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(54) **COMPOSITION TO IMPROVE LOW TEMPERATURE PROPERTIES AND OXIDATION STABILITY OF VEGETABLE OILS AND ANIMAL FATS**

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(57) **ABSTRACT**

The present invention describes a composition comprising: (A) at least one polyalkyl (meth) acrylate polymer having a number average molecular weight M_n of from 15000 to 75000 g/mol; (B) at least one ethylene vinyl acetate copolymer comprising units being derived from at least one alkyl (meth) acrylate having 1 to 30 carbon atoms in the alkyl residue; (C) a phenolic type anti-oxidant; (D) a mixture stabilizer; and (E) a glycol ether solvent. The composition is useful as cold flow improver and oxidation stabilizer in vegetable oils and animal fats.

COMPOSITION TO IMPROVE LOW TEMPERATURE PROPERTIES AND OXIDATION STABILITY OF VEGETABLE OILS AND ANIMAL FATS

[0001] The present invention relates to an additive composition to improve low temperature properties and oxidation stability of vegetable oils and animal fats.

[0002] Due to growing environmental concerns, there has been an increasing interest and demand for environmental-friendly and bio-compatible products, which could find applications in lubrication industry (e.g. "engine lubricants" such as gasoline engine oils, diesel engine oils, two-stroke engine oils, marine diesel oils, aviation engine oils, etc and "non-engine" lubricants such as transmission fluid, gear oils, metalworking fluids, greases etc.). Besides lubrication industry, environmental-friendly products are also in demand from the other sectors, which could function as transformer oils, dielectric fluids, refrigeration oils, etc. One such example disclosing a vegetable oil based dielectric fluid for use in electrical appliances is given in U.S. Pat. No. 6,398,986 B1 (Cooper Industries, Inc.).

[0003] One of the most abundant sources for the development of environmental-friendly products is "nature-derived", in the form of natural oils and fats. For example, the natural oil can be a vegetable oil such as sunflower oil, rapeseed oil, soya oil, coconut oil, corn oil, cottonseed oil, jojoba oil, jatropa oil, olive oil etc, and an animal fat can be tallow, lard, chicken oil, whale sperm, etc. Natural oils and fats offer a few advantages over mineral oils, such as their high flash points, low emissions of toxic substances, higher viscosity index, biodegradability, etc.

[0004] The major constituent of vegetable oils and animal fats is triglyceride, which is an ester, derived from glycerol and one or more free fatty acids. The number of carbon atoms and the amount of saturation and unsaturation in the fatty acid chain define the properties, such as low temperature behaviour and oxidation stability of fats and oils. The number of carbon atoms in fatty acids found in plants and animals ranges from C10 to C30 (most usual is C12 to C18). The melting point of the fatty acids increases with an increasing number of carbon atoms in the fatty acid chain (molecular weight). The extent of saturation and unsaturation in the fatty acid chains of triglycerides can vary significantly depending upon the sources of oils and fats. The saturated fatty acids have a higher melting point as compared to an unsaturated fatty acid chain. For example, Lauric acid (saturated and C12) has a melting point of 44° C. and Arachidonic acid (unsaturated and C20) has a melting point of −50° C., which means that it is liquid at room temperature. Thus, the higher the melting point of oils and fats the better is the cold flow property of the feedstock.

[0005] The oxidation stability of the oils and fats decreases with increasing amount of unsaturation in the fatty acid chains. For example, the oxidation stability of a coconut oil is better as compared to soya oil, as the latter has larger amount of unsaturation. Oils and fats usually have issues with respect to their cold temperature properties, oxidative instability and show poor hydrolytic stability. To overcome these shortcomings, additives such as cold flow improvers and anti-oxidants, detergents, dispersants, pour point depressants, emulsifiers etc. are often added to oils and fats. However, it is known that oils and fats are not as responsive to the conventional pour point depressants compared to mineral oil-treatment. Also large dosages on antioxidants are required in order to acquire oxidation stability.

[0006] The improvement of the cold flow activity of certain vegetable oils by adding polyalkyl (meth)acrylates (PAMAs) without the presence of methyl (meth)acrylate (methyl (meth)acrylate copolymer is disclosed in U.S. Pat. No. 5,696,066 A (Rohm and Hass Company)). Another ingredient, which is widely used as cold flow improver (CFI), are the poly(meth)acrylate and styrene esters as disclosed in U.S. Pat. No. 5,338,471 A (The Lubrizol Corporation). Besides this, the use of cold flow improvers based on ethylene vinyl acetate (EVA) copolymers is disclosed in U.S. Pat. No. 7,276,264 (Clariant GmbH). U.S. Pat. No. 6,565,616 (Clariant GmbH) discloses an additive for improving the cold flow properties containing a blend of EVA and copolymers containing maleic anhydride or alkyl acrylates. EP 0 406 684 B1 (Röhm GmbH) discloses a flow improver additive containing a mixture of EVA copolymer and PAMA. U.S. Pat. No. 4,932,980 (Röhm GmbH) discloses flow improvers based on a graft polymer consisting of 80-20% EVA copolymer as the backbone and 20-80% alkyl (meth)acrylate as the grafting monomer. EP 2 305 753 B1 (RohMax Additives GmbH) discloses a composition of cold flow additives derived from a mixture of PAMA and EVA-graft-(meth)acrylates which gives a boost in the cold flow performance of fossil fuel oil and biodiesel fuel oil.

[0007] The use of a variety of natural and synthetic antioxidants is mentioned improving the oxidation stability of vegetable oils. H. Sanders Gwin, Jr. have reported the use of anti-oxidants, such as butylated hydroxyl anisole (BHA), butylated hydrotoluene, tertiary butyl hydroquinone (TBHQ), tertiary hydrobutrophenone, ascorbyl palmitate, propyl gallate and alpha-, beta-, or delta-tocopherol to improve the oxidation stability of one or more vegetable oils in a dielectric fluid.

[0008] As most of these antioxidant components are solid particles and contain polar functional groups, the finding of solvents that will carry higher concentrations of these antioxidants along with other additives, including CFIs, while being miscible with oils and fats is a challenge.

[0009] There is a continued need for new formulation containing concentrated antioxidants and CFIs in solution form. Patent application publication WO 2009/108851 A1 (Novus International Inc.) discloses compositions containing at least one phenolic antioxidant and at least one ethylene amine in aromatic solvents. Patent application No. US 2007/0197412 A1 (Eastman Chemical Co.) describes the use of various organic solvents, including monofunctional alcohols, polyol, esters, ethers, glycol ethers, ketones and their combinations, to formulate concentrated phenolic antioxidants and metal-chelating compounds.

[0010] US Patent Application No. 2008/0274921 A1 (Luedeka, Neely & Graham, P.C.) describes additive compositions for an environmentally compatible lubricant of PAMA-based PPD and antioxidants besides a number of other tribologically functional components. This application also describes the composition of an environmentally compatible lubricant comprising a vegetable oil together with the additive composition as described earlier.

[0011] Patent application publication no. WO 02/00815 A2 (Renewable Lubricants, Inc.) discloses biodegradable vegetable oil compositions comprising at least on vegetable oil, wherein the latter comprises at least one genetically modified vegetable oil, a PPD, which comprises alkylated polystyrene or PAMA, and amine based antioxidant.

[0012] Based on the objectives mentioned above, a further improvement of the oxidation stability and the cold flow properties is an enduring challenge. Preferably, the combination of a cold flow improver and an antioxidant should provide a synergistic improvement. At least, no essential decrease in any of these properties should be achieved.

[0013] The present invention highlights additive formulations containing cold flow improver and antioxidant in stable, miscible solution, which offers significant cold flow improvement (pour point depressant (PPD) activity) and enhanced oxidation stability of natural oils and fats.

[0014] The presence of EVA-graft-PAMA is essential in order to maintain homogeneity of the additive formulation, i.e. keeping the individual components together in one phase. According to the second finding, the presence of EVA-graft-PAMA provides a boost in cold flow improvement of the oil.

[0015] There are documents describing vegetable oil compositions comprising one or more vegetable oils, one or more PPDs, one or more antioxidants and other additives such as dispersants, friction modifiers, inhibitors, anti-wear and extreme pressure agents, detergents etc.

