

USE OF COLD FLOW IMPROVER COMPOSITIONS FOR FUELS, BLENDS THEREOF WITH BIOFUELS AND FORMULATIONS THEREOF

The present invention relates to the use of polyalkyl(meth)acrylates as an additive to fuels, especially middle distillate fuels and blends thereof. The present invention further relates to the use of a composition comprising polyalkyl(meth)acrylates as dispersing species susceptible to disperse waxes and sludgy material at low temperatures and a hydrocarbon solvent or an oil for improving the cold flow properties of fuel oil and fuel oil compositions.

The present invention further relates to the use of these compositions as an additive to fuels, especially in the function of paraffin dispersant, to such fuels themselves and to fuel additive concentrates which comprise this composition dissolved in a hydrocarbon solvent or an oil.

Fuels are nowadays typically obtained from fossil sources. However, these resources are limited, so that replacements are being sought. Therefore, interest is rising in renewable raw materials which can be used to produce fuels. A very interesting replacement is in particular biodiesel fuel.

The term biodiesel is in many cases understood to mean a mixture of fatty acid esters, usually fatty acid methyl esters (FAMEs), with chain lengths of the fatty acid fraction of 14 to 24 carbon atoms with 0 to 3 double bonds. The higher the carbon number and the fewer double bonds are present, the higher is the melting point of the FAME. Typical raw materials are vegetable oils (i.e. glycerides) such as rapeseed oils, sunflower oils, soya oils, palm oils, coconut oils and, in isolated cases, even used vegetable oils. These are converted to the corresponding FAMEs by transesterification, usually with methanol under basic catalysis.

The FAME content also affects the cold flow properties of the feedstock. The lower the carbon number and the lower the degree of saturation is in the fatty acid chains, the better is the cold flow property of the feedstock. The common methods to evaluate the cold flow quality are: pour point (PP) test as mentioned in ASTM D97, filterability limit via cold filter plugging point (CFPP) test measured to DIN EN 116 or ASTM D6371, and cloud point (CP) test as described in ASTM D2500.

Currently rapeseed oil methyl ester (RME) is the preferred stock for biodiesel production in Europe as rapeseed allows producing biodiesel fuel with relatively good cold flow properties. However with the high price level of RME, mixtures of RME with other feedstock, such as soybean (SME) or palm methyl ester (PME), have been exploited as well. Soybean is the preferred feedstock in the Americas and palm oil is preferred in Asia. In addition to the utilization of 100% biodiesel, mixtures with fossil diesel, i.e. the middle distillate of crude oil distillation, and biodiesel are also of interest owing to the improved low-temperature properties and better combustion characteristics.

10 In view of the declining ecological quality and decreasing world crude oil reserves, the use of pure biodiesel (B100) has been an important target in many countries. However, many issues, ranging from different combustion characteristics to corrosion of seal materials, have been reported as hindrances to the use of biodiesel as a replacement for fossil diesel.

15 Middle distillate fuels of fossil origin, especially gas oils, diesel oils or extra light heating oils, which are obtained from mineral oil, have different composition depending on the origin of the crude oil and the refinery process.

It has long been known that suitable additives can modify the crystal growth of the n-paraffins in middle distillate fuels. Very effective additives prevent middle distillate fuels from becoming solid even at temperatures a few degrees Celsius below the temperature at which the first paraffin crystals crystallize out. Instead, fine, readily crystallizing, separate paraffin crystals are formed which pass through filters in motor vehicles and heating systems or at least form a filter cake which is permeable to the liquid portion of the middle distillates, so that disruption-free operation is ensured.

The effectiveness of the cold flow improvers is expressed in accordance to European Standard EN 116 indirectly by measuring the cold filter plugging point (CFPP).

30 Ethylene-vinyl carboxylate copolymers have been used for some time as cold flow improvers (CFI) or middle distillate flow improvers (MDFI). One disadvantage of these additives is that the precipitated paraffin crystals, owing to their higher density compared to the liquid portion, tend to settle out more and more at the bottom of the vessel in the course of storage. As a

result, a homogenous low-paraffin phase forms in the upper part of the vessel and a biphasic paraffin-rich layer at the bottom.

5 Since the fuel is usually drawn off just above the vessel bottom both in fuel tanks and in storage or supply tanks of mineral oil dealers, there is a risk that the high concentration of solid n-paraffins leads to plugging of filters and metering devices. The further the storage temperature is below the precipitation temperature of the paraffins and the longer storage times at such temperature are the greater this risk becomes, since the amount of precipitated paraffin increases with falling temperature. In particular, fractions of biodiesel might also
10 enhance this undesired tendency of the middle distillate fuel to n-paraffin sedimentation.

The afore mentioned problems can be reduced significantly by virtue of the additional use of paraffin dispersants or wax anti-settling additives (WASA).

15 As the temperature of the fuel is reduced to below the cloud point, e.g. to the cold filter plugging point, small particles appear in the fuel, which tend to agglomerate and precipitate as large, plate-like or spherulites of wax. These wax crystals increase the difficulties to transport the fuel through lines and pumps and tend to plug fuel lines, screens and filters. The wax from a diesel fuel is primarily an n-alkane wax, crystallizes as platelets whereas the
20 wax coming from biodiesel consists mainly of co-crystallized saturated fatty acid methyl esters (FAME). These problems are well-recognized and various additives have been proposed.

Certain additives, called middle distillate cold flow improvers (MDFI) or biodiesel flow
25 improvers (BDFI), reduce the size and change the shape, from plate-like to needle-like structures, of the wax crystals that do form. Smaller size crystals are desirable since they are less likely to clog the filter whereas needle-like structure are being more likely to pass through a filter, or form a porous layer of crystals on the filter. Other additives may also have the effect of retaining the wax crystals in suspension in the fuel, reducing settling and thus
30 also assisting in the prevention of blockages. These types of additives are often termed "wax anti-settling agents" (WASA).

Many WASA have been described over the past years for avoiding the sedimentation of wax crystals inside a fuel.

For example, US Patent No. 4,400,2708 discloses the efficiency of single molecules based on dialkyl amine derivatives of phthalic acid (PA derivatives). In particular are mentioned N,N-dioctadecyl phthalamic acid, N,N-diarachidyl phthalamic acid and phthalic acid bis-
5 dioctadecyl amide.

Another example, EP Patent No. 1 935 968 describes suitable wax anti-settling agents to be oil-soluble polar nitrogen of which substituents may be in the form of cations. The WASA are condensates of carboxylic acids or their anhydrides with primary or secondary amines
10 containing at least one straight chain C₈₋₄₀ alkyl segment. In particular, the preferred compound is the amide-amine salt formed by reacting 1 molar portion of phthalic anhydride with 2 molar portions of di-(hydrogenated tallow) amine.

In WO International Publication No. 2007/147753 (BASF) a blend of 2 to 3 components is
15 used to stabilize wax crystals in fuels and mixes thereof with biofuels (from B0.1 to B75). The blend consists of 5% to 95% by weight of polar molecule (which is not one of following), 1 to 50% by weight of an amid molecule made from the condensation of a polyamine structure (having 2 to 1000 N-atoms) and with C₈₋₃₀ fatty acids, and which may be mixed with 0 to 50% by weight of a condensate of α,β -dicarboxylic acid (having 4 to 300 C-atoms) and primary
20 amine. As example is given a condensate of ethylenediaminetetraacetic acid (EDTA) with ditallow amine (50 mol%) blended with a condensate of diethylene triamine and oleic acid (37.5 mol%) and a condensate of maleic acid anhydride with tridecylamine (12.5 mol%).

EP Patent No. 1 451 271 describes the use of oil soluble nitrogen compounds obtained by
25 reaction of aliphatic or aromatic amines with aliphatic or aromatic mono, di-, tri-, or tetracarboxylic acids or their anhydrides. In particular, two different types of WASA chemistries are cited as part of the WAFI formulation (wax antissettling and flow improver). One of the chemistry is based on alkenyl-spirolactone reacted with secondary fatty amines having 8 to 36 carbon atoms. Example is given by dodecenyl-spirobis lactone condensed with
30 primary and secondary tallow amines. The second chemistry is provided by a terpolymer of vinyl monomers statistically copolymerized with allyl polyglycol ether and maleic acid anhydride and condensated with primary amines and/or aliphatic alcohol. To illustrate the patent, a terpolymer of C₁₄/C₁₆- α -olefin, maleic anhydride and allylpolyglycol reacted with 2 moles of ditallow amines is mentioned as useful wax stabilizer.

