud point (CP): $+6^{\circ}\text{C}$;

Cold filter plugging point (CFPP): $+2^{\circ}\text{C}$.

Lubricity test: 563 μm

[0197] Distillation analysis:

Distilled quantity (vol. %)/temperature ($^{\circ}\text{C}$.)										
IBP	10%	20%	30%	40%	50%	60%	70%	80%	90%	FBP
189	243	259	271	281	292	303	317	334	357	385

9.1.2 Additive Component a)

[0198] Ethylene-vinylacetate copolymer wax (manufactured by LEUNA Polymer GmbH, vinyl acetate content 32 mass %, molecular mass weight average 2300 g/mol).

9.1.3 Additive Component d2)

[0199] Wax ester with vaseline-like consistency, acid number 7.9 mg KOH/g, saponification number 113 mg KOH/g, kinematic viscosity 20.6 mm^2/s , solidification point 34.5°C .

Production of Additive Component d2)

[0200] A mixture of 25 kg dimeric acid (dimerization product from unsaturated C_{18} -fatty acids, mean carbon num-

9.2 Production of Solutions Containing the Additive Components in Mineral Oil Middle Distillates

[0202] 25 kg of a 40% solution of additive component d2) in C_8 - C_9 -diesel aromatic fraction, 50 kg of a 50% solution of additive component a) in an aromatic hydrocarbon mixture (Solvesso), and 15 kg of a 20% solution of another additive component, ethylacrylate-ethylhexylacrylate copolymer in toluene are intermixed in a stirred tank reactor for 90 minutes at 65°C ., and the mixture is transferred into a storage tank.

9.3 Production of the Mineral Oil Composition

[0203] The additive solution according to 9.2 is injected at 0.48 kg/min into a product stream of diesel without additives, batch 16080601, flowing at 800 kg/min and the mixture is transferred into a storage tank.

[0204] Testing the mineral oil formulation for low-temperature resistance revealed a CFPP value of -14°C . The lubricity test shows a "wear scar diameter" of 412 μm .

[0205] If a mineral oil composition containing only the unmodified copolymer wax a) as an additive is produced under the same conditions, the CFPP value is -3°C .

Example 10

10.1 Starting Materials

10.1.1 Diesel without Additives

Batch: 030210 test DF 2

Characterization:

Cloud point (CP): $+7^{\circ}\text{C}$;

Cold filter plugging point (CFPP): $+2^{\circ}\text{C}$.

Lubricity test: 556 μm

[0206] Distillation analysis:

Distilled quantity (vol. %)/temperature ($^{\circ}\text{C}$.)										
IBP	10%	20%	30%	40%	50%	60%	70%	80%	90%	FBP
235	266	279	291	301	310	320	337	342	357	374

ber 36), 5 kg of stearyl alcohol, and 7 kg of cetyl alcohol are dissolved by heat in a 70 l stirred tank reactor at 120°C . with inert gas introduction and reacted while adding 50 g H_2SO_4 and removing the reaction water until an acid number of 7.9 mg KOH/g is reached. After allowing the melt to cool down, the catalyst is neutralized with 0.5 l of 10% NaHCO_3 , the aqueous phase is separated, and the wax ester drawn off.

9.1.4 Other Additive Components

[0201] Ethylacrylate-ethylhexylacrylate copolymer (mole ratio 3:2, molecular mass number average 13500)

10.1.2 Additive Component a)

[0207] 20 mass % of a partially saponified ethylene-vinylacetate copolymer wax (molecular mass weight average 1600 g/mol, vinyl acetate content of the unsaponified ethylene-vinylacetate copolymer wax 32 mass %, degree of saponification 15 mole %) and 80 mass % of an ethylene-vinylacetate copolymer wax (manufactured by LEUNA Polymer GmbH, vinylacetate content 32 mass %, molecular mass weight average 2300 g/mol) are intermixed.

10.1.3 Additive Component d2)

[0208] Wax ester with vaseline-like consistency, acid number 8.6 mg KOH/g, saponification number 118 mg KOH/g, kinematic viscosity 23.1 mm²/s, solidification point 35.2° C.