[0016] A first embodiment of the present invention is therefore directed to an additive composition, comprising:

[0017] (A) 35% to 50% by weight of at least one polyalkyl (meth)acrylate polymer having a number average molecular weight M_n of from 15000 to 75000 g/mol;

[0018] (B) 5% to 15% by weight of at least one ethylene vinyl acetate copolymer comprising units being derived from at least one alkyl (meth)acrylate having 1 to 30 carbon atoms in the alkyl residue;

[0019] (C) 10% to 20% by weight of a phenolic type antioxidant;

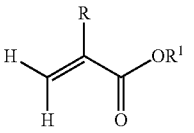
[0020] (D) 10% to 25% by weight of a mixture stabilizer; and

[0021] (E) 10% to 20% by weight of a glycol ether solvent, wherein the sum of all components (A) to (E) of the composition add up to 100% by weight.

[0022] According to a preferred aspect of the present invention, the composition of the present invention preferably comprises at least one polyalkyl(meth)acrylate polymer having a number average molecular weight M_n of from 15000 to 75000 g/mol and a polydispersity M_w/M_n of from 1 to 8. The combination of a polyalkyl(meth)acrylate polymer having the properties mentioned above with an ethylene vinyl acetate copolymer provides a synergistic improvement in oxidation stability and low temperature flow properties of vegetable oils and animal fats.

[0023] Polyalkyl(meth)acrylate polymers are polymers comprising units being derived from alkyl(meth)acrylate monomers. The term (meth)acrylates includes methacrylates and acrylates as well as mixtures thereof. These monomers are well known in the art. The alkyl residue of the ester compounds can be linear, cyclic or branched. The monomers can be used individually or as mixtures of different alkyl (meth)acrylate monomers to obtain the polyalkyl(meth)acrylate polymers useful for the present invention. Usually the polyalkyl(meth)acrylate polymers comprise at least 50% by weight, preferably at least 70% by weight and more preferably at least 90% by weight alkyl(meth)acrylate monomers having 7 to 20, preferably 7 to 15 carbon atoms in the alkyl residue.

[0024] According to a preferred aspect of the present invention, the polyalkyl(meth)acrylate polymers of component (A) useful for the present invention may comprise units being derived from one or more alkyl(meth)acrylate monomers of formula (I)



(I)

wherein

[0025] R denotes hydrogen or methyl and

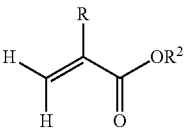
[0026] R^1 denotes a linear, branched or cyclic alkyl residue with 1 to 6 carbon atoms, especially 1 to 5 and preferably 1 to 3 carbon atoms.

[0027] Examples of monomers according to formula (I) are, among others, (meth)acrylates which derived from saturated alcohols such as methyl (meth)acrylate, ethyl (meth) acrylate, n-propyl (meth)acrylate, isopropyl (meth)acrylate, n-butyl (meth)acrylate, tert-butyl (meth)acrylate, pentyl (meth)acrylate and hexyl (meth)acrylate; cycloalkyl (meth) acrylates, like cyclopentyl (meth)acrylate and cyclohexyl (meth)acrylate. Preferably, the polymer comprises units being derived from methyl methacrylate.

[0028] The polyalkyl(meth)acrylate polymers useful for the present invention may comprise 0 to 40% by weight, preferably 0.1 to 30% by weight, in particular 0.5 to 20% by weight of units derived from one or more alkyl(meth)acrylate monomers of formula (I) based on the total weight of the polymer.

[0029] The polyalkyl(meth)acrylate polymer may be obtained preferably by free-radical polymerization. Accordingly the weight fraction of the units of the polyalkyl(meth) acrylate polymer as mentioned in the present application is a result of the weight fractions of corresponding monomers that are used for preparing the inventive polymer.

[0030] Preferably, the polyalkyl(meth)acrylate polymer comprises units of one or more alkyl(meth)acrylate monomers of formula (II)



(II)

wherein

[0031] R denotes hydrogen or methyl and

[0032] R^2 denotes a linear, branched or cyclic alkyl residue with 7 to 15 carbon atoms.

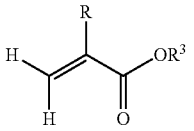
[0033] Examples of component (II) include (meth)acrylates that derive from saturated alcohols, such as 2-ethylhexyl (meth)acrylate, heptyl (meth)acrylate, 2-tert-butylheptyl (meth)acrylate, n-octyl (meth)acrylate, 3-isopropylheptyl (meth)acrylate, nonyl (meth)acrylate, 2-propylheptyl (meth)acrylate, decyl (meth)acrylate, undecyl (meth) acrylate, 5-methylundecyl (meth)acrylate, n-dodecyl (meth) acrylate, 2-methyldodecyl (meth)acrylate, tridecyl (meth) acrylate, 5-methyltridecyl (meth)acrylate, n-tetradecyl (meth)acrylate, pentadecyl (meth)acrylate;

(meth)acrylates which derive from unsaturated alcohols, for example oleyl (meth)acrylate;

cycloalkyl (meth)acrylates such as cyclohexyl (meth)acrylate having a ring substituent, like tert-butylcyclohexyl (meth) acrylate and trimethylcyclohexyl (meth)acrylate, bornyl (meth)acrylate and isobornyl (meth)acrylate.

[0034] According to a preferred aspect of the present invention, the polymer comprises preferably about 40 to 99% by weight, more preferably about 60 to 95% by weight of units derived from monomers according to formula (II).

[0035] Furthermore, the polyalkyl(meth)acrylate polymers useful for the present invention may comprise units being derived from one or more alkyl(meth)acrylate monomers of formula (III)



(III)

wherein

[0036] R denotes hydrogen or methyl and

[0037] R^3 denotes a linear, branched or cyclic alkyl residue with 16 to 30 carbon atoms.

[0038] Examples of component (III) include (meth)acrylates which derive from saturated alcohols, such as hexadecyl (meth)acrylate, 2-methylhexadecyl (meth)acrylate, heptadecyl (meth)acrylate, 5-isopropylheptadecyl (meth)acrylate, 4-tert-butyloctadecyl (meth)acrylate, 5-ethyloctadecyl (meth)acrylate, 3-isopropyloctadecyl (meth)acrylate, octadecyl (meth)acrylate, nonadecyl (meth)acrylate, eicosyl (meth) acrylate, cetyleicosyl (meth)acrylate, stearyleicosyl (meth) acrylate, docosyl (meth)acrylate and/or eicosyltetratriacontyl (meth)acrylate;

cycloalkyl (meth)acrylates such as 2,4,5-tri-t-butyl-3-vinylcyclohexyl (meth)acrylate, 2,3,4,5-tetra-t-butylcyclohexyl (meth)acrylate.

[0039] The polyalkyl(meth)acrylate polymers useful for the present invention may comprise 0.1 to 40% by weight, in particular 0.5 to 35% by weight of units derived from one or more alkyl(meth)acrylate monomers of formula (III) based on the total weight of the polymer.

[0040] The ester compounds with a long-chain alcohol residue, especially monomers according to formulae (II) and (III), can be obtained, for example, by reacting (meth)acrylates and/or the corresponding acids with long chain fatty alcohols, where in general a mixture of esters such as (meth) acrylates with different long chain alcohol residues results. These fatty alcohols include, among others, Oxo Alcohol® 7911 and Oxo Alcohol® 7900, Oxo Alcohol® 1100 (Monsanto); Alphanol® 79 (ICI); Nafol® 1620, Alfol® 610 and Alfol® 810 (Sasol); Epal® 610 and Epal® 810 (Ethyl Corporation); Linevol® 79, Linevol® 911 and Dobanol® 25L (Shell AG); Lial 125 (Sasol); Dehydad® and Dehydad® and Lorol® (Cognis).

[0041] The polymer may contain units derived from comonomers as an optional component.