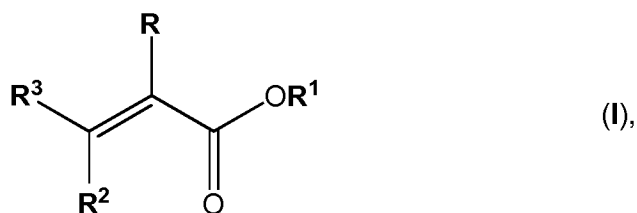
As most of the commercial WASA are based on blends of single modified molecules (like NTA, EDTA and PSA) or on modified poly- α -olefins, we propose as new WASA, a PAMA-based polymeric material having amino functionalities (e.g. for monomers

5 dimethylaminoethylmethacrylate (DMAEMA) or dimethylpropylmethacrylamide (DMPMAm)). These compounds have good handling properties compared to state of the art components and are moreover useful to stabilize wax in fuels or blends thereof.

Summary of the Invention

10 In accordance with a first aspect of the invention, there is provided the use of a polyalkyl(meth)acrylate comprising monomer units of:

- (a) 0% to 40% by weight of one or more ethylenically unsaturated ester compounds of
- 15 formula (I)



wherein

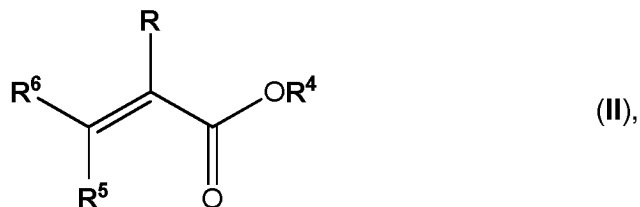
R is H or CH₃,

R¹ represents a linear or branched, saturated or unsaturated alkyl group with 1 to 9 carbon atoms or a cycloalkyl group with 3 to 9 carbon atoms,

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R² and **R**³ independently represent H or a group of the formula -COOR', wherein **R'** is H or a linear or branched, saturated or unsaturated alkyl group with 1 to 9 carbon atoms or a cycloalkyl group with 3 to 9 carbon atoms,

- 25 (b) 20% to 98% by weight of one or more ethylenically unsaturated ester compounds of formula (II)



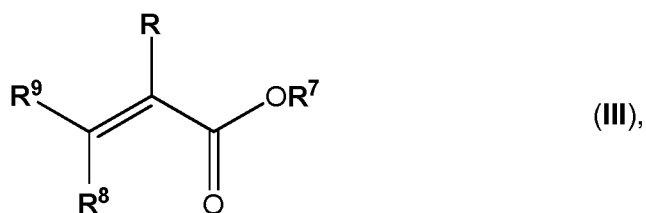
wherein

R is H or CH₃,

R⁴ represents a linear or branched, saturated or unsaturated alkyl group with 10 to 22 carbon atoms,

R⁵ and **R**⁶ independently represent H or a group of the formula -COOR'', wherein **R**'' is H or a linear or branched, saturated or unsaturated alkyl group with 10 to 22 carbon atoms,

- 10 (c) 0% to 10% by weight of one or more ethylenically unsaturated ester compounds of formula (III)



wherein

R is H or CH₃,

R⁷ represents a linear or branched, saturated or unsaturated alkyl group with 23 to 40 carbon atoms,

R⁸ and **R**⁹ independently represent H or a group of the formula -COOR''' wherein **R**''' is H or a linear or branched, saturated or unsaturated alkyl group with 23 to 40 carbon atoms,

- (d) 0% to 30% by weight of vinyl aromatic monomers, and

- (e) 2% to 80% by weight of at least one N-dispersant monomer,

wherein components (a) to (e) add up to 100% by weight, for improving the cold flow properties of fuel oil compositions.

Detailed description of the invention

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Within the context of the present invention, the term "alkyl (meth)acrylate" refers to both the alkyl acrylate and the alkyl methacrylate species or a mixture thereof. Alkyl methacrylates are preferred.

- 10 Non-limiting examples of component (a) include (meth)acrylates, fumarates and maleates which derive 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, hexyl (meth)acrylate, 2-ethylhexyl (meth)acrylate, heptyl (meth)acrylate, octyl (meth)acrylate and nonyl (meth)acrylate; cycloalkyl (meth)acrylates, like cyclopentyl (meth)acrylate, cyclohexyl (meth)acrylate and 3-vinylcyclohexyl (meth)acrylate; (meth)acrylates that derive from unsaturated alcohols like 2-propynyl (meth)acrylate, allyl (meth)acrylate and vinyl (meth)acrylate; and the corresponding fumarates and maleates.
- 15
- 20 Monomer (a) is present in an amount of 0% to 40% by weight, preferably 0% to 20% by weight based on the total weight of components (a), (b), (c), (d) and (e).

In one embodiment, the amount of monomer (a) is at least 0.1% by weight, preferably at least 0.5% by weight.

- 25 In a preferred embodiment the amount of monomer (a) is 0%.

- Non-limiting examples of component (b) include (meth)acrylates, fumarates and maleates that derive from saturated alcohols, such as 2-tert-butylheptyl (meth)acrylate, 3-isopropylheptyl (meth)acrylate, 2-n-propylheptyl (meth)acrylate, decyl (meth)acrylate, undecyl (meth)acrylate, 5-methylundecyl (meth)acrylate, dodecyl (meth)acrylate, 2-methyldodecyl (meth)acrylate, tridecyl (meth)acrylate, 5-methyltridecyl (meth)acrylate, tetradecyl (meth)acrylate, pentadecyl (meth)acrylate, hexadecyl (meth)acrylate, 2-methylhexadecyl (meth)acrylate, heptadecyl (meth)acrylate, 5-isopropylheptadecyl (meth)acrylate, 4-tert-butyloctadecyl (meth)acrylate, 5-ethyloctadecyl (meth)acrylate,
- 30

3-isopropyloctadecyl (meth)acrylate, octadecyl (meth)acrylate, nonadecyl (meth)acrylate, eicosyl (meth)acrylate or docosyl (meth)acrylate; (meth)acrylates that derive from unsaturated alcohols, such as oleyl (meth)acrylate; cycloalkyl (meth)acrylates such as bornyl (meth)acrylate, 2,4,5-tri-tert-butyl-3-vinylcyclohexyl (meth)acrylate,
 5 2,3,4,5-tetra-tert-butylcyclohexyl (meth)acrylate; oxiranyl methacrylates such as 10,11-epoxyhexadecyl methacrylate; and the corresponding fumarates and maleates.

Monomer (b) is present in an amount of 20% to 98% by weight, preferably 50% to 95% by weight, more preferably 70% to 90% by weight based on the total weight of components (a),
 10 (b), (c), (d) and (e).

In a preferred embodiment monomer (b) is a C₈₋₁₅-alkyl (meth)acrylate, preferably commercial lauryl(meth)acrylate, or a C₁₀₋₁₅-alkyl (meth)acrylate fraction. More preferably the backbone monomer is a C₈₋₁₅-alkyl methacrylate, preferably commercial lauryl methacrylate
 15 or a C₁₀₋₁₅-alkyl methacrylate fraction.

Non-limiting examples of component (c) include (meth)acrylates that derive from saturated alcohols, such as cetylcicosyl (meth)acrylate, stearylcicosyl (meth)acrylate and/or eicosyltetratricontyl (meth)acrylate; as well as the corresponding fumarates and maleates.

In accordance with the invention, aromatic groups denote radicals of monocyclic or polycyclic aromatic compounds having preferably 6 to 20, more particularly 6 to 12, C atoms, such as, for example, phenyl, naphthyl or biphenyl, preferably phenyl.

25 Heteroaromatic groups identify aryl radicals in which at least one CH group is replaced by N and/or at least two adjacent CH groups are replaced by S, NH or O. These radicals include, among others, groups derived from thiophene, furan, pyrrole, thiazole, oxazole, imidazole, isothiazole, isoxazole, pyrazole, 1,3,4-oxadiazole, 1,3,4-thiadiazole, 1,3,4-triazole, 1,2,4-oxadiazole, 1,2,4-thiadiazole, 1,2,4-triazole, 1,2,3-triazole, 1,2,3,4-tetrazole, benzo[b]thiophene,
 30 benzo[b]furan, indole, benzo[c]thiophene, benzo[c]furan, isoindole, benzoxazole, benzothiazole, benzimidazole, benzisoxazole, benzisothiazole, benzopyrazole, benzothiadiazole, benzotriazole, dibenzofuran, dibenzothiophene, carbazole, pyridine, pyrazine, pyrimidine, pyridazine, 1,3,5-triazine, 1,2,4-triazine, 1,2,4,5-triazine, quinoline, isoquinoline, quinoxaline, quinazoline, cinnoline, 1,8-naphthyridine, 1,5-naphthyridine,

1,6-naphthyridine, 1,1'-naphthyridine, phthalazine, pyridopyrimidine, purine, pteridine or 4H-quinolizine.