Production of Additive Component d2)

[0209] A mixture of 25 kg dimeric acid (dimerization product from unsaturated C₁₈-fatty acids, mean carbon number 36), 5 kg of stearyl alcohol, and 8 kg of eicosane alcohol are dissolved by heat in a 70 l stirred tank reactor at 120° C. with inert gas introduction and reacted while adding 50 g H₂SO₄ and removing the reaction water until an acid number of 8.6 mg KOH/g is reached. After allowing the melt to cool down, the catalyst is neutralized with 1.0 l of 10% NaHCO₃, the aqueous phase is separated, and the wax ester drawn off.

10.1.4 Other Additive Components

[0210] Triesters of pentaerythrite with oleic acid

10.2 Production of Solutions Containing the Additive Components in Mineral Oil Middle Distillates

[0211] 22 kg of a 50% solution of additive component d2) in 2-ethyl hexanol, 50 kg of a 60% solution of additive component a) in C₈-C₉-diesel aromatic fraction, and 20 kg of a triester of pentaerythrite with oleic acid as other additive component are introduced into a stirred tank reactor, stirred for 90 minutes at 65° C., and the mixture is transferred into a storage tank.

10.3 Production of the Mineral Oil Composition

[0212] Additive solution according to 10.2 is injected at 0.30 kg/min into a product stream of diesel without additives, batch 030210, flowing at 800 kg/min and the mixture is transferred into a storage tank.

[0213] Testing the mineral oil composition for low-temperature resistance revealed a CFPP value of -8° C. The lubricity test shows a "wear scar diameter" of 425 µm.

[0214] If a mineral oil composition that only contains the unmodified copolymer wax a) as an additive is produced under the same conditions, the CFPP value is -5° C. and the "wear scar diameter" is 528 µm.

Example 11

11.1 Starting Materials

11.1.1 Heating Oil without Additives

Batch: 030225 test HEL 1

Characterization:

Cloud point (CP): +1° C.;

Cold filter plugging point (CFPP): -1° C.

[0215] Distillation analysis:

11.1.2 Additive Component a)

[0216] 25 mass % of an oxidized ethylene-vinylacetate copolymer wax (molecular mass weight average 950 g/mol, acid number 18 mg KOH/g, OH number 70 mg KOH/g) and 75 mass % of an unoxidized ethylene-vinylacetate copolymer wax (manufactured by LEUNA Polymer GmbH, vinyl acetate content 32 mass %, molecular mass weight average 2300 g/mol) are intermixed.

11.1.3 Additive Component d1)

[0217] Oligomeric ester, acid number 12 mg KOH/g, saponification number 175 mg KOH/g, kinematic viscosity (100° C.) 65 mm²/s, solidification point 42° C., produced in accordance with EP 0 934 921 A1 from glyceryl monostearate and dimeric acid (dimerization product from unsaturated C₁₈-fatty acids, mean carbon number 36) by solvent-free oligocondensation with acid catalysis.

11.1.4 Other Additive Components

[0218] N-(2-hydroxyethyl)oleylamine

11.2 Production of solutions containing the additive components in mineral oil middle distillates

[0219] 50 kg of a 60% solution of additive component a) in C₈-C₉-diesel aromatic fraction, and 3 kg of another additive component, N-(2-hydroxyethyl) oleylamine, are added to a stirred tank reactor containing 23 kg of a 40% solution of additive component d1) in C₈-C₉-diesel aromatic fraction at 65° C., stirred for 90 minutes at 65° C., and the mixture is transferred into a storage tank.

11.3 Production of the Mineral Oil Composition

[0220] The additive solution according to 11.2 is injected at 0.28 kg/min into a product stream of heating oil without additives, batch 030225, flowing at 800 kg/min, and the mixture is transferred into a storage tank.

[0221] Testing the mineral oil formulation for low-temperature resistance revealed a CFPP value of -16° C.

[0222] If a mineral oil composition containing only the unmodified copolymer wax a) as an additive is produced under the same conditions, the CFPP value is -13° C.

Example 12

12.1 Starting Materials

12.1.1 Diesel without Additives

Batch: 16080601 test DF 1

Characterization:

Cloud point (CP): +6° C.;

Cold filter plugging point (CFPP): +2° C.

Distilled quantity (vol. %)/temperature (° C.)