[0042] These comonomers include hydroxyalkyl (meth) acrylates like 3-hydroxypropyl (meth)acrylate, 3,4-dihydroxybutyl (meth)acrylate, 2-hydroxyethyl (meth)acrylate, 2-hydroxypropyl (meth)acrylate, 2,5-dimethyl-1,6-hexanediol (meth)acrylate, 1,10-decanediol (meth)acrylate;

aminoalkyl (meth)acrylates and aminoalkyl (meth)acrylamides like N-(3-dimethyl-aminopropyl)methacrylamide, 3-diethylaminopentyl (meth)acrylate, 3-dibutyl-aminohexadecyl (meth)acrylate;

nitriles of (meth)acrylic acid and other nitrogen-containing (meth)acrylates like N-(methacryloyloxyethyl)diisobutylketimine, N-(methacryloyloxyethyl)dihexadecylketimine, (meth)acryloylamidoacetonitrile, 2-methacryloyloxyethylmethylcyanamide, cyanomethyl (meth)acrylate;

aryl (meth)acrylates like benzyl (meth)acrylate or phenyl (meth)acrylate, where the acryl residue in each case can be unsubstituted or substituted up to four times;

carbonyl-containing (meth)acrylates like 2-carboxyethyl (meth)acrylate, carboxymethyl (meth)acrylate, oxazolidinylethyl (meth)acrylate, N-methyacryloyloxy)-formamide, acetonyl (meth)acrylate, N-methacryloylmorpholine, N-methacryloyl-2-pyrrolidinone, N-(2-methyacryloxyoxyethyl)-2-pyrrolidinone, N-(3-methacryloyloxy-propyl)-2-pyrrolidinone, N-(2-methyacryloyloxypentadecyl(-2-pyrrolidinone, N-(3-methacryloyloxyheptadecyl-2-pyrrolidinone;

(meth)acrylates of ether alcohols like tetrahydrofurfuryl (meth)acrylate, methoxyethoxyethyl (meth)acrylate, 1-butoxypropyl (meth)acrylate, cyclohexyloxyethyl (meth)acrylate, propoxyethoxyethyl (meth)acrylate, benzyloxyethyl (meth)acrylate, furfuryl (meth)acrylate, 2-butoxyethyl (meth)acrylate, 2-ethoxy-2-ethoxyethyl (meth)acrylate, 2-methoxy-2-ethoxypropyl (meth)acrylate, ethoxylated (meth)acrylates, 1-ethoxybutyl (meth)acrylate, methoxyethyl (meth)acrylate, 2-ethoxy-2-ethoxy-2-ethoxyethyl (meth)acrylate, esters of (meth)acrylic acid and methoxy polyethylene glycols;

(meth)acrylates of halogenated alcohols like 2,3-dibromopropyl (meth)acrylate, 4-bromophenyl (meth)acrylate, 1,3-dichloro-2-propyl (meth)acrylate, 2-bromoethyl (meth) acrylate, 2-iodoethyl (meth)acrylate, chloromethyl (meth) acrylate;

oxiranyl (meth)acrylate like 2,3-epoxybutyl (meth)acrylate, 3,4-epoxybutyl (meth)acrylate, 10,11 epoxyundecyl (meth) acrylate, 2,3-epoxycyclohexyl (meth)acrylate, oxiranyl (meth)acrylates such as 10,11-epoxyhexadecyl (meth)acrylate, glycidyl (meth)acrylate;

phosphorus-, boron- and/or silicon-containing (meth)acrylates like 2-(dimethyl-phosphato)propyl (meth)acrylate, 2-(ethylphosphito)propyl (meth)acrylate, 2-dimethylphosphinomethyl (meth)acrylate, dimethylphosphonoethyl (meth)acrylate, diethylmethacryloyl phosphonate, dipropylmethacryloyl phosphate, 2-(dibutylphosphono)ethyl (meth) acrylate, 2,3-butylenemethacryloylethyl borate, methyldiethoxymethacryloylethoxysiliane, diethylphosphatoethyl (meth)acrylate;

sulfur-containing (meth)acrylates like ethylsulfinylethyl (meth)acrylate, 4-thio-cyanatobutyl (meth)acrylate, ethylsulfonylethyl (meth)acrylate, thiocyanatomethyl (meth)acrylate, methylsulfinylmethyl (meth)acrylate, bis(methacryloyloxyethyl) sulfide;

heterocyclic (meth)acrylates like 2-(1-imidazolyl)ethyl (meth)acrylate, 2-(4-morpholinyl)ethyl (meth)acrylate and 1-(2-methacryloyloxyethyl)-2-pyrrolidone;

maleic acid and maleic acid derivatives such as mono- and diesters of maleic acid, maleic anhydride, methylmaleic

anhydride, maleinimide, methylmaleinimide; fumaric acid and fumaric acid derivatives such as, for example, mono- and diesters of fumaric acid;

vinyl halides such as, for example, vinyl chloride, vinyl fluoride, vinylidene chloride and vinylidene fluoride;

vinyl esters like vinyl acetate;

vinyl monomers containing aromatic groups like styrene, substituted styrenes with an alkyl substituent in the side chain, such as alpha-methylstyrene and alpha-ethylstyrene, substituted styrenes with an alkyl substituent on the ring such as vinyltoluene and p-methylstyrene, halogenated styrenes such as monochlorostyrenes, dichlorostyrenes, tribromostyrenes and tetrabromostyrenes;

heterocyclic vinyl compounds like 2-vinylpyridine, 3-vinylpyridine, 2-methyl-5-vinylpyridine, 3-ethyl-4-vinylpyridine, 2,3-dimethyl-5-vinylpyridine, vinylpyrimidine, vinylpiperidine, 9-vinylcarbazole, 3-vinylcarbazole, 4-vinylcarbazole, 1-vinylimidazole, 2-methyl-1-vinylimidazole, N-vinylpyrrolidone, 2-vinylpyrrolidone, N-vinylpyrrolidine, 3-vinylpyrrolidine, N-vinylcaprolactam, N-vinylbutyrolactam, vinyloxolane, vinylfuran, vinylthiophene, vinylthiolane, vinylthiazoles and hydrogenated vinylthiazoles, vinyloxazoles and hydrogenated vinyloxazoles;

vinyl and isoprenyl ethers;

methacrylic acid and acrylic acid.

[0043] The comonomers and the ester monomers of the formulae (I), (II) and (III) can each be used individually or as mixtures.

[0044] The proportion of comonomers can be varied depending on the use and property profile of the polymer. In general, this proportion may be in the range from 0 to 60% by weight, preferably from 0.01 to 20% by weight and more preferably from 0.1 to 10% by weight. Owing to the combustion properties and for ecological reasons, the proportion of the monomers which comprise aromatic groups, heteroaromatic groups, nitrogen-containing groups, phosphorus-containing groups and sulphur-containing groups should be minimized. The proportion of these monomers can therefore be restricted to 1% by weight, in particular 0.5% by weight and preferably 0.01% by weight.

[0045] Preferably, the polyalkyl(meth)acrylate polymer comprises units derived from hydroxyl-containing monomers and/or (meth)acrylates of ether alcohols. According to a preferred aspect of the present invention, the polyalkyl(meth) acrylate polymer preferably comprises 0.1 to 40% by weight, especially 1 to 20% by weight and more preferably 2 to 10% by weight of hydroxyl-containing monomer and/or (meth) acrylates of ether alcohols based on the weight of the polymer. The hydroxyl-containing monomers include hydroxyalkyl (meth)acrylates and vinyl alcohols. These monomers have been disclosed in detail above.

[0046] The polyalkyl(meth)acrylate polymers of component (A) preferably have a number average molecular weight M_n in the range of 15000 to 75000 g/mol

[0047] The polydispersity M_w/M_n of the polyalkyl(meth) acrylate polymers preferably is in the range from of 1 to 8, especially from 1.05 to 6.0, more preferably from 1.1 to 5.0 and most preferably from 1.1 to 4. The weight average molecular weight M_w, the number average molecular weight M_n and the polydispersity M_w/M_n can be determined by GPC using a methyl methacrylate polymer as standard.

[0048] The architecture of the polyalkyl(meth)acrylate polymers is not critical for many applications and properties. Accordingly, these polymers may be random copolymers, gradient copolymers, block copolymers and/or graft copolymers. Block copolymers and gradient copolymers can be obtained, for example, by altering the monomer composition discontinuously during the chain growth.

[0049] According to a preferred embodiment, the present composition comprises at least one ethylene vinyl acetate copolymer comprising units being derived from at least one alkyl (meth)acrylate having 1 to 30 carbon atoms in the alkyl residue as component (B).

[0050] Polymers comprising units being derived from ethylene, vinyl acetate and at least one alkyl (meth)acrylate having 1 to 30 carbon atoms in the alkyl residue can be obtained by the polymerisation of corresponding monomer compositions. Ethylene and vinyl acetate are commercially available from a number of suppliers. Alkyl (meth)acrylates having 1 to 30 carbon atoms in the alkyl residue are described below and above and reference is made thereto.

[0051] These ethylene vinyl acetate copolymers may contain 1 to 60% by weight, particularly 5 to 40% by weight, preferably 10 to 20% by weight of units being derived from ethylene based on the total of the repeating units. Particular preference is given to ethylene vinyl acetate copolymers containing preferably 0.5 to 60% by weight, especially 2 to 40% by weight or 3 to 40% by weight and more preferably 5 to 10% by weight of vinyl acetate based on the total of the repeating units.

[0052] Preferably, the amount of alkyl (meth)acrylates having 1 to 30 carbon atoms in the alkyl residue is in the range of from 10% by weight to 90% by weight, especially in the range of from 30 to 80% by weight and more preferably in the range of from 60 to 80% by weight based on the total of the repeating units.