The preferred alkyl groups include the methyl, ethyl, propyl, isopropyl, 1-butyl, 2-butyl, 2-methylpropyl, tert-butyl, pentyl, 2-methylbutyl, 1,1-dimethylpropyl, hexyl, heptyl, octyl, 1,1,3,3-tetramethylbutyl, nonyl, 1-decyl, 2-decyl, undecyl, dodecyl, pentadecyl and the eicosyl group.

The preferred cycloalkyl groups include the cyclopropyl, cyclobutyl, cyclopentyl, cyclohexyl, cycloheptyl and the cyclooctyl group, which are unsubstituted or substituted by branched or non-branched alkyl groups.

The preferred alkenyl groups include the vinyl, allyl, 2-methyl-2-propene, 2-butenyl, 2-pentenyl, 2-decenyl and the 2-eicosenyl group.

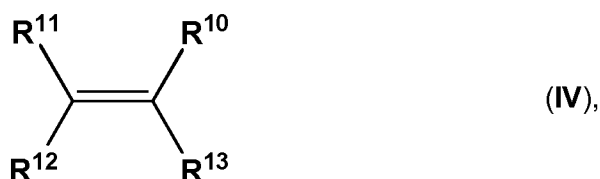
Monomer (c) is present in an amount of 0% to 10% by weight based on the total weight of components (a), (b), (c), (d) and (e).

In one embodiment, the amount of monomer (c) is at least 0.1% by weight, preferably at least 0.5% by weight.

Monomer (d), when present may be a vinyl aromatic monomer such as styrene and substituted styrenes although other vinyl monomers can also be used. The substituted styrenes include styrenes which are substituted with one or more substituents selected from the group consisting of halogen, amino, alkoxy with 1 to 12 carbon atoms in the alkyl residue, carboxy, hydroxy, sulfonyl, hydrocarbyl with 1 to 12 carbon atoms and other substituents. Exemplary of the hydrocarbyl-substituted styrenes are alpha-methylstyrene, *para*-tert-butylstyrene, alpha-ethylstyrene, and *para*-lower alkoxy styrene having 1 to 12 carbon atoms. Mixtures of two or more vinyl monomers can be used. Styrene is preferred.

The amount of vinyl monomer used is from 0% to 30% by weight, and when present, preferably from 5% to 25% by weight, more preferably 10% to 20% by weight, based on the total weight of components (a), (b), (c), (d) and (e).

Monomer (e) is at least one monomer selected from the group consisting of N-vinyllic monomers, (meth)acrylic esters, (meth)acrylic amides and (meth)acrylic imides each with dispersing moieties in the side chain and may be an N-dispersant monomer of the formula (IV)



5 wherein

R^{10} , R^{11} and R^{12} independently are H or a linear or branched, saturated or unsaturated alkyl group with 1 to 5 carbon atoms and

10 R^{13} is either a group selected from $-\text{C}(\text{O})-\text{O}-\text{R}^{14}$, $-\text{C}(\text{O})-\text{NH}-\text{R}^{14}$, $-\text{C}(\text{NR}^{15})-\text{O}-\text{R}^{14}$, $-\text{C}(\text{NR}^{15})-\text{NH}-\text{R}^{14}$ and $-\text{C}(\text{O})-[\text{NH}-\text{C}_{2-10}\text{-alkylene}]_x-\text{NR}^{16}\text{R}^{17}$, wherein

R^{15} represents a linear or branched, saturated or unsaturated alkyl group with 1 to 5 carbon atoms or an aryl group and

15 R^{14} represents a linear or branched alkyl group with 1 to 20 carbon atoms which is unsubstituted or substituted by a group $-\text{NR}^{16}\text{R}^{17}$, wherein R^{16} and R^{17} independently represent H or a linear or branched alkyl group with 1 to 8 carbon atoms, or wherein R^{16} and R^{17} are part of a 4- to 8-membered saturated or unsaturated ring containing optionally one or more hetero atoms chosen from the group consisting of nitrogen, oxygen or sulphur, wherein
20 said ring may be further substituted with alkyl or aryl groups, and x represents a number 1, 2, 3 or 4, or

R^{13} is a group $-\text{NR}^{18}\text{R}^{19}$, wherein R^{18} and R^{19} are part of a 4- to 8-membered saturated or unsaturated ring, containing at least one carbon atom as part of the ring which forms a
25 double bond to a hetero atom chosen from the group consisting of nitrogen, oxygen or sulphur, wherein said ring may be further substituted with alkyl or aryl groups.

In one embodiment, R^{14} represents H or a linear or branched alkyl group with 2 to 6 carbon atoms.

30

Non-limiting examples of N-dispersant monomers include those selected from the group consisting of vinyl substituted nitrogen heterocyclic monomers, for example vinyl pyridine and N-vinyl-substituted nitrogen heterocyclic monomers, for example, N-vinyl imidazole, N-vinyl pyrrolidinone (NVP), morpholinoethyl methacrylate and N-vinyl caprolactam,

5 dialkylaminoalkyl acrylate and methacrylate monomers, for example N,N-dialkylaminoalkyl (meth)acrylates, for example N,N-dimethylaminoethyl methacrylate (DMAEMA), tert-butyl aminoethyl methacrylate, dialkylaminoalkyl acrylamide and methacrylamide monomers, for example di-lower alkylaminoalkylacrylamide, especially where each alkyl or aminoalkyl group contains from 1 to 8 carbon atoms, especially from 1 to 3 carbon atoms, for example N,N-di
10 lower alkyl, especially, N,N-dimethylaminopropylmethacrylamide (DMAPMAM), dimethylaminopropylacrylamide, dimethylaminoethylacrylamide, N-tertiary alkyl acrylamides and corresponding methacrylamides, for example tertiary butyl acrylamide, vinyl substituted amines, and N-vinyl lactam such as N-vinyl pyrrolidone (NVP).

15 By virtue to the presence of basic nitrogen groups in the polymer, it is readily apparent that some or all of the nitrogen atoms may be converted to a salt form by reaction with an acid. Accordingly, the polymer may be partially or completely neutralized by reaction with acidic compounds and still be within the scope of the invention.

20 In another embodiment, the N-dispersant monomer may comprise a combination of

(i) acrylamide based N-dispersant monomer of the formula (IV)



wherein

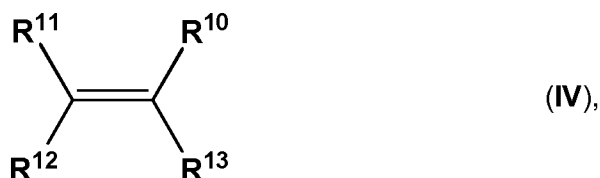
25 R^{10} , R^{11} and R^{12} are independently H or a linear or branched, saturated or unsaturated alkyl group with 1 to 5 carbon atoms and

R^{13} is a group selected from $-\text{C}(\text{O})-\text{O}-\text{R}^{14}$, $-\text{C}(\text{O})-\text{NH}-\text{R}^{14}$, $-\text{C}(\text{NR}^{15})-\text{O}-\text{R}^{14}$, $-\text{C}(\text{NR}^{15})-\text{NH}-\text{R}^{14}$ and $-\text{C}(\text{O})-[\text{NH}-\text{C}_{2-10}\text{-alkylene}]_x-\text{NR}^{16}\text{R}^{17}$, wherein

R^{15} is an alkyl or aryl group and R^{14} represents a linear or branched alkyl group with 1 to 20 carbon atoms which is unsubstituted or substituted by a group $-NR^{16}R^{17}$ wherein R^{16} and R^{17} independently represent H or a linear or branched alkyl group with 1 to 8 carbon atoms, or wherein R^{16} and R^{17} are part of a 4 to 8 membered saturated or unsaturated ring containing optionally one or more hetero atoms chosen from the group consisting of nitrogen, oxygen or sulphur, wherein said ring may be further substituted with alkyl or aryl groups, and x represents a number 1, 2, 3 or 4,

and

(ii) an N-dispersant monomer of the formula (IV)



wherein

R^{10} , R^{11} and R^{12} independently are H or an alkyl group with 1 to 5 carbon atoms and R^{13} is a group $-NR^{18}R^{19}$, wherein R^{18} and R^{19} are part of a 4- to 8-membered saturated or unsaturated ring, containing at least one carbon atom as part of the ring which forms a double bond to a hetero atom chosen from the group consisting of nitrogen, oxygen or sulphur, wherein said ring may be further substituted with alkyl or aryl groups.