IBP	10%	20%	30%	40%	50%	60%	70%	80%	90%	FBP
165	196	213	230	249	269	290	310	327	344	363

[0223] Distillation analysis:

Distilled quantity (vol. %)/temperature (° C.)										
IBP	10%	20%	30%	40%	50%	60%	70%	80%	90%	FBP
189	243	259	271	281	292	303	317	334	357	385

12.1.2 Additive Component a)

[0224] Ethylene-vinylacetate copolymer wax (manufactured by LEUNA Polymer GmbH, vinyl acetate content 32 mass %, molecular mass weight average 2300 g/mol).

12.1.3 Additive Component d1)

[0225] Oligomeric ester, acid number 14 mg KOH/g, saponification number 185 mg KOH/g, kinematic viscosity (100° C.) 76 mm²/s, solidification point 42° C., produced in accordance with EP 0 934 921 A1 from glyceryl monostearate and dimeric acid (dimerization product from unsaturated C₁₈-fatty acids, mean carbon number 36) by solvent-free oligocondensation with acid catalysis.

12.1.4 Other Additive Components

[0226] Mixture of C₃-oxyalkyl-bridged unsaturated C₁₈-C₂₄-carboxylic acids, degree of esterification 92 mol %, content of C₁₈-unsaturated fatty acids 32 mass %, content of C₂₂-unsaturated fatty acids 48 mass %, iodine number 96

[0227] Ethylacrylate-octadecylacrylate copolymer (mole ratio 4:1, molecular mass number average 8400)

12.2 Production of Solutions Containing the Additive Components in Mineral Oil Middle Distillates

[0228] 25 kg of a 50% solution of additive component d1) in C₈-C₉-diesel aromatic fraction, 50 kg of a 50% solution of additive component a) in an aromatic hydrocarbon mixture (Solvesso), 12 kg of a mixture of C₃-oxyalkyl-bridged unsaturated C₁₈-C₂₄-carboxylic acids as other additive component and 15 kg of a 20% solution of another additive component, ethylacrylate-octadecylacrylate copolymer in toluene are intermixed in a stirred tank reactor for 90 minutes at 65° C., and the mixture is transferred into a storage tank.

12.3 Production and Testing of the Mineral Oil Composition

[0229] The additive solution according to 12.2 is injected at 0.52 kg/min into a product stream of diesel without additives, batch 16080601, flowing at 800 kg/min and the mixture is transferred into a storage tank.

[0230] Testing the mineral oil formulation for low-temperature resistance revealed a CFPP value of -18° C.

[0231] If a mineral oil composition containing only the unmodified copolymer wax a) as an additive is produced under the same conditions, the CFPP value is -3° C.

1. Compositions of mineral oil as the main component and trace portions of an additive mixture wherein the additive mixture comprises the additive components

- a) ethylene-vinylester copolymers with molecular mass weight averages from 3000 to 50000 and an ethylene proportion of 50 to 90 mass %,

and

- b) mixed esters of glycerine in which 50 to 80 mol % of the hydroxy groups are esterified with unsaturated C₁₂-C₄₀ monocarboxylic acids and 20 to 50 mol % of the hydroxy groups are esterified with partially imidated and/or partially esterified maleic anhydride copolymers,

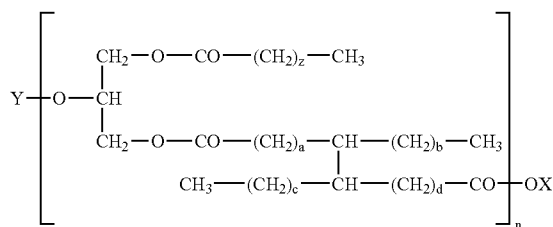
and/or

- c) partially and/or completely imidated copolymers of maleic anhydride and α -methylstyrene with molecular mass number averages from 1500 to 15000 and at least one terminal group based on dimeric α -methylstyrene,

and/or

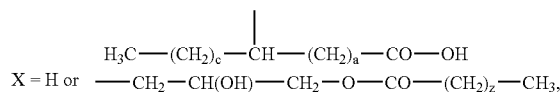
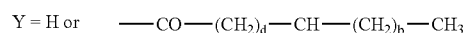
- d) wax compositions based on natural starting materials of type

- d1) wax-like oligomeric esters based on glyceryl monostearate and dimeric acid in which the conversion product corresponds to the