[0053] According to a special embodiment of the present invention, the ethylene vinyl acetate copolymers preferably comprise from 30 to 90% by weight, more preferably from 60 to 80% by weight, of units being derived from at least one alkyl (meth)acrylate having 7 to 15 carbon atoms in the alkyl residue.

[0054] Preferably, the molar ratio of ethylene to vinyl acetate of the ethylene vinyl acetate copolymer could be in the range of 100:1 to 1:2, more preferably in the range of 20:1 to 2:1, especially preferably 10:1 to 3:1. The molar ratio of alkyl (meth)acrylates having 1 to 30 carbon atoms in the alkyl residue to vinyl acetate of the ethylene vinyl acetate copolymer is preferably in the range of 50:1 to 1:2, more preferably in the range of 10:1 to 1:1, especially preferably 5:1 to 2:1. Particularly, the molar ratio of ethylene to alkyl (meth)acrylates having 1 to 30 carbon atoms in the alkyl residue of the ethylene vinyl acetate copolymer is preferably in the range of 10:1 to 1:20, more preferably in the range of 2:1 to 1:10, especially preferably 1:1 to 1:5.

[0055] In addition to the monomers mentioned above and below, the ethylene vinyl acetate copolymer may contain further comonomers. These monomers are mentioned above and below and reference is made thereto. Especially preferred are vinyl esters and olefins. Suitable vinyl esters derive from fatty acids having linear or branched alkyl groups having 2 to 30 carbon atoms. Examples include vinyl propionate, vinyl butyrate, vinyl hexanoate, vinyl heptanoate, vinyl octanoate, vinyl laurate and vinyl stearate, and also esters of vinyl alcohol based on branched fatty acids, such as vinyl isobutyrate, vinyl pivalate, vinyl 2-ethylhexanoate, vinyl isononanoate, vinyl neononanoate, vinyl neodecanoate and vinyl neounde-

canoate. Suitable olefins include propene, butene, isobutylene, hexene, 4-methylpentene, octene, diisobutylene and/or norbornene.

[0056] Particularly, ethylene vinyl acetate copolymer may comprise from 0 to 20% by weight and more preferably from 1 to 10% by weight of units being derived from comonomers.

[0057] The architecture of the ethylene vinyl acetate copolymers is not critical for many applications and properties. Accordingly, the ester-comprising polymers may be random copolymers, gradient copolymers, block copolymers and/or graft copolymers.

[0058] According to a special aspect of the present invention, ethylene vinyl acetate copolymers is a graft copolymer having an ethylene vinyl acetate copolymer as graft base and an alkyl (meth)acrylate having 1 to 30 carbon atoms in the alkyl residue as graft layer. Preferably, the weight ratio of graft base to graft layer is in the range of from 1:1 to 1:20 more preferably 1:2 to 1:10.

[0059] The polydispersity M_w/M_n of the ethylene vinyl acetate copolymers may be in the range from of 1 to 8, preferably from 1.05 to 6.0 and most preferably from 1.2 to 5.0. The weight average molecular weight M_w, the number average molecular weight M_n and the polydispersity M_w/M_n can be determined by GPC using a methyl methacrylate polymer as standard.

[0060] The ethylene vinyl acetate copolymers to be used in accordance with the invention can be prepared by the free radical polymerization method mentioned above and reference is made thereto. Preferably, the ethylene vinyl acetate copolymers can be manufactured according to the method described in EP-A 406684 (Röhm GmbH).

[0061] According to a preferred aspect of the present invention, the ethylene vinyl acetate copolymer is a graft copolymer having an ethylene vinyl acetate copolymer as graft base. The ethylene vinyl acetate copolymer useful as graft base preferably have a number average molecular weight M_n in the range of 1000 to 100 000 g/mol, especially in the range of 5000 to 80 000 g/mol and more preferably in the range of 10 000 to 50 000 g/mol.

[0062] The preparation of the polyalkyl(meth)acrylate polymers and the ethylene vinyl acetate copolymer comprising units being derived from at least one alkyl (meth)acrylate from the above-described monomers is known per se. Thus, these polymers can be obtained in particular by free-radical polymerization and related processes, for example ATRP (=Atom Transfer Radical Polymerization), RAFT (=Reversible Addition Fragmentation Chain Transfer) or NMP processes (nitroxide-mediated polymerization). In addition thereto, these polymers are also available by anionic polymerisation.

[0063] Customary free-radical polymerization is described, inter alia, in Ullmann's Encyclopedia of Industrial Chemistry, Sixth Edition. In general, a polymerization initiator is used for this purpose. The usable initiators include the azo initiators widely known in the technical field, such as 2,2'-azo-bis-isobutyronitrile (AIBN), 2,2'-azo-bis-(2-methylbutyronitrile) (AMBN) and 1,1-azobiscyclohexanecarbonitrile, and also peroxy compounds such as methyl ethyl ketone peroxide, acetylacetone peroxide, dilauryl peroxide, tert-butyl peroxypivalate, tert-butyl peroxy-2-ethyl hexanoate, tert-amyl peroxy-2-ethyl hexanoate, ketone peroxide, tert-butyl peroctoate, methyl isobutyl ketone peroxide, cyclohexanone peroxide, dibenzoyl peroxide, tert-butyl-peroxybenzoate, tert-butyl-peroxyisopropylcarbonate, 2,5-bis(2-ethylhexanoyl-peroxy)-2,5-dimethylhexane, tert-butyl-peroxy-2-ethylhexanoate, tert-butyl-peroxy-3,5,5-trimethylhexanoate, dicumyl peroxide, 1,1-bis(tert-butyl-peroxy)cyclohexane, 1,1-bis(tert-butyl-peroxy)-3,3,5-trimethylcyclohexane, cumyl hydroperoxide, tert-butyl-hydroperoxide, bis(4-tert-butylcyclohexyl) peroxydicarbonate, mixtures of two or more of the aforementioned compounds with one another, and mixtures of the aforementioned compounds with compounds which have not been mentioned but can likewise form free radicals. Furthermore a chain transfer agents can be used. Suitable chain transfer agents are in particular oil-soluble mercaptans, for example dodecyl mercaptan or 2-mercaptoethanol, or else chain transfer agents from the class of the terpenes, for example terpineols.

[0064] Preferably, the polymers can be achieved by using high amounts of initiator and low amounts of chain transfer agents. Especially, the mixture to obtain the polyalkyl(meth) acrylate polymer useful for the present invention may comprise 1 to 15% by weight, preferably 2 to 10% by weight and more preferable 4 to 8% by weight initiator based on the amount of monomers. The amount of chain transfer agents can be used in an amount of 0 to 2% by weight, preferably 0.01 to 1% by weight and more preferable 0.02 to 0.1% by weight based on the amount of monomers.

[0065] The ATRP process is known per se. It is assumed that it is a "living" free-radical polymerization, without any intention that this should restrict the description of the mechanism. In these processes, a transition metal compound is reacted with a compound which has a transferable atom group. This transfers the transferable atom group to the transition metal compound, which oxidizes the metal. This reaction forms a radical which adds onto ethylenic groups. However, the transfer of the atom group to the transition metal compound is reversible, so that the atom group is transferred back to the growing polymer chain, which forms a controlled polymerization system. The structure of the polymer, the molecular weight and the molecular weight distribution can be controlled correspondingly. This reaction is described, for example, by J S. Wang, et al., J. Am. Chem. Soc., vol. 117, p. 5614-5615 (1995), by Matyjaszewski, Macromolecules, vol. 28, p. 7901-7910 (1995). In addition, the patent applications WO 96/30421, WO 97/47661, WO 97/18247, WO 98/40415 and WO 99/10387 disclose variants of the ATRP explained above.

[0066] Preferably, catalytic chain transfer processes using cobalt (II) chelates complex can be used to prepare the polymers useful for the present invention as disclosed in U.S. Pat. No. 4,694,054 (Du Pont Co) or U.S. Pat. No. 4,526,945 (SCM Co).

[0067] In addition, the polymers may be obtained, for example, also via RAFT methods. This process is presented in detail, for example, in WO 98/01478 and WO 2004/083169, to which reference is made explicitly for the purposes of disclosure.

[0068] In addition, the polymers are also obtainable by NMP processes (nitroxide-mediated polymerization), which is described, inter alia, in U.S. Pat. No. 4,581,429.

[0069] These methods are described comprehensively, in particular with further references, inter alia, in K. Matyjazewski, T. P. Davis, Handbook of Radical Polymerization, Wiley Interscience, Hoboken 2002, to which reference is made explicitly for the purposes of disclosure.