The N-dispersant monomer may specifically be at least one monomer selected from the group consisting of N-vinyl pyrrolidinone, N,N-dimethylaminoethyl methacrylate and N,N-dimethylaminopropylmethacrylamide or a mixture thereof.

The amount of N-dispersant monomer is typically from 2% to 80%, preferably from 5% to 50% by weight, and even more preferably from 10% to 30% by weight, based on the total weight of components (a), (b), (c), (d) and (e).

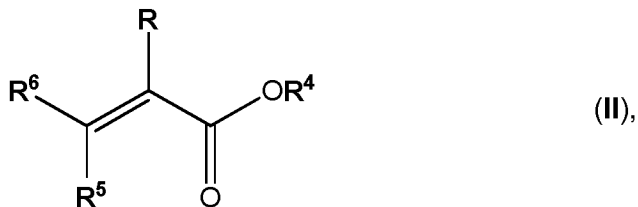
It may be beneficial to use at least two N-dispersant monomers, especially when the total amount of N-dispersant monomer is at the low end of the recited range.

The polyalkyl(meth)acrylate typically have a number average molecular weight M_n of from 1000 to 1000000 g/mol, preferably 2000 to 100000 g/mol, more preferably 2500 to 100000 g/mol, even more preferably 2500 to 50000 g/mol and especially preferred 4000 to 20000 g/mol as measured by size exclusion chromatography, calibrated versus a polystyrene standard.

The polydispersity M_w/M_n of the polyalkyl(meth)acrylate polymers preferably is in the range of from 1 to 8, especially from 1.05 to 6.0, more preferably from 1.1 to 5.0 and most preferably from 1.3 to 2.5. 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.

As a preferred first aspect of the invention, there is provided the use of a polyalkyl(meth)acrylate comprising monomer units of:

- (a) 20% to 98% by weight of one or more ethylenically unsaturated ester compounds of formula (II)



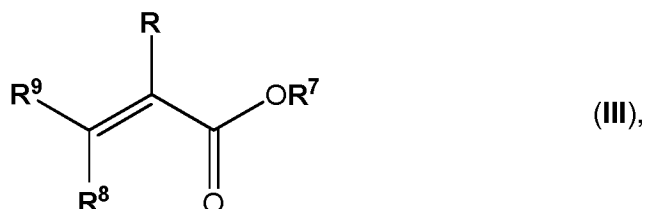
wherein

R is H or CH₃,

R⁴ represents a linear or branched, saturated or unsaturated alkyl group with 10 to 22 carbon atoms,

R⁵ and **R**⁶ independently represent H or a group of the formula -COOR'', wherein **R**'' is H or a linear or branched, saturated or unsaturated alkyl group with 10 to 22 carbon atoms,

- (b) 0% to 10% by weight of one or more ethylenically unsaturated ester compounds of formula (III)



wherein

R is H or CH₃,

R⁷ represents a linear or branched, saturated or unsaturated alkyl group with 23 to 40 carbon atoms,

R⁸ and **R**⁹ independently represent H or a group of the formula -COOR''' wherein **R**''' is H or a linear or branched, saturated or unsaturated alkyl group with 23 to 40 carbon atoms,

(c) 0% to 30% by weight of vinyl aromatic monomers, and

(d) 2% to 80% by weight of at least one N-dispersant monomer,

wherein components (a) to (e) add up to 100% by weight, for improving the cold flow properties of fuel oil compositions.

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. According to the present invention, the polymers are preferably random copolymers.

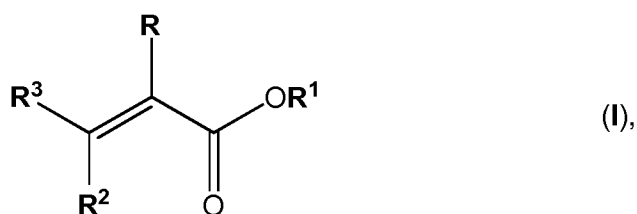
The combination according to the present invention is suitable as an additive to fuels, especially middle distillate fuels. Middle distillate fuels are often referred to as fuels oils. They find use in particular in gas oils, petroleum, diesel oils or diesel fuels or light and extra light heating oils and have generally boiling points from 150°C to 400°C.

The combination according to the present invention can be added to the fuels directly and undiluted or as concentrate (solution) in a suitable solvent, typically a hydrocarbon solvent.

A further embodiment of the present invention comprises the use of a concentrate, comprising:

5 (A) 30% to 90% by weight of a polyalkyl(meth)acrylate comprising monomer units of:

(a) 0% to 40% by weight of one or more ethylenically unsaturated ester compounds of formula (I)



wherein

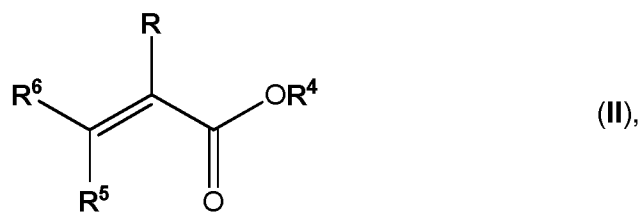
R is H or CH₃,

R¹ represents a linear or branched, saturated or unsaturated alkyl group with 1 to 9 carbon atoms or a cycloalkyl group with 3 to 9 carbon atoms,

R² and **R**³ independently represent H or a group of the formula -COOR', wherein **R**' is

H or a linear or branched, saturated or unsaturated alkyl group with 1 to 9 carbon atoms or a cycloalkyl group with 3 to 9 carbon atoms,

(b) 20% to 98% by weight of one or more ethylenically unsaturated ester compounds of formula (II)



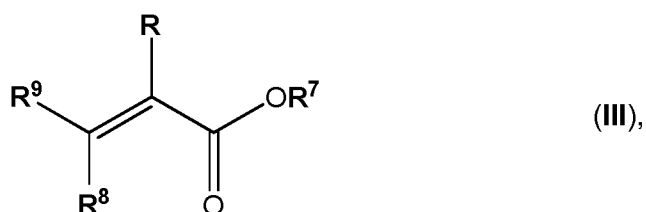
wherein

R is H or CH₃,

R⁴ represents a linear or branched, saturated or unsaturated alkyl group with 10 to 22 carbon atoms,

R^5 and R^6 independently represent H or a group of the formula $-COOR''$, wherein R'' is H or a linear or branched, saturated or unsaturated alkyl group with 10 to 22 carbon atoms,

- 5 (c) 0% to 10% by weight of one or more ethylenically unsaturated ester compounds of formula (III)



wherein

R is H or CH_3 ,

- 10 R^7 represents a linear or branched, saturated or unsaturated alkyl group with 23 to 40 carbon atoms,

R^8 and R^9 independently represent H or a group of the formula $-COOR'''$ wherein R''' is H or a linear or branched, saturated or unsaturated alkyl group with 23 to 40 carbon atoms,

- 15 (d) 0% to 30% by weight vinyl aromatic monomers, and
- (e) 2% to 80% by weight of at least one N-dispersant monomer,

20 wherein components (a) to (e) add up to 100 weight%; and

(B) 10% to 70% by weight of a hydrocarbon solvent/an oil

as an additive to fuels, especially middle distillate fuels, for improving the cold flow properties
25 of fuel oil compositions.

Common hydrocarbon solvents in this context are aliphatic or aromatic hydrocarbons such as xylenes or mixtures of high-boiling aromatics as for example Solvent Naphtha. Middle distillate fuels themselves may also be used as the solvent for such concentrates.

The concentrate may comprise from 10% to 70% by weight, preferably from 30% to 65% by weight, and more preferred from 45% to 60% by weight, based on the total amount of the concentrate, of the inventive polyalkyl(meth(acrylate) as described above.

5 In a preferred embodiment, the inventive concentrate is used as an additive to fuels which consists of

(i) 0% to 99% by weight, preferably 0.5% to 75% by weight, of at least one biofuel oil which is based on fatty acid esters and

10

(ii) 1% to 100% by weight, preferably 25% to 99.5% by weight, of middle distillates of fossil origin and/or of vegetable and/or animal origin, which are essentially hydrocarbon mixtures and are free of fatty acid esters.

15 The fuel component (i) shall be understood to mean middle distillate fuels boiling in the range of from 120°C to 450°C. Such middle distillate fuels are used in particular as diesel fuel, heating oil or kerosene. Preference is given to diesel fuel and heating oil.