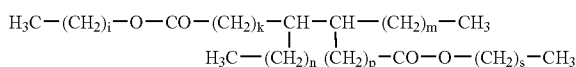
structure by at least 90 mass %,

where n=1 to 20, the total of a+b+c+d=30, z=12 to 20



and/or

- d2) wax esters with vaseline-like consistency based on at least two different straight-chain and/or branched C₁₄-C₃₆ alcohols and dimeric acids in which the conversion product corresponds to the



structure by at least 80 mass %,

where $i=13$ to 35 ; $s=13$ to 35 ,

the total of $k+m+n+p$ is 30 to 34 , and $(\text{CH}_2)_i$ or $(\text{CH}_2)_s$ are straight-chain or straight-chain and branched,

whereby the content of the additive mixture in the mineral oil is 0.005 to 1 mass % and the mass proportion of the additive components a/b or a/c or a/d is in the range from $10:90$ to $90:10$, respectively.

2. The compositions according to claim 1 wherein the ethylene-vinylester copolymers of the additive mixture are ethylene-vinylacetate copolymers with a vinylacetate content of 12 to 50 mass %.

3. The compositions according to claim 1 wherein the ethylene-vinylester copolymers of the additive mixture are mixtures of 10 to 90 mass % of unmodified ethylene-vinylester copolymers and 90 to 10 mass % of ethylene-vinylester copolymers modified by polar groups.

4. The compositions according to claim 3 wherein the modified ethylene-vinylester copolymers of the additive mixture are oxidized ethylene-vinylester copolymers, partially saponified ethylene-vinylester copolymers, hemiacetals of partially saponified ethylene-vinylester copolymers and/or ethylene-vinylester copolymers grafted with polar unsaturated monomers of the vinyl ester, (meth)acryl ester, and/or vinyl ether type.

5. The compositions according to one or several of claim 1 wherein the C_{12} - C_{40} -monocarboxylic acids contained as esterifying components in the mixed esters of glycerine of the additive mixture consist of 45 to 52 mass % C_{22} -monocarboxylic acids in relation to the overall weight of the C_{12} - C_{24} -monocarboxylic acids, and wherein the partially imidated maleic anhydride copolymers contained as esterifying components are maleic anhydride- α -methylstyrene copolymers partially imidated with C_6 - C_{40} -monoalkylamines in which the mole ratio of anhydride groups in the copolymer/ C_6 - C_{24} -monoalkylamine bound in the copolymer is in the range of from $8:1$ to $1.3:0.1$.

6. The compositions according to claim 1 wherein the partially imidated copolymer of maleic anhydride and α -methylstyrene as additive component c) are maleic anhydride- α -methylstyrene copolymers partially imidated with C_6 - C_{24} monoalkylamines in which the mole ratio of anhydride groups in the copolymer/bound C_6 - C_{24} monoalkylamine in the copolymer is from $8:1$ to $1.3:1$.

7. Compositions according to claim 1 wherein the wax esters with vaseline-like consistency as additive component d2) are wax esters based on Guerbet alcohols of the 2-hexyldecane-1-ol, 2-octyldecane-1-ol or 2-octyldecane-1-ol type and dimeric acids obtained by splitting vegetable oils with a high oleic acid content and subsequent catalytic dimerization.

8. Compositions of mineral oil according to claim 1 wherein the mineral oils are crude oils or fuel oils from a middle distillate with a sulfur content under 0.05 mass %, preferably heating oils, gas oils, or diesel oils.

9. Compositions of mineral oil according to claim 1 wherein the mineral oil compositions contain a total of 0 up to 200 mass % in relation to the additive components $a+b$, $a+c$, $a+d$, $a+b+c$, $a+b+c+d$, or $a+c+d$ of other additive components such as fatty acid mixtures, polar nitrogen compounds, preferably polyamines, etheramines, amino alcohols, amine salts, amides or imides of multivalent carboxylic acids; modified copolymers of ethylenically unsaturated C_4 - C_{20} -dicarboxylic anhydrides, non-modified ethylene-vinylester copolymers, C_7 - C_{30} -alcohols, polyalkylene glycols, esters or ethers of polyoxyalkylene compounds, C_2 - C_6 -oxyalkyl-bridged C_{12} - C_{40} -monocarboxylic acids, preferably C_3 - C_4 -oxyalkyl-bridged unsaturated C_{16} - C_{24} -monocarboxylic acids with a content of C_{22} -monocarboxylic acids in relation to the overall weight of the C_{16} - C_{24} -monocarboxylic acids of 45 to 52 mass %, hydrocarbon polymers, alkylphenol-aldehyde copolymers, aromatic compounds with C_8 - C_{100} -alkyl substituents, carboxylated polyamines, detergents, corrosion inhibitors, demulsifiers, metal deactivators, cetane number improvers, defoaming agents and/or cosolvents.