[0070] The anionic polymerisation is well known in the art and described, inter alia, in Ullmann's Encyclopedia of Industrial Chemistry, Sixth Edition. According to a preferred aspect of the present invention, the polyalkyl(meth)acrylate polymer can be obtained according to a method described in U.S. Pat. No. 4,056,559 (Rohm & Haas Co) Particularly, potassium methoxide solution can be used as initiator.

[0071] The polymerization may be carried out at standard pressure, reduced pressure or elevated pressure. The polymerization temperature too is uncritical. However, it is generally in the range of −200° C. to 200° C., especially 0° C. to 190° C., preferably 60° C. to 180° C. and more preferably 120° C. to 170° C. Higher temperatures are especially preferred in free radical polymerizations using high amounts of initiators.

[0072] The polymerization may be carried out with or without solvent. The term solvent is to be understood here in a broad sense.

[0073] The polymerization is preferably carried out in a nonpolar solvent. These include hydrocarbon solvents, for example aromatic solvents such as toluene, benzene and xylene, saturated hydrocarbons, for example cyclohexane, heptane, octane, nonane, decane, dodecane, which may also be present in branched form. These solvents may be used individually and as a mixture. Particularly preferred solvents are mineral oils, diesel fuels of mineral origin, naphthenic solvents, natural vegetable and animal oils, biodiesel fuels and synthetic oils (e.g. ester oils such as dinonyl adipate), and also mixtures thereof. Among these, very particular preference is given to mineral oils, mineral diesel fuels and naphthenic solvent (e.g. commercially available Shellsol® A150, Solvesso® A150).

[0074] In addition to the ethylene vinyl acetate copolymer comprising units being derived from at least one alkyl (meth) acrylate having 1 to 30 carbon atoms in the alkyl residue as described above, the composition of the present invention may preferably comprise at least one polyalkyl(meth)acrylate polymer. As mentioned above, also the polyalkyl(meth)acrylate polymer may comprise units being derived from ethylene and vinyl acetate as comonomers. However, the ethylene vinyl acetate copolymer differs from the polyalkyl(meth) acrylate copolymer. Especially, the amounts of ethylene and/or vinyl acetate in the ethylene vinyl acetate copolymer are higher than in the polyalkyl(meth)acrylate polymer. Therefore the present composition may preferably comprise at least two polymers being different in their ethylene and/or vinyl acetate proportion.

[0075] The weight ratio of both polymers may be in a wide range. Preferably, the weight ratio of the polyalkyl(meth) acrylate polymer having a number average molecular weight M_n of from 15000 to 75000 g/mol and a polydispersity M_w/M_n of from 1 to 8 to the ethylene vinyl acetate copolymer comprising units being derived from at least one alkyl (meth) acrylate having 1 to 30 carbon atoms in the alkyl residue is in the range of from 40:1 to 1:10, particularly 20:1 to 1:2, especially 15:1 to 1:1, more preferably 10:1 to 3:1 and most preferably 6:1 to 5:1.

[0076] The inventive composition further comprises at least one antioxidant as component (C). The antioxidant used in the present invention is in the general class known as free radical inhibitors and/or antioxidants. More specifically the antioxidants used are well known as disclosed in the documents mentioned above.

[0077] Preferred antioxidants useful for the present invention are disclosed in US patent application publication no. 2004/0139649, US 2006/0219979 and US 2009/094887A1 and international publication WO 2009/108747 A1.

[0078] The antioxidants are generally commercially available. For more details it is herein referred to known prior art, in particular to Römpp-Lexikon Chemie; Editor: J. Falbe, M. Regitz; Stuttgart, N.Y.; 10. version (1996); keyword "antioxidants" and the at this site cited literature references.

[0079] Antioxidants include e.g. aromatic compounds and/or nitrogen containing compounds.

[0080] Organic nitrogen compounds being useful as antioxidant are known in themselves. Besides one or more nitrogen atoms, they contain alkyl, cycloalkyl or aryl groups, and the nitrogen atom may also be a member of a cyclic group.

[0081] Preferably, nitrogen containing compounds include amine-containing antioxidant components. Examples include naphthylamine derivative, diphenylamine derivative, p-phenylene diamine derivative, and quinoline derivative as mentioned e.g. in CN 101353601 A, nitro-aromatics, e.g. nitro benzene, di-nitrobenzene, nitro-toluene, nitro-napthalene, and di-nitro-napthalene and alkyl nitro benzenes and poly aromatics as mentioned e.g. in WO 2008/056203 A2 and aliphatic amine as described e.g. in WO 2009/016400 A1.

[0082] Preferred antioxidants comprise amines, such as thiodiphenylamine and phenothiazine; and/or p-phenylene diamines, such as N,N'-diphenyl-p-phenylene diamine, N,N'-di-2-naphthyl-p-phenylene diamine, N,N'-di-p-tolyl-p-phenylene diamine, N-1,3-dimethylbutyl-N'-phenyl-p-phenylene diamine and N-1,4-dimethylpentyl-N'-phenyl-p-phenylene diamine.

[0083] In a very preferred embodiment of the invention, the antioxidant is an aromatic compound. These aromatic compounds comprise phenolic compounds; especially sterically hindered phenols, such as 2,4-di-t-butylhydroxytoluene (BHT), 2,4-dimethyl-6-tert-butylphenol or 2,6-ditert-butyl-4-methylphenol; tocopherol-compounds, preferably alpha-tocopherol; and/or hydroquinone ethers, such as hydroquinone monomethylether, 2-tert-Butyl-4-hydroxyanisole and 3-tert-butyl-4-hydroxyanisole.

[0084] Especially preferred phenolic compounds have 2 or more hydroxyl groups such as dihydroxybenzenes, preferably hydroquinone or derivatives thereof, such as alkyl hydroquinones, e.g. tert-butylhydroquinone (TBHQ), 2,6-di-tert-butylhydroquinone (DTBHQ), 2,5-di-tert-butylhydroquinone or pyrocatechol or alkyl pyrocatechols, e.g. di-tert-butylbrenzcatechine.

[0085] Furthermore, phenolic compounds having 3 or more hydroxyl groups are preferred. These compounds include e.g. propyl gallate and pyrogallol.

[0086] Regarding the antioxidants mentioned, phenolic compounds are especially preferred.

[0087] The antioxidants can be used individually or as a mixture. Surprising results could be achieved with mixtures comprising phenolic compounds having at least two hydroxyl groups such as hydroquinones, propyl gallate and pyrogallol; and phenolic compounds having exactly one hydroxyl groups such as hydroquinone ethers, sterically hindered phenols, such as 2,4-di-tert-butylhydroxytoluene (BHT), 2,4-dimethyl-6-tert-butylphenol or 2,6-di-tert-butyl-4-methylphenol; and/or tocopherol-compounds, preferably alpha-tocopherol. According to a very preferred embodiment, the mixture may preferably comprise phenolic compounds having at least three hydroxyl groups such as propyl gallate and

pyrogallol; and phenolic compounds having exactly two hydroxyl groups such as hydroquinone or derivatives thereof.

[0088] If more than one antioxidant is used, the two antioxidants can preferably be at a weight ratio of in the range of about 20:1 to 1:20, especially more preferably 10:1 to 1:10, more preferably 5:1 to 1:5. Depending on the desired characteristics of the biodiesel, one skilled in the art, in view of the present disclosure, would be able to select appropriate concentrations and ratios of antioxidants.

[0089] According to a preferred aspect of the present invention, the composition comprises a mixture stabilizer as component (D), preferably phenolic compounds having exactly one hydroxyl groups such as hydroquinone ethers, sterically hindered phenols, such as 2,4-di-tert-butylhydroxytoluene (BHT), 2,4-dimethyl-6-tert-butylphenol or 2,6-di-tert-butyl-4-methylphenol; and/or tocopherol-compounds, preferably alpha-tocopherol. Preferably sterically hindered phenols, such as 2,4-di-tert-butylhydroxytoluene (BHT), 2,4-dimethyl-6-tert-butylphenol or 2,6-di-tert-butyl-4-methylphenol can be used as mixture stabilizer with 2,4-di-tert-butylhydroxytoluene being more preferred.

[0090] Preferably, the composition according to the present invention can be prepared by mixing the components mentioned above. Solvents can be used for accomplishing the mixing. Preferred solvents are polar organic solvents, especially ethers and esters. Preferably, ethers and esters comprise glycol groups.