The fuel composition of the present invention may comprise diesel fuel of mineral origin, i.e. diesel, gas oil or diesel oil. Mineral diesel fuel is widely known per se and is commercially available. This is understood to mean a mixture of different hydrocarbons which is suitable as a fuel for a diesel engine. Diesel can be obtained as a middle distillate, in particular by distillation of crude oil. The main constituents of the diesel fuel preferably include alkanes, cycloalkanes and aromatic hydrocarbons having about 10 to 22 carbon atoms per molecule.

25

Preferred diesel fuels of mineral origin boil in the range of 120°C to 450°C, more preferably 170°C and 390°C. Preference is given to using those middle distillates which contain 0.2% by weight of sulphur and less, preferably less than 0.05% by weight of sulphur, more preferably less than 350 ppm of sulphur, in particular less than 200 ppm of sulphur and in special cases less than 50 ppm of sulphur, for example less than 10 ppm of sulphur. They are preferably those middle distillates which have been subjected to refining under hydrogenating conditions, and which therefore contain only small proportions of polyaromatic and polar compounds. They are preferably those middle distillates which have 95% distillation points below 370°C, in particular below 350°C and in special cases below 330°C.

30

Synthetic fuels, as obtainable, for example, by the Fischer-Tropsch process or gas to liquid processes (GTL), are also suitable as diesel fuels of mineral origin.

5 The kinematic viscosity of diesel fuels of mineral origin to be used with preference is in the range of 0.5 to 8 mm²/s, more preferably 1 to 5 mm²/s, and especially preferably 2 to 4.5 mm²/s or 1.5 to 3 mm²/s, measured at 40°C to ASTM D 445.

The fuel compositions of the present invention may comprise at least 20% by weight, in particular at least 30% by weight, preferably at least 50% by weight, more preferably at least 10 70% by weight and most preferably at least 80% by weight of diesel fuels of mineral origin.

Furthermore, the present fuel composition may comprise at least one biodiesel fuel component. Biodiesel fuel is a substance, especially an oil, which is obtained from vegetable or animal material or both, or a derivative thereof which can be used in principle as a 15 replacement for mineral diesel fuel.

In a preferred embodiment, the biodiesel fuel, which is frequently also referred to as "biodiesel" or "biofuel" comprises fatty acid alkyl esters formed from fatty acids having preferably 6 to 30, more preferably 12 to 24 carbon atoms, and monohydric alcohols having 20 1 to 4 carbon atoms. In many cases, some of the fatty acids may contain one, two or three double bonds. The monohydric alcohols include in particular methanol, ethanol, propanol and butanol, methanol being preferred.

Examples of oils which derive from animal or vegetable material and which can be used in 25 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, oils which are derived from animal tallow, especially beef tallow, bone oil, fish oils and used cooking oils. Further examples include oils which derive from cereal, wheat, jute, sesame, rice husks, jatropha, algae, arachis oil and linseed oil. The 30 fatty acid alkyl esters to be used with preference may be obtained from these oils by processes known in the prior art.

Preference is given in accordance with the invention to highly C16:0/C18:0-glyceride-containing oils, such as palm oils and oils which are derived from animal tallow, and also

derivatives thereof, especially the palm oil alkyl esters which are derived from monohydric alcohols. Palm oil (also: palm fat) is obtained from the fruit flesh of the palm fruits. The fruits are sterilized and pressed. Owing to their high carotene content, fruits and oils have an orange-red colour which is removed in the refining. The oil may contain up to 80% C18:0-glyceride.

Particularly suitable biodiesel fuels are lower alkyl esters of fatty acids. Useful examples here are commercial mixtures of the ethyl, propyl, butyl and especially methyl esters of fatty acids having 6 to 30, preferably 12 to 24, more preferably 14 to 22 carbon atoms, for example of caprylic acid, capric acid, lauric acid, myristic acid, palmitic acid, margaric acid, stearic acid, arachic acid, behenic acid, lignoceric acid, cerotic acid, palmitoleic acid, stearic acid, oleic acid, elaidic acid, petroselic acid, ricinoleic acid, elaeostearic acid, linoleic acid, linolenic acid, eicosanoic acid, gadoleic acid, docosanoic acid or erucic acid.

In a particular aspect of the present invention, a biodiesel fuel is used which comprises preferably at least 10% by weight, more preferably at least 30% by weight and most preferably at least 40% by weight of saturated fatty acid esters which are derived from methanol and/or ethanol. Especially, these esters have at least 16 carbon atoms in the fatty acid part. These include in particular the esters of palmitic acid and stearic acid.

The inventive fuel composition may comprise further additives in order to achieve specific solutions to problems. These additives include other cold flow improvers different than those described above, dispersants, for example wax dispersants and dispersants for polar substances, conductivity improvers, demulsifiers, defoamers, lubricity additives, additional antioxidants, cetane number improvers, detergents, dyes, corrosion inhibitors, metal deactivators, metal passivators and/or odourants.

A further object of the present invention is directed to a method for improving the cold flow properties of fuel oil compositions, comprising the steps of adding at least one polyalkyl(meth)acrylate as described above to fuels, especially to middle distillate fuels and blends thereof, and mixing the resulting composition. The addition is preferably done at temperatures above the cloud point of the used fuels.

A further object of the present invention is directed to a method for improving the cold flow properties of fuel oil compositions, comprising the steps of:

adding a concentrate comprising

(i) at least one polyalkyl(meth)acrylate as described above and

5 (ii) a hydrocarbon solvent/an oil

to fuels, especially to middle distillate fuels and blends thereof; and

(finally) reducing the tendency of sedimentation of paraffin waxes and sludgy material in the fuels at low temperatures.

10 **Process for Preparing PAMAs**

The monomer mixtures described above can be polymerized by methods known in the art.

The copolymers of this invention may be prepared by processes comprising reacting

monomers (a) to (e) in the presence of a free radical initiator and optionally in the presence

15 of a chain transfer agent. The monomers may be reacted concurrently.

Conventional radical initiators can be used to perform a classic radical polymerization. These initiators are well known in the art. Examples for these radical initiators are azo initiators like

2,2'-azodiisobutyronitrile (AIBN), 2,2'-azobis(2-methylbutyronitrile) and

20 1,1-azobiscyclohexane carbonitrile; peroxide compounds, e.g. methyl ethyl ketone peroxide, acetyl acetone peroxide, dilauryl peroxide, tert-butyl per-2-ethyl hexanoate, ketone peroxide, methyl isobutyl ketone peroxide, cyclohexanone peroxide, dibenzoyl peroxide, tert-butyl perbenzoate, tert-butyl peroxy isopropyl carbonate, 2,5-bis(2-ethylhexanoyl-peroxy)-

25 2,5-dimethyl hexane, tert-butyl peroxy 2-ethyl hexanoate, tert-butyl peroxy-3,5,5-trimethyl hexanoate, dicumene peroxide, 1,1-bis(tert-butyl peroxy) cyclohexane, 1,1-bis(tert-butyl peroxy) 3,3,5-trimethyl cyclohexane, di-tert-butyl peroxide, cumene hydroperoxide and tert-butyl hydroperoxide.

Low molecular weight poly(meth)acrylates can be obtained by using chain transfer agents.

30 This technology is ubiquitously known and practiced in the polymer industry and is described in Odian, Principles of Polymerization, 1991. Examples of chain transfer agents are

aldehydes or sulphur containing compounds such as thiols, e.g. n- and tert-dodecanethiol, 2-mercaptoethanol, and mercapto carboxylic acid esters, e.g. methyl-3-mercaptopropionate.

Preferred chain transfer agents contain up to 20, especially up to 15 and more preferably up

to 12 carbon atoms. Furthermore, chain transfer agents may contain at least 1, especially at least 2 oxygen atoms.