10. A method for producing compositions of mineral oil as the main component and trace portions of an additive mixture wherein the additive mixture, which comprises the additive components

a) ethylene-vinylester copolymers with molecular mass weigh averages from 3000 to 50000 and an ethylene proportion of 50 to 90 mass %,

and

b) mixed esters of glycerine in which 50 to 80 mol % of the hydroxy groups are sterified with unsaturated C_6 - C_{40} monocarboxylic acids and 20 to 50 mol % of the hydroxy groups are esterified with partially imidated and/or partially esterified maleic anhydride copolymers,

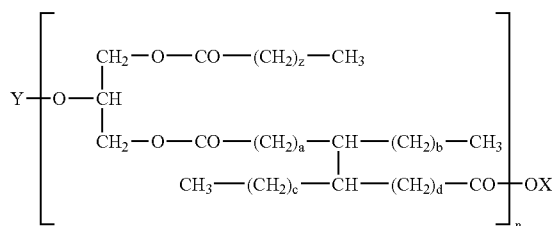
and/or

c) partially and/or completely imidated copolymers of maleic anhydride and α -methylstyrene with molecular mass number averages from 1500 to 15000 and at least one terminal group based on dimeric α -methylstyrene,

and/or

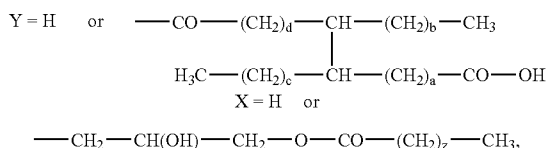
d) wax compositions based on natural starting materials of type

d1) wax-like oligomeric esters based on glyceryl monostearate and dimeric acid in which the conversion product corresponds to the



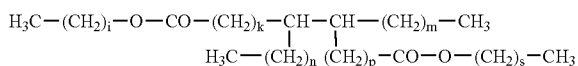
structure by at least 90 mass %,

where $n=1$ to 20, the total of $a+b+c+d=30$, $z=12$ to 20



and/or

d2) wax esters with vaseline-like consistency based on at least two different straight-chain and/or branched C_{14} - C_{36} alcohols and dimeric acids in which the conversion product corresponds to the



structure by at least 80 mass %,

where $i=13$ to 35; $s=13$ to 35,

the total of $k+m+n+p$ is 30 to 34, and

$(\text{CH}_2)_i$ or $(\text{CH}_2)_s$ are straight-chain or straight-chain and branched,

whereby the content of the additive mixture in the mineral oil is 0.005 to 1 mass % and the mass proportion of the additive components a/b or a/c or a/d is in the range from 10:90 to 90:10, respectively, are produced in a prehomogenization process in which

solutions containing 1 to 60 mass % of additive components in mineral oil middle distillates are produced at 20 to 90° C. in a first process step, and

the solutions containing the additive components are homogenized with the mineral oil as the main component in a second process step,

while other additive components of a total of 0 to 200 mass % in relation to the additive components a+b, a+c, a+d, a+b+c, a+b+c+d, or a+c+d are added to the mineral oil in the first and/or second process step.

11. Use of compositions according to claim 1 as flowable media to be transported at low-temperatures and as mineral oil fuel with high lubricity and flowability.

12. The compositions according to claim 2 wherein the ethylene-vinylester copolymers of the additive mixture are mixtures of 10 to 90 mass % of unmodified ethylene-vinylester copolymers and 90 to 10 mass % of ethylene-vinylester copolymers modified by polar groups.

13. The compositions according to claim 12 wherein the modified ethylene-vinylester copolymers of the additive mixture are oxidized ethylene-vinylester copolymers, partially saponified ethylene-vinylester copolymers, hemiacetals of partially saponified ethylene-vinylester copolymers

and/or ethylene-vinylester copolymers grated with polar unsaturated monomers of the vinyl ester, (meth)acryl ester, and/or vinyl ether type.