[0091] Preferred solvents of component (E) include ethers, more preferably glycol ethers such as ethylene glycol monomethyl ether (2-methoxyethanol), ethylene glycol monoethyl ether (2-ethoxyethanol), ethylene glycol monopropyl ether (2-propoxyethanol), ethylene glycol monoisopropyl ether (2-isopropoxyethanol), ethylene glycol monobutyl ether (2-butoxyethanol), ethylene glycol monophenyl ether (2-phenoxyethanol), ethylene glycol monobenzyl ether (2-benzyloxyethanol), diethylene glycol monomethyl ether (2-(2-methoxyethoxyl)ethanol), diethylene glycol monoethyl ether (2-(2-ethoxyethoxyl)ethanol, diethylene glycol mono-n-butyl ether (2-(2-butoxyethoxyl) ethanol), ethylene glycol dimethyl ether (dimethoxyethane), ethylene glycol diethyl ether (diethoxyethane) and ethylene glycol dibutyl ether (dibutoxyethane). Regarding the ethers diethylene glycol solvents are preferred, especially diethylene glycol monobutyl ether.

[0092] Preferred esters having glycol groups include ethylene glycol methyl ether acetate (2-methoxyethyl acetate), ethylene glycol monoethyl ether acetate (2-ethoxyethyl acetate) and ethylene glycol monobutyl ether acetate (2-butoxyethyl acetate).

[0093] The mixture achieved can be used as an additive composition.

[0094] Preferably, an additive composition comprises at most 70% by weight, especially at most 50% by weight and more preferably at most 30% by weight of solvent. Preferably, an additive composition comprises at least 2% by weight, especially at least 5% by weight and more preferably at least 10% by weight of mixture stabilizer. Preferably, an additive composition comprises at least 2% by weight, especially at least 5% by weight and more preferably at least 10% by weight of mixture antioxidant. Preferably, an additive composition comprises at least 10% by weight, especially at least 20% by weight and more preferably at least 25% by weight of cold flow improver. According to a special aspect of the present invention, the cold flow improver comprises a mixture of more preferably a mixture of at least one polyalkyl (meth)acrylate polymer having a number average molecular weight M_n of from 15000 to 75000 g/mol and a polydispersity M_w/M_n of from 1 to 8 and at least one ethylene vinyl acetate copolymer comprising units being derived from at least one alkyl (meth)acrylate having 1 to 30 carbon atoms in the alkyl residue. The compositions provide homogenous miscible mixture which can improve both cold flow and oxidation stability of vegetable oils and animal fats.

[0095] According to a preferred embodiment, the mixture stabilizer and the cold flow improver are mixed as a first solution, while the antioxidant is solved in a solvent to form a second solution. The first and the second solution can be mixed, preferably at a temperature in the range of 40 to 100° C., more preferably at a temperature in the range of 60 to 80° C. to form a homogenous additive mixture which can improve both cold flow and oxidation stability of vegetable oils and animal fats. The ethylene vinyl acetate copolymer comprising units being derived from at least one alkyl (meth)acrylate having 1 to 30 carbon atoms in the alkyl residue can be added to the first and/or second solution.

[0096] Surprisingly an additive composition comprising a mixture of at least one polyalkyl(meth)acrylate polymer having a number average molecular weight M_n of from 15000 to 75000 g/mol and a polydispersity M_w/M_n of from 1 to 8 and at least one ethylene vinyl acetate copolymer comprising units being derived from at least one alkyl (meth)acrylate having 1 to 30 carbon atoms in the alkyl residue provides a stable liquid composition. The stability and miscibility can be improved by using a mixture stabilizer and/or a solvent.

[0097] Examples of vegetable oils which can be used in accordance with the invention are palm oil, rapeseed oil, coriander oil, soya oil, cottonseed oil, sunflower oil, castor oil, olive oil, groundnut oil, corn oil, almond oil, palm kernel oil, coconut oil, mustard seed oil, jojoba oil, jatropa oil, olive oil etc. Examples of animal fats which can be used in accordance with the invention are oils which are derived from animal tallow, especially beef tallow, bone oil, fish oils, lard, chicken oil, whale sperm, etc. and used cooking oils. Further examples include oils which derive from cereal, wheat, jute, sesame, rice husks, jatropha, arachis oil and linseed oil.

[0098] The common methods to evaluate the cold flow quality are pour point (PP) tests as mentioned in ASTM D97. Oxidation stability of oils and fats is normally evaluated via Rancimat test (EN 14112), measured at 110° C. In this test, a purified air stream is fed through the sample to induce the formation of volatile acids formed from the oxidation process. These volatile acids are then distilled into a measurement vessel containing deionised water, in which the conductivity of the solution is measured. The end of induction period is measured as the conductivity increases. Typical induction periods for rapeseed oil are 5 to 7 h and 1 to 2 h for sunflower oil. A few examples of antioxidants include BHA (butylated hydroxy anisole), BHT (butylated hydroxy toluene), TBHQ (tertiary butylated hydroxy quinone) etc., which are successfully used to improve the cold flow behaviour of vegetable oils and animal fats.

[0099] The use of antioxidants and ethylene vinyl acetate copolymer comprising units being derived from at least one alkyl (meth)acrylate having 1 to 30 carbon atoms in the alkyl residue in a concentration of 0.01 to 4% by weight, preferably 0.05 to 2% by weight, as a flow improver in fuel compositions which comprise vegetable oils and/or animal fats accordingly

provides lubricant compositions with exceptional properties, especially a high oxidation stability and good cold flow properties.

[0100] The invention will be illustrated in detail hereinafter with reference to examples and comparative examples, without any intention that this should impose a restriction. Unless otherwise specified, the percentages are weight percent.

EXAMPLES

[0101] The following different types of vegetable oils were used in the examples:

Oil/Fat	Pour Point (PP)	Rancimat induction period (IP)
Sunflower oil	−15° C.	~1.2 hours
High oleic sunflower oil	−18° C.	~6.5 hours
Soybean oil	−9° C.	~4.5 hours
Canola oil-II	−18° C.	~8.5 hours
High oleic canola oil	−18° C.	~15 hours

General Method to Prepare the CFI and the Additive Containing CFI and Antioxidant

Example 1

Preparation of PAMA-I

[0102] PAMA-I, which has a number average molecular weight (M_n) in the range of 35000 g/mol to 75000 g/mol, can be prepared by the following method:

A reaction vessel was charged with 10.24 g stearyl methacrylate (SMA), 52.7 g dodecyl pentadecyl methacrylate (DPMA), 7 g methyl methacrylate (MMA), and 0.2 g n-dodecyl mercaptan. The resulting mixture was stirred under nitrogen inert conditions and heated up to a reaction temperature of 115° C. An initiator mixture containing 0.18 g tert-butyl-per-2-ethyl-hexanoate and 7.8 g diisononyladipate was separately prepared. The initiator mixture was fed to the reaction mixture for 150 minutes in two steps. Step-1: 2.0 gram of initiator mixture over 90 minutes at 115° C., step-2: 3.35 gram of initiator mix over 60 minutes at 115° C. Later, 0.24 g of tert-butyl-per-2-ethyl-hexanoate was added in the remaining initiator mix and was fed for 60 minutes at 105° C. The reaction was held for another 30 minutes at 105° C. Thereafter, 22.2 g of rapeseed oil was added to the product in order to bring it to a desired dilution.

Example 2

Preparation of PAMA-II

[0103] PAMA-II, which has a number average molecular weight (M_e) in the range of 35000 g/mol to 75000 g/mol, can be prepared by the following method:

A reaction vessel was charged with 50.4 g lauryl methacrylate (LMA), 19.6 g SMA and 0.35 g n-dodecyl mercaptan. The resulting mixture was stirred under nitrogen inert conditions and heated up to a reaction temperature of 120° C. An initiator mixture containing 0.143 g tert-butyl-per-2-ethyl-hexanoate and 0.445 g canola oil was separately prepared. The initiator mixture was fed to the reaction mixture for 100 minutes in three steps. Step-1: 0.06 gram of initiator mixture over 30 minutes at 120° C., step-2: 0.12 gram of initiator mixture over 40 minutes at 120° C., step-3: 0.42 gram of initiator mixture over 30 minutes at 105° C. The reaction was held for another 30 minutes at 105° C. Thereafter, 29.05 gram of Canola oil was added to bring the product to a desired dilution.

[0104] The molecular weights of PAMA-I and PAMA-II were determined by SEC (Size Exclusion Chromatography):

[0105] Columns: 5 SDV columns 8×300 mm resp. 8×50 mm (company PSS at Mainz), 1 solvent-peak separation column 8×100 mm (company Shodex)

[0106] Instrument: Agilent 1100 Series

[0107] Oven: 35° C.

[0108] Eluent: tetrahydrofuran

[0109] Flow rate: 1 mL/min

[0110] Injected volume: 100 μL

[0111] RI detection at 40° C.