- Furthermore, novel polymerization techniques such as ATRP (Atom Transfer Radical Polymerization) and or RAFT (Reversible Addition Fragmentation Chain Transfer) can be applied to obtain useful poly(meth)acrylates. These methods are well known. The ATRP reaction method is described, for example, by J.-S. Wang, et al., J. Am. Chem. Soc., Vol. 117, pp. 5614-5615 (1995), and by Matyjaszewski, Macromolecules, Vol. 28, pp. 7901-7910 (1995). Moreover, the patent applications WO 96/30421, WO 97/47661, WO 97/18247, WO 98/40415 and WO 99/10387 disclose variations of the ATRP explained above to which reference is expressly made for purposes of the disclosure. The RAFT method is extensively presented in WO 98/01478, for example, to which reference is expressly made for purposes of the disclosure.
- 15 The polymerization can be carried out at normal pressure, reduced pressure or elevated pressure. The polymerization temperature is also not critical. However, in general it lies in the range of -20°C to 200°C, preferably 0°C to 130°C and especially preferably 60°C to 120°C, without any limitation intended by this.
- 20 The polymerization can be carried out with or without solvents. The term solvent is to be broadly understood here.
- Preferably, the polymerization is carried out in a nonpolar solvent. Among these solvents are hydrocarbon solvents, such as aromatic solvents like toluene, benzene and xylene, saturated hydrocarbons such as cyclohexane, heptane, octane, nonane, decane, dodecane, which can also occur in branched form. These solvents can be used individually and as a mixture. Especially preferred solvents are mineral oils and synthetic oils and mixtures of these. Of these, mineral oils are most preferred.
- 30 Mineral oils are substantially known and commercially available. They are generally obtained from petroleum or crude oil by distillation and/or refining and optionally additional purification and processing methods, especially the higher-boiling fractions of crude oil or petroleum fall under the concept of mineral oil. In general, the boiling point of the mineral oil is higher than 200°C, preferably higher than 300°C, at 50 mbar. Preparation by low temperature distillation

of shale oil, coking of hard coal, distillation of lignite under exclusion of air as well as hydrogenation of hard coal or lignite is likewise possible. To a small extent, mineral oils are also produced from raw materials of plant origin (for example jojoba, rapeseed oil) or animal origin (for example neatsfoot oil). Accordingly, mineral oils exhibit different amounts of aromatic, cyclic, branched and linear hydrocarbons in each case, according to origin.

Natural oils include animal oils and vegetable oils (e.g., castor oil, lard oil); liquid petroleum oils and hydro-refined, solvent-treated or acid-treated mineral oils of the paraffinic, naphthenic and mixed paraffinic-naphthenic types.

These solvents can be used, among other ways, in an amount of 1% to 99% by weight, preferably 5% to 95% weight, especially preferably 5% to 60% by weight and most preferably 10% to 50% by weight, with respect to the total weight of the mixture, without any limitation intended to be implied by this.

In one embodiment, the process comprises reacting a mixture of the monomers, often by first heating a portion, often from about 20% to about 60%, of the mixture until reaction is evident, usually by noting an exotherm, then adding and reacting the balance of the mixture of monomers, either portion wise, or all at once.

Experimental Part

Sedimentation tests were carried out with state of the art WASA, based on either ethylenediaminetetraacetic acid (EDTA), phthalic anhydride (PA) or Alpha-olefin and with the products of the invention. The list of tested WASA components is given below. For all polymers used in this study, the number average molecular weight M_n of the polymer is around 5000 g/mol and the mass average molecular weight M_w of the polymer is around 9000 g/mol. If there is any exception in the molecular weight, then WASA are noted with (*).

Component A: EDTA condensed with 4 moles of di-tallow amine in solvent Naphta; product content = 70%

Component B: Phthalic acid anhydride condensed with 2 moles of di-tallow amine in solvent Naphta;

product content = 70%

Component C: Alpha-olefin-stat-MA condensed with di-tallow amine in solvent Naphta;
polymer content = 70%

5

Component D: dodecyl/pentadecyl methacrylate
polymer content = 70% in Shellsol A 150 ND

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Component E: dodecyl/pentadecyl methacrylate-stat-2-
dimethylaminoethylmethacrylate (70/30 wt%);
polymer content = 70% in Shellsol A 150 ND

15

Component F: dodecyl/pentadecyl methacrylate-stat-2-
dimethylaminoethylmethacrylate (85/15 wt%);
polymer content = 70% in Shellsol A 150 ND

20

Component G: lauryl methacrylate/stearyl methacrylate-stat-
dimethylaminoethylmethacrylate (70/30 wt%);
polymer content = 70% in Shellsol A 150 ND

Component H: dodecyl/pentadecyl methacrylate-stat-
dimethylaminopropylmethacrylamide (70/30 wt%);
polymer content = 70% in Shellsol A 150 ND

25 Table 1 below gives an overview of the different WASA combinations tested.

	W1	W2	W3	W4	W5	W6	W7	W8
Component A	100							
Component B		100						
Component C			100					
Component D				100				
Component E					100			
Component F						100		
Component G							100	
Component H								100

Table 1: compositions tested as WASA. Values given in wt%.

W1 to W4 represent comparative examples and W5 to W8 represent examples of the invention.

Components preparation

Component A:

10 12.5 g EDTA, 77.5 g ditallow amine and 0.014 g p-toluene sulfonic acid were molten at temperature of 150°C. The reaction was allowed to take place during 30 minutes, and after cooling down, was diluted in solvent Naphta to 70 wt%.

Component B:

15 35.0 g PSA, 213.2 g ditallow amine and 62.1 g solvent naphtha were molten at temperature of 150°C. The reaction was allowed to take place during 180 minutes, and after cooling down, was further diluted in solvent Naphta to 70 wt%.

Component C:

20 88.1 g solvent naphtha, 10.5 g maleic anhydride and 11.1 g C_{16/18}-alpha olefin were charged in the kettle and heated up to 140°C. A mixture of C_{16/18}-alpha olefin (188.4 g) and a 50% concentrated solution of 2,2-bis-(tert-butylperoxy)butane (3.8 g) was continuously added over 3.5 h. After 1.5 h, the temperature was reduced to 100°C, where 0.42 g tert.-butylper-2-ethylhexanoat was added. The batch was stirred over night at 100°C. All steps were done in
25 an inert gas atmosphere. Then, 150 g of the C_{16/18}-alpha olefin-maleic anhydride copolymer

was added to 59.6 g ditallow amine and 25.5 g solvent naphtha. The solution was heated up to 140°C and stirred over night. The forming water was removed directly with a permanent inert gas flow.

5 Component D:

107.5 g solvent naphtha was charged in the kettle and heated up to 140°C. A mixture of dodecyl/pentadecyl methacrylate (262.5 g) and a 50% concentrated solution of 2,2-bis-(tert-butylperoxy)butan (10.0 g) were continuously added over 5 h. After 1.5 h, the temperature was reduced to 100°C, and 0.5 g tert-butylper-2-ethylhexanoat was added. The batch was
10 stirred over night at 100°C. All steps were done in an inert gas atmosphere.

Component E:

143.4 g solvent naphtha was charged in the kettle and heated up to 140°C. A mixture of dodecyl/pentadecyl methacrylate (245.0 g), 2-dimethylaminoethylmethacrylate (105.0 g) and
15 a 50% concentrated solution of 2,2-bis-(tert-butylperoxy)butan (13.3 g) was continuously added over 5 h. After 1.5 h, the temperature was reduced to 100°C, and 0.7 g tert-butylper-2-ethylhexanoat was added. The batch was stirred over night at 100°C. All steps were done in an inert gas atmosphere.

20 Component F:

143.4 g solvent naphtha was charged in the kettle and heated up to 140°C. A mixture of dodecyl/pentadecyl methacrylate (297.5 g), 2-dimethylaminoethylmethacrylate (52.5 g) and a 50% concentrated solution of 2,2-bis-(tert-butylperoxy)butan (13.3 g) was continuously added over 5 h. After 1.5 h, the temperature was reduced to 100°C, and 0.7 g tert-butylper-2-ethylhexanoat was added. The batch was stirred over night at 100°C. All steps were done in
25 an inert gas atmosphere.

Component G:

143.4 g solvent naphtha was charged in the kettle and heated up to 140°C. A mixture of
30 lauryl methacrylate/stearyl methacrylate (245.0 g), 2-dimethylaminoethylmethacrylate (105.0 g) and a 50% concentrated solution of 2,2-bis-(tert-butylperoxy)butan (13.3 g) was continuously added over 5 h. After 1.5 h, the temperature was reduced to 100°C, and 0.7 g tert-butylper-2-ethylhexanoat was added. The batch was stirred over night at 100°C. All steps were done in an inert gas atmosphere.

Component H:

143.4 g solvent naphtha was charged in the kettle and heated up to 140°C. A mixture of dodecyl/pentadecyl methacrylate (245.0 g), dimethylaminopropylmethacrylamide (105.0 g) and a 50% concentrated solution of 2,2-bis-(tert-Butylperoxy)butan (13.3 g) were continuously added over 5 h. After 1.5 h, the temperature was reduced to 100°C, and 0.7 g tert-butylper-2-ethylhexanoat was added. The batch was stirred over night at 100°C. All steps were done in an inert gas atmosphere.