14. The compositions according to claim 2 wherein the C_{12} - C_{40} -monocarboxylic acids contained as esterifying components in the mixed esters of glycerine of the additive mixture consist of 45 to 52 mass % C_{22} -monocarboxylic acids in relation to the overall weight of the C_{12} - C_{40} -monocarboxylic acids, and wherein the partially imidated maleic anhydride copolymers contained as esterifying components are maleic anhydride- α -methylstyrene copolymers partially imidated with C_6 - C_{40} -monoalkylamines in which the mole ratio of anhydride groups in the copolymer/ C_6 - C_{24} -monoalkylamine bound in the copolymer is in the range of from 8:1 to 1.3:01.

15. The compositions according to claim 3 wherein the C_{12} - C_{40} -monocarboxylic acids contained as esterifying components in the mixed esters of glycerine of the additive mixture consist of 45 to 52 mass % C_{22} -monocarboxylic acids in relation to the overall weight of the C_{12} - C_{40} -monocarboxylic acids, and wherein the partially imidated maleic anhydride copolymers contained as esterifying components are maleic anhydride- α -methylstyrene copolymers partially imidated with C_6 - C_{40} -monoalkylamines in which the mole ratio of anhydride groups in the copolymer/ C_6 - C_{24} -monoalkylamine bound in the copolymer is in the range of from 8:1 to 1.3:01.

16. The compositions according to claim 4 wherein the C_{12} - C_{40} -monocarboxylic acids contained as esterifying components in the mixed esters of glycerine of the additive mixture consist of 45 to 52 mass % C_{22} -monocarboxylic acids in relation to the overall weight of the C_{12} - C_{40} -monocarboxylic acids, and wherein the partially imidated maleic anhydride copolymers contained as esterifying components are maleic anhydride- α -methylstyrene copolymers partially imidated with C_6 - C_{40} -monoalkylamines in which the mole ratio of anhydride groups in the copolymer/ C_6 - C_{24} -monoalkylamine bound in the copolymer is in the range of from 8:1 to 1.3:01.

17. The compositions according to claim 12 wherein the C_{12} - C_{40} -monocarboxylic acids contained as esterifying components in the mixed esters of glycerine of the additive mixture consist of 45 to 52 mass % C_{22} -monocarboxylic acids in relation to the overall weight of the C_{12} - C_{40} -monocarboxylic acids, and wherein the partially imidated maleic anhydride copolymers contained as esterifying components are maleic anhydride- α -methylstyrene copolymers partially imidated with C_6 - C_{40} -monoalkylamines in which the mole ratio of anhydride groups in the copolymer/ C_6 - C_{24} -monoalkylamine bound in the copolymer is in the range of from 8:1 to 1.3:01.

18. The compositions according to claim 13 wherein the C_{12} - C_{40} -monocarboxylic acids contained as esterifying components in the mixed esters of glycerine of the additive mixture consist of 45 to 52 mass % C_{22} -monocarboxylic acids in relation to the overall weight of the C_{12} - C_{40} -monocarboxylic acids, and wherein the partially imidated maleic anhydride copolymers contained as esterifying components are maleic anhydride- α -methylstyrene copolymers partially imidated with C_6 - C_{40} -monoalkylamines in which the mole ratio of anhydride groups in the copolymer/ C_6 -

C₂₄-monoalkylamine bound in the copolymer is in the range of from 8:1 to 1.3:01.

19. The compositions according to claim 2 wherein the partially imidated copolymer of maleic anhydride and α -methylstyrene as additive component c) are maleic anhydride- α -methylstyrene copolymers partially imidated with C₆-C₂₄ monoalkylamines in which the mole ratio of anhydride groups in the copolymer/bound C₆-C₂₄ monoalkylamine in the copolymer is from 8:1 to 1.3:1.

20. The compositions according to claim 3 wherein the partially imidated copolymer of maleic anhydride and α -methylstyrene as additive component c) are maleic anhydride- α -methylstyrene copolymers partially imidated with C₆-C₂₄ monoalkylamines in which the mole ratio of anhydride groups in the copolymer/bound C₆-C₂₄ monoalkylamine in the copolymer is from 8:1 to 1.3:1.

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