[0112] Concentration of sample solution: 2 g/L

[0113] Standards: PMMA (PSS Mainz or Polymer Laboratories)

Example 3

Preparation of EVA-Graft-PAMA as Disclosed in U.S. Pat. No. 4,906,682 (RöHm GmbH)

[0114] Dissolve 20 g of EVA copolymer in 150 gram dilution oil by stirring the mixture at 100° C. overnight. Adjust the temperature to 90° C. Start feeding 80 g of dodecyl pentadecyl methacrylate (DPMA) containing 0.5% tert-butylperoxy-2-ethyl-hexanoate to the EVA copolymer solution over 3.5 hours. Hold the reaction by stirring the mixture at 90° C. for another 2 hours. Add 0.2% tert-butylperoxy-2-ethyl-hexanoate and hold for another 45 minutes.

Example 4

Preparation of CFI-I (Cold Flow Improver-I) Additive Containing PAMA-I and EVA-Graft-PAMA

[0115] Mix 85 g of CFI-I and 15 g of p(EVA-g-DPMA). Blend the mixture by stirring at 60° C. for a minimum of 1 hour. The blend appears homogeneous and colourless.

Example 5

Preparation of CFI-II Additive Containing PAMA-II and EVA-Graft-PAMA

[0116] Mix 85 g of CFI-1 and 15 g of p(EVA-g-DPMA). Blend the mixture by stirring at 60° C. for a minimum of 1 hour. The blend appears homogeneous and colourless.

Example 6

Preparation of Additive Composition Containing Antioxidants and Cold Flow Improvers (Additive A-1)

[0117] In a 50 mL reaction flask, dissolve 15 g of TBHQ in 15 g of diethylene glycol monobutyl ether at 60° C. under nitrogen inert conditions for a minimum of one hour. The latter solution is termed as solution I. In a separate 150 mL reaction flask, blend 50 g of CFI-I and 20 g of BHT at 60° C. under nitrogen inert for a minimum of one hour. The latter mixture is termed as solution II. Later mix solution I and solution II at 60° C. under nitrogen inert conditions for

another one hour. The final mixture contains 50% CFI-I, 15% TBHQ, 15% diethylene glycol monobutyl ether and 20% BHT (Additive A-1).

Example 7

Preparation of Additive Composition Containing Antioxidants and Cold Flow Improvers (Additive A-2)

[0118] In a 50 mL reaction flask, dissolve 15 g of TBHQ in 15 g of diethylene glycol monobutyl ether at 60° C. under nitrogen inert conditions for a minimum of one hour. The latter solution is termed as solution I. In a separate 150 mL reaction flask, blend 50 g of CFI-II and 20 g of BHT at 60° C. under nitrogen inert conditions for a minimum of one hour. The latter mixture is termed as solution II. Later mix solution I and solution II at 60° C. under nitrogen inert conditions for another one hour. The final mixture contains 50% CFI-II, 15% TBHQ, 15% diethylene glycol monobutyl ether and 20% BHT (Additive A-2).

Example 8

Comparative Examples

[0119] Comparative examples B1 to B6 were all prepared in the similar manner to the preparation of Additive A-1 and Additive A-2.

[0120] The details of the variations in the recipe are described in table 1.

TABLE 1

Comparative Example	Antioxidant	Solvent	CFI	Mixture stabilizer
B-1	15% TBHQ	15% diethylene glycol monobutyl ether	42.5% PAMA (biodiesel flow improver palm methyl ester) + 7.5% EVA-graft-PAMA	15% diethylene glycol monobutyl ether
B-2	15% TBHQ	15% diethylene glycol monobutyl ether	42.5% PAMA (biodiesel flow improver rapeseed methyl ester) + 7.5% EVA-graft-PAMA	15% diethylene glycol monobutyl ether
B-3	15% TBHQ	15% diethylene glycol monobutyl ether	47% PAMA II + 3% high oleic sunflower oil	15% diethylene glycol monobutyl ether
B-4	15% TBHQ	15% diethylene glycol monobutyl ether	42.5% PAMA II + 7.5% high oleic sunflower oil	15% diethylene glycol monobutyl ether
B-5	15% TBHQ	15% diethylene glycol monobutyl ether	47% PAMA II + 3% soybean oil	15% diethylene glycol monobutyl ether
B-6	15% TBHQ	15% diethylene glycol monobutyl ether	42.5% PAMA II + 7.5% soybean oil	15% diethylene glycol monobutyl ether

[0121] 42.5% PAMA in comparative example B-1, which is a cold flow improver for fossil diesel oil and biodiesel oil, uses greater C16 and C18 fractions compared to A-1 and A-2. 42.5% PAMA in comparative example B-2, which is also a cold flow improver for fossil diesel oil and biodiesel oil, has a number average molecular weight below 10,000 g/mol, which is significantly lower as compared to A-1 and A-2. The comparative examples B-3 to B-6 consist of CFI (cold flow improver) combinations, which exclude EVA-graft-PAMA. The comparative example B-3 and B-5 used 47% PAMA-II that equals the polymer actives in comparison to the CFI combination used in A-2. Whereas, in the comparative example B-4 and B-6 simply replaces the EVA-graft-PAMA fraction by high oleic sunflower oil and soybean oil, respectively.

Visual Appearance of the Additives

[0122] Visual appearances of Additives A-1, A-2 and Comparative Examples B-1 to B-6 are summarized in Table 2.

TABLE 2

Additive	Visual Appearance		
	After 1 day	After 1 week	After 2 weeks
A-1	miscible and hazy	miscible and hazy	miscible and hazy
A-2	miscible and hazy	miscible and hazy	miscible and hazy
B-1	miscible and hazy	miscible and hazy	miscible and hazy
B-2	miscible and hazy	miscible but start to re-crystallize	presence of two phases
B-3	Immiscible	Clear phase separation	Clear phase separation
B-4	Immiscible	Clear phase separation	Clear phase separation
B-5	Immiscible	Clear phase separation	Clear phase separation
B-6	Immiscible	Clear phase separation	Clear phase separation

[0123] As described earlier in Table 1, the comparative examples B-3 to B-6 do not contain EVA-graft-PAMA. As shown in the Table 2, it is clearly indicates that the without the presence of EVA-graft-PAMA, the individual components in the additive formulation are immiscible.

Influence of EVA-Graft-PAMA on the Cold Flow Improvement of Oils and Fats

[0124] In Table 3, examples C-1 and C-2 are PAMA formulations with and without presence of EVA-graft-PAMA. C-1 and C-2 were then evaluated with respect to the pour point activity in 2011/53.

TABLE 3

Example	PAMA II [wt %]	EVA-graft-PAMA [wt %]	Sunflower Oil (2011/553) [wt %]	treat rate [ppm]	PP [° C.]
C-1	42.5	7.5	50	0	−15
C-1	42.5	7.5	50	2000	−24
C-2	42.5	—	57.5	0	−15
C-2	42.5	—	57.5	2000	−21

[0125] As shown in Table 3, the presence of EVA-graft-PAMA (C−1) gives a boost in the pour point activity in comparison to C-2, which doesn't have EVA-graft-PAMA.

Cold Flow and Oxidation Stability of Natural Vegetable Oils with the Addition of the Additives

[0126] Cold flow ability (pour point, PP) and oxidation stabilities (reported as induction period measured by Rancimat test) of different vegetable oils (2012/301, 2012/302, 2012/303 and 2012/304) using the inventive additives are summarized in Table 4. The performance tests using additives B-2, B-3, B-4, B-5 and B-6 were carried out not during the same period to that of additives A-1, A-2 and B-1. Therefore, the Rancimat value of the neat vegetable oils (2012/301 and 2012/302) were measured before treating the oils with B-2, B-3, B-4, B-5 and B-6.