10 Handling properties:

The handling properties, i.e. temperature limits for handling of the different WASA have been compared by determining cloud and pour points (according to ASTM D97 and D2500 respectively). For the tests, WASA are dissolved in Shellsol A 150N D at a concentration of 70% (as mentioned above in the "components" part).

15

In the Table 2 below, we can clearly see that W1 to W4 (reference WASA) display much higher CP and PP than the products of the invention W5 and W8 and therefore showing poorer handling properties. Moreover invention examples are clear without any turbidity whereas references are hazy or solid at room temperature.

20

Table 2: Cold flow properties of the WASA 70% in Shellsol A 150 ND.

WASA	PP [°C]	CP [°C]	visual appearance after 3 days
W1	33.0	35.0	solid at RT
W2	6.0	13.0	liquid & strongly hazy
W3	30.0	31.0	solid at RT
W5	-57.0	-53.0	liquid & clear
W8	-48.0	-45.0	liquid & clear

Anti-sedimentation properties

- 5 The sedimentation tests were carried out in B0 and B10 diesel based on three different fossil diesel fuels (see characteristics displayed below).

DK1: CP (ISO 3015) = -3.3°C; CFPP (EN 116) = -10°C; Density d15 (DIN 51577) = 0.8257 g/ml; Distillation begin & end = 163°C & 364°C; n-Paraffin content = 25 wt%.

- 10 DK2: CP (ISO 3015) = -2.3°C; CFPP (EN 116) = -5°C; Density d15 (DIN 51577) = 0.8284 g/ml; Distillation begin & end = 170°C & 356°C; n-Paraffin content = 18 wt%.

DK3: CP (ISO 3015) = -8.1°C; CFPP (EN 116) = -12°C; Density d15 (DIN 51577) = 0.8282 g/ml; Distillation begin & end = 245°C & 340°C; n-Paraffin content = 25 wt%

- 15 In a typical sedimentation test, 500 mL glassware containing the fuel blended with the additives to be tested (250 ppm of EVA-based MDFI and 150 ppm of WASA) is plunged in an ethanol bath. Before sedimentation, CP, CFPP and PP of the sample are measured. The ethanol bath is cooled down to a certain temperature depending on the CP and PP of

the fuel + additives as the sample should not freeze (temperature well above PP and below CP). Cooling rate is of 0.24°C/min and the sample is let at temperature 16 hours long. After this period of time, 80% of the upper volume contained in the glassware, the upper phase, is carefully removed and with the remaining 20%, the bottom phase, CP was determined after homogenization.

ΔCP describes the difference between CP "20% remaining" and CP "initial". The smaller the ΔCP is the more efficient the wax anti-settling agent is. In general it is expected that a good WASA provides ΔCP of 2°C or below.

Table 3: ΔCP of B0 and B10 DK1 treated with WASA comparative examples (W1 and W3) and invention products (W5-8). WASA with * have M_n around 24000 g/mol.

Fuel type	EVA MDFI	WASA type	ΔCP
DK1 <i>cool down to - 16 °C</i>	250	W3	0.9
	250	W5	0.9
	250	W5*	1.2
	250	W6	1.1
	250	W7	1.1
	250	W8	0.4
	250	W8*	1.0
DK1/RME (90/10) <i>cool down to - 16 °C</i>	250	W1	0.5
	250	W3	2.1
	250	W5	0.7
	250	W6	0.5
	250	W7	0
	250	W8	0.5

From Table 3 it is obvious that the products of the invention, W5 to W8 show similar performances in B0 DK1 as the comparative examples. Moreover W8 even shows better efficiency than W1-3. Even higher molecular weight WASAs, W5* and W8* (M_n around 24000 g/mol), show very good anti-settling performance.

In blends made of DK1 and 10% of RME, the WASA of the invention display same performance as EDTA-based reference, and interestingly, all new WASA outperform the comparative example W3 (alpha-olefin-based).

Table 4: Δ CP of B0 and B10 DK2 treated with WASA comparative examples (W1 to W4) and invention products (W5 to W8). WASA component with * have M_n around 24000 g/mol.

Fuel type	EVA MDFI	WASA type	Δ CP
DK2 <i>cool down to - 16 °C</i>	250	W2	2.3
	250	W3	3.7
	250	W5	2.6
	250	W6	2.2
	250	W7	2.5
	250	W8	1.4
DK2/RME (90/10) <i>cool down to - 16 °C</i>	250	W1	2.4
	250	W2	3.9
	250	W3	4.5
	250	W4	5.5
	250	W7	1.2
	250	W8	1.0
	250	W8*	2.3

5

In Table 4 are displayed the Δ CP values obtained during the sedimentation tests in fuel DK2 and blend thereof with 10% RME. In B0, products of the invention show Δ CP values between 2.2°C and 2.8°C which is comparable to the performance obtained using comparative examples W2 and W3 with 2.3°C and 3.7°C respectively. In this type of fuel, W8 provides the best wax stabilization as Δ CP of 1.4°C was measured.

10

In B10 RME, W1 to W4 show very poor efficiency without exceptions. It is interesting to notice that the reference WASA W4 differs from the inventive examples as it does not possess N-dispersant functionality. On the contrary, inventive WASA W7, W8 and W8* display much better Δ CP values of 1.2 and 1.0°C for number molecular weight of 5000 g/mol and of 2.3°C for 24000 g/mol.

15

Table 5: Δ CP of B0 and B10 DK3 treated with WASA comparative examples (W1, W3 and W4) and invention products (W5 to W8). WASA component with * have M_n around 24000 g/mol

Fuel type	EVA MDFI	WASA type	ΔCP
DK3 <i>cool down to - 11 °C</i>	500	W3	5.4
	500	W4	4.1
	500	W7	3.2
	500	W8	3.5
DK3/RME (90/10) <i>cool down to - 11 °C</i>	500	W1	3.0
	500	W3	4.7
	500	W4	3.5
	500	W7	1.2
	500	W8	2.4
	500	W8*	1.7
DK3/RME (90/10) <i>cool down to - 8 °C</i>	500	W1	8.1
	500	W7	1.2
	500	W8	3.2

In DK3 B0, the reference WASA, W3 and W4, display ΔCP of 5.4 and 4.1°C, respectively whereas a neat improvement, on the average, of more than 1°C lower was measured when using W7 and W8 (DMAEMA and DMAPMAM respectively).

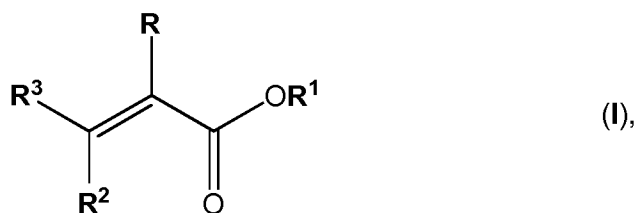
- 5 Sedimentation tests carried out in RME/DK3 blends at –11°C show the same ranking with even more pronounced decrease of the ΔCP values, on the average, of 2°C. When the same blend is cooled down to –8°C, again, W7 and W8 clearly outperform the results obtained by using W1 (EDTA-based WASA) of more than 5°C.

Claims

1. Use of a polyalkyl(meth)acrylate comprising monomer units of:

5

- (a) 0% to 40% by weight of one or more ethylenically unsaturated ester compounds of formula (I)



wherein

10

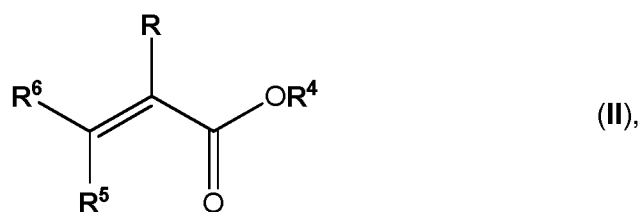
R is H or CH₃,

R¹ represents a linear or branched, saturated or unsaturated alkyl group with 1 to 9 carbon atoms or a cycloalkyl group with 3 to 9 carbon atoms,

R² and **R**³ independently represent H or a group of the formula -COOR', wherein **R**' is H or a linear or branched, saturated or unsaturated alkyl group with 1 to 9 carbon atoms or a cycloalkyl group with 3 to 9 carbon atoms,

15

- (b) 20% to 98% by weight of one or more ethylenically unsaturated ester compounds of formula (II)



wherein

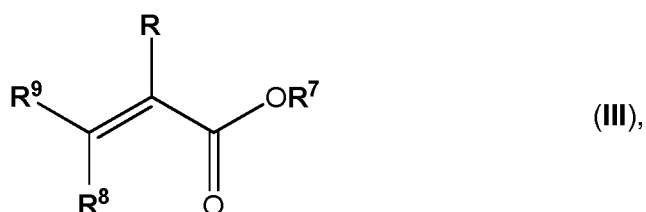
20

R is H or CH₃,

R⁴ represents a linear or branched, saturated or unsaturated alkyl group with 10 to 22 carbon atoms,

R^5 and R^6 independently represent H or a group of the formula $-COOR''$, wherein R'' is H or a linear or branched, saturated or unsaturated alkyl group with 10 to 22 carbon atoms,

- 5 (c) 0% to 10% by weight of one or more ethylenically unsaturated ester compounds of formula (III)



wherein

R is H or CH_3 ,

- 10 R^7 represents a linear or branched, saturated or unsaturated alkyl group with 23 to 40 carbon atoms,

R^8 and R^9 independently represent H or a group of the formula $-COOR'''$ wherein R''' is H or a linear or branched, saturated or unsaturated alkyl group with 23 to 40 carbon atoms,

15

- (d) 0% to 30% by weight of vinyl aromatic monomers, and

- (e) 2% to 80% by weight of at least one N-dispersant monomer,

- 20 wherein components (a) to (e) add up to 100% by weight, for improving the cold flow properties of fuel oil compositions.

2. Use according to claim 1, characterized in that the polyalkyl(meth)acrylate has a number average molecular weight M_n of from 2500 to 100000.

25

3. Use according to claim 1, characterized in that the polyalkyl(meth)acrylate has a number average molecular weight M_n of from 4000 to 20000.

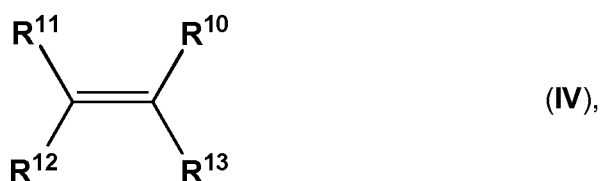
4. Use according to claim 1, characterized in that the polydispersity M_w/M_n of the polyalkyl(meth)acrylate is in the range of from 1 to 8.

30

5. Use according to claim 1, characterized in that the polydispersity M_w/M_n of the polyalkyl(meth)acrylate is in the range of from 1.3 to 2.5.

5 6. Use according to claim 1, characterized in that the vinyl aromatic monomer (d) is selected from the group consisting of styrene and substituted styrene.

7. Use according to claim 1, characterized in that the N-dispersant monomer of component (e) is a monomer of the formula (IV)



10 wherein

R^{10} , R^{11} and R^{12} independently are H or a linear or branched, saturated or unsaturated alkyl group with 1 to 5 carbon atoms and

15 R^{13} is either a group selected from $-C(O)-O-R^{14}$, $-C(O)-NH-R^{14}$, $-C(NR^{15})-O-R^{14}$, $-C(NR^{15})-NH-R^{14}$ and $-C(O)-[NH-C_{2-10}\text{-alkylene}]_x-NR^{16}R^{17}$, wherein

R^{15} represents a linear or branched, saturated or unsaturated alkyl group with 1 to 5 carbon atoms or an aryl group and

20 R^{14} represents a linear or branched alkyl group with 1 to 20 carbon atoms which is unsubstituted or substituted by a group $-NR^{16}R^{17}$, wherein R^{16} and R^{17} independently represent H or a linear or branched alkyl group with 1 to 8 carbon atoms, or wherein R^{16} and R^{17} are part of a 4- to 8-membered saturated or unsaturated ring containing optionally one or more hetero atoms chosen from the group consisting of nitrogen, oxygen or sulphur, wherein
25 said ring may be further substituted with alkyl or aryl groups, and x represents a number 1, 2, 3 or 4, or

R^{13} is a group $-NR^{18}R^{19}$, wherein R^{18} and R^{19} are part of a 4- to 8-membered saturated or unsaturated ring, containing at least one carbon atom as part of the ring which forms a

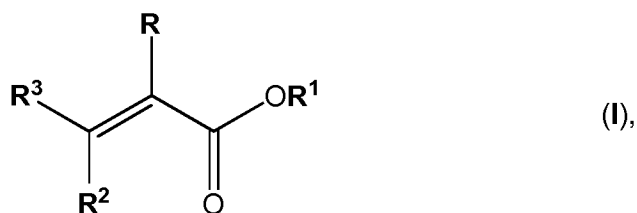
double bond to a hetero atom chosen from the group consisting of nitrogen, oxygen or sulphur, wherein said ring may be further substituted with alkyl or aryl groups.

8. Use according to claim 1, characterized in that the N-dispersant monomer of component (e) is selected from the group consisting of vinyl substituted nitrogen heterocyclic monomers, N-vinyl-substituted nitrogen heterocyclic monomers, dialkylaminoalkyl acrylate and methacrylate monomers, methacrylamide monomers, N-tertiary alkyl acrylamides and corresponding methacrylamides, vinyl substituted amines and N-vinyl lactams.

9. Use of a concentrate, comprising:

(A) 30% to 90% by weight of a polyalkyl(meth)acrylate comprising monomer units of:

(a) 0% to 40% by weight of one or more ethylenically unsaturated ester compounds of formula (I)



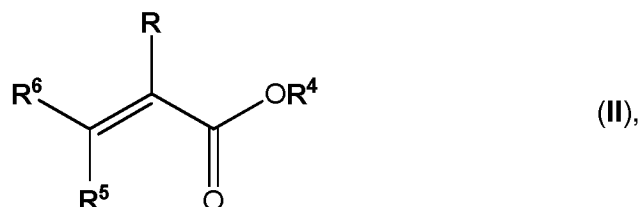
wherein

R is H or CH₃,

R¹ represents a linear or branched, saturated or unsaturated alkyl group with 1 to 9 carbon atoms or a cycloalkyl group with 3 to 9 carbon atoms,

R² and **R**³ independently represent H or a group of the formula -COOR', wherein **R'** is H or a linear or branched, saturated or unsaturated alkyl group with 1 to 9 carbon atoms or a cycloalkyl group with 3 to 9 carbon atoms,

(b) 20% to 98% by weight of one or more ethylenically unsaturated ester compounds of formula (II)



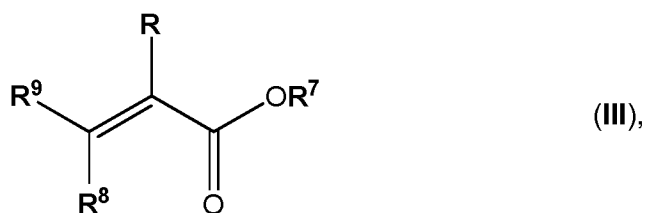
wherein

R is H or CH₃,

R⁴ represents a linear or branched, saturated or unsaturated alkyl group with 10 to 22 carbon atoms,

R⁵ and **R**⁶ independently represent H or a group of the formula -COOR'', wherein **R**'' is H or a linear or branched, saturated or unsaturated alkyl group with 10 to 22 carbon atoms,

- 10 (c) 0% to 10% by weight of one or more ethylenically unsaturated ester compounds of formula (III)



wherein

R is H or CH₃,

R⁷ represents a linear or branched, saturated or unsaturated alkyl group with 23 to 40 carbon atoms,

R⁸ and **R**⁹ independently represent H or a group of the formula -COOR''' wherein **R**''' is H or a linear or branched, saturated or unsaturated alkyl group with 23 to 40 carbon atoms,

- (d) 0% to 30% by weight vinyl aromatic monomers, and

- (e) 2% to 80% by weight of at least one N-dispersant monomer,

wherein components (a) to (e) add up to 100 weight%; and

(B) 10% to 70% by weight of a hydrocarbon solvent/an oil

as an additive to fuels, especially middle distillate fuels, for improving the cold flow properties
5 of fuel oil compositions.

10. Use of a fuel, comprising:

(a) from 0% to 99% by weight of at least one biofuel oil which is based on fatty acid
10 esters,

(b) from 1% to 100% by weight of middle distillates of fossil origin and/or of vegetable
and/or animal origin, which are essentially hydrocarbon mixtures and are free of fatty
acid esters, and
15

(c) the concentrate according to claim 9

for improving the cold flow properties.

20 11. Use according to claim 14, characterized in that one or more additives selected from
the group consisting of additional cold flow improvers, dispersants, conductivity improvers,
demulsifiers, defoamers, lubricity additives, antioxidants, cetane number improvers,
detergents, dyes, corrosion inhibitors, metal deactivators, metal passivators and/or odourants
are present.

25