TABLE 4

Oil	Additive	treat rate [ppm]	PP [° C.]	IP [hour]	ΔIP
High oleic sunflower oil	A-1	0	−18	6.28	0.00
		500	−21	10.99	4.71
		1000	−21	14.14	7.86
		5000	−24	31.19	24.91
		10000	−24	44.17	37.89
	A-2	0	−18	6.28	0.00
		500	−24	11.21	4.93
		1000	−24	14.50	8.22
		5000	−24	30.82	24.54
		10000	−24	43.84	37.56
	B-1	0	−18	6.28	0.00
		500	−21	11.31	5.03
		1000	−21	14.47	8.19
		5000	−21	30.59	24.31
		10000	−21	41.82	35.54
	B-2	0	−15	3.95	0.00
		500	−21	6.46	2.51
		1000	−21	9.54	5.59
		5000	−21	22.16	18.21
		10000	−21	35.24	31.29
	B-3	0	−15	3.95	0.00
		500	−24	7.15	3.20
		1000	−24	9.75	5.80
		5000	−24	22.48	18.53
		10000	−24	34.08	30.13
	B-4	0	−15	3.95	0.00
		500	−24	6.99	3.04
		1000	−24	9.77	5.82
		5000	−24	22.80	18.85
		10000	−24	33.56	29.61
Soybean oil	A-1	0	−9	4.45	0.00
		500	−12	7.91	3.46
		1000	−12	10.43	5.98
		5000	−15	20.07	15.62
		10000	−24	29.04	24.59
	A-2	0	−9	4.45	0.00
		500	−12	7.77	3.32
		1000	−12	9.85	5.40
		5000	−18	15.63	11.18
		10000	−21	28.20	23.75
Soybean oil	B-1	0	−9	4.45	0.00
		500	−9	6.12	1.67
		1000	−12	7.75	3.30
		5000	−12	15.59	11.14
		10000	−9	27.22	22.77
	B-2	0	−9	3.28	0.00
		500	−9	4.55	1.27
		1000	−9	5.30	2.02
		5000	−9	11.80	8.52
		10000	−9	23.22	19.94
	B-5	0	−9	3.28	0.00
		500	−12	4.45	1.17
		1000	−15	5.73	2.45
		5000	−18	13.46	10.18
		10000	−21	16.25	12.97
	B-6	0	−9	3.28	0.00
		500	−12	4.35	1.07
		1000	−15	6.04	2.76
		5000	−18	12.75	9.47
		10000	−21	20.30	17.02
Canola oil-II	A-1	0	−18	5.93	0.00
		500	−30	8.90	2.97
		1000	−33	12.30	6.37
		5000	−33	16.95	11.02
		10000	−33	29.12	23.19
	A-2	0	−18	5.93	0.00
		500	−30	9.68	3.75
		1000	−30	10.53	4.60
		5000	−33	15.81	9.88
		10000	−33	26.15	20.22
High oleic canola oil	A-1	0	−18	9.65	0.00
		500	−24	15.30	5.65
		1000	−27	17.48	7.83
		5000	−30	35.86	26.21
		10000	−30	48.34	38.69
	A-2	0	−18	9.65	0.00
		500	−27	15.59	5.94
		1000	−27	18.47	8.82
		5000	−30	37.69	28.04
		10000	−30	50.11	40.46

[0127] By evaluating the data presented in 3.4, 3.5 and 3.6, the following values of the additive formulation can be obtained:

[0128] The visual appearance study as summarized in Table 2, i.e. comparing additive A-1 and A-2 against B-2, B-3, B-4, B-5 and B-6, indicates that the presence of EVA-graft-PAMA component is essential to obtain a stable and homogeneous additive formulation over a longer period of time.

[0129] The presence of EVA-graft-PAMA not only stabilizes the additive formulation, but also boosts the pour point of the oils and fats, as shown in Table 3.

[0130] The additive formulation, which is a homogenous solution, can be used to improve the pour point and the oxidation stability of various oils and fats, without any antagonistic effects, as shown in Table 4.

[0131] The choice of PAMA used in the CFI composition is critically important. The use of an inappropriate choice can lead to an antagonistic effect both in cold flow improvement and oxidation stability (see example A-1, A-2 against B-1, B-2).

1. A composition, comprising

(A) 35% to 50% by weight of a polyalkyl (meth)acrylate polymer;

(B) 5% to 15% by weight of an ethylene vinyl acetate copolymer comprising a unit derived from at least one alkyl (meth)acrylate having 1 to 30 carbon atoms in the alkyl residue;

(C) 10% to 20% by weight of a phenolic type antioxidant;

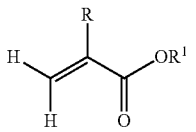
(D) 10% to 25% by weight of a mixture stabilizer; and

(E) 10% to 20% by weight of a glycol ether solvent

wherein the sum of all components (A) to (E) of the composition adds up to 100% by weight.

2. The composition according to claim **1**, wherein the polyalkyl (meth)acrylate polymer of component (A) comprises:

(a) 0 to 40% by weight, based on the total weight of the polymer, of a unit derived from one or more alkyl(meth) acrylate monomers of formula (I)



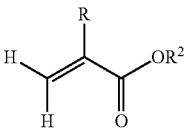
(I)

wherein

R denotes hydrogen or methyl and

R^1 denotes a linear, branched or cyclic alkyl residue with 1 to 6 carbon atoms;

(b) 40 to 99% by weight, based on the total weight of the polymer, of a unit derived from one or more alkyl(meth) acrylate monomers of formula (II)



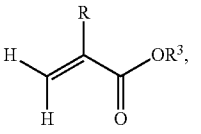
(II)

wherein

R denotes hydrogen or methyl and

R^2 denotes a linear, branched or cyclic alkyl residue with 7 to 15 carbon atoms; and

(c) 0.1 to 40% by weight, based on the total weight of the polymer, of a unit derived from one or more alkyl(meth) acrylate monomers of formula (III)



(III)

wherein

R denotes hydrogen or methyl and

R^3 denotes a linear, branched or cyclic alkyl residue with 16 to 30 carbon atoms, wherein the sum of all components (a) to (c) adds up to 100% by weight.

3. The composition according to claim **1**, wherein the ethylene vinyl acetate copolymer of component (B) comprises:

(i) from 2 to 40% by weight of vinyl acetate;

(ii) from 30 to 80% by weight of a unit derived from at least one alkyl (meth)acrylate having 1 to 30 carbon atoms in the alkyl residue; and

(iii) from 5 to 40% by weight of a unit derived from ethylene,

wherein the sum of all components (i) to (iii) adds up to 100% by weight.

4. The composition according to claim **1**, wherein the ethylene vinyl acetate copolymer of component (B) comprises from 30 to 90% by weight of a unit derived from at least one alkyl (meth)acrylate having 7 to 20 carbon atoms in the alkyl residue.

5. The composition according to claim **1**, wherein the ethylene vinyl acetate copolymer of component (B) is a graft copolymer having an ethylene vinyl acetate copolymer as graft base and an alkyl (meth)acrylate having 1 to 30 carbon atoms in the alkyl residue as graft layer.

6. The composition according to claim **5**, wherein the weight ratio of graft base to graft layer is in the range of from 1:1 to 1:20.

7. The composition according to claim **1**, wherein the polyalkyl(meth)acrylate polymer of component (A) comprises at least 50% by weight of a unit derived from an alkyl (meth) acrylate having 7 to 20 carbon atoms in the alkyl residue.

8. The composition according to claim **7**, wherein the polydispersity M_w/M_n of said polyalkyl(meth)acrylate polymer is in the range of from 1.1 to 5.

9. The composition according claim **1**, wherein the weight ratio of the polyalkyl(meth)acrylate polymer of component (A) to the ethylene vinyl acetate copolymer of component (B) is in the range of from 15:1 to 1:1.

10. The composition according to claim **1**, wherein the weight ratio of the phenolic type antioxidant of component (C) to the ethylene vinyl acetate copolymer of component (B) is in the range of from 5:1 to 1:5.

11. The composition according to claim **1**, wherein the phenolic type antioxidant of component (C) is a phenolic compound having 2 or more hydroxyl groups.

12. The composition according to claim **1**, wherein the mixture stabilizer of component (D) is a sterically hindered phenol.

13. The composition according to claim **12**, wherein said sterically hindered phenol is 2,4-di-tert-butylhydroxytoluene.

14. The composition according to claim **1**, further comprising at least one additive selected from the group consisting of a dispersant, a demulsifier, a defoamer, a lubricity additive, an additional antioxidant, a cetane number improver, a detergent, a dye, a corrosion inhibitor, a metal deactivator, a metal passivator and an odorant.

15. A method of lowering a pour point of a vegetable oil or an animal fat, the method comprising adding the composition of claim **1** to a vegetable oil or an animal fat.

16. A method of improving an oxidation stability of a vegetable oil or an animal fat, the method comprising adding the composition of claim **1** to a vegetable oil or an animal fat.

17. A lubricant, comprising:

(I) 0.01 to 4% by weight of the composition according to claim **1**, based on the total weight of the lubricant; and

(II) 96 to 99.9% by weight of a vegetable or an animal fat, based on the total weight of the lubricant.

18. The lubricant according to claim **17**, wherein component (I) is present in an amount of 0.05% by weight and component (II) is present in an amount of 98 to 99.5% by weight, each based on the total weight of the lubricant.

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