Current fuel specifications limit the sulfur content to a few ppm. That means that additives which are added to stabilize fuels or otherwise improve the performance of fuels should preferably not contain any sulfur.

It is commonly known that polymers containing basic nitrogen substituents can be used as oil-soluble surface-active agents (C.B. Biswell et al, "New Polymeric Dispersants for Hydrocarbon Systems", Industrial and Engineering Chemistry 1955, 47, 8, 1598-1601). Such N-dispersant polymers can be prepared by copolymerizing N-containing monomers. Current dispersant products contain approximately 750 ppm of sulfur.

US Patent No. 5,035,719 describes the use of dispersant polyalkyl (meth)acrylates for the improvement of middle distillate storage stability. The patent makes no claim to the sulfur content of the prepared polymers, nor does it suggest a process to prepare said polymers.

It was therefore an object of the ~~present invention~~embodiments disclosed herein to find a process for preparing an almost sulfur-free N-dispersant polyalkyl (meth)acrylate.

The inventive process should include as key steps:

- the use of polymerization and dilution oils with a low sulfur content;
- removal of thiol chain transfer agents from the recipe; and
- modifying the process conditions in order to control the molecular weight after the removal of the thiol chain transfer agent.

Summary ~~of the Invention~~

~~In accordance with a first aspect of the invention, T~~there is provided a process for preparing grafted polyalkyl (meth)acrylate copolymers (A), containing as a polymer backbone monomer units comprising:

(A1) 0% to 40% by weight of one or more ethylenically unsaturated ester compounds of formula (I)

(b) preparing a monomer mixture of monomer units (A1) to (A4) as hereinbefore described and a first reaction initiator;

(c) adding the mixture as prepared under step (b) to the mineral oil of step (a), preferably over the course of 1 to 5 hours, more preferably over the course of 2 to 3 hours;

(d) polymerizing the mixture as obtained under step (c), preferably in the absence of any chain transfer agent;

(e) optionally isolating the polymer as obtained under step (c);

(f) adding monomer units (A5) as hereinbefore described;

(g) adding a second reaction initiator;

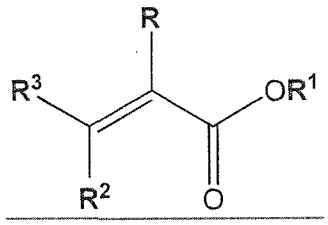
(h) polymerizing the mixture as obtained under step (g);

(i) optionally isolating the polymer as obtained under step (h); and/or

(j) diluting the polymer mixture as obtained under step (h) or the isolated polymer obtained under step (i) with a mineral oil to achieve the desired concentration of polymer in oil.

In a first aspect, there is provided a process for preparing grafted polyalkyl (meth)acrylate copolymers (A), containing a polymer backbone comprising the following monomers units (A1) to (A4):

(A1) 0% to 40% by weight of one or more ethylenically unsaturated ester compounds of formula (I)



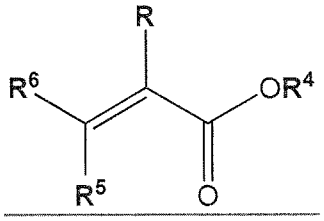
(I),

wherein

R is H or CH_3,

R^1 represents a linear or branched, saturated or unsaturated alkyl group with 1 to 5 carbon atoms or a cycloalkyl group with 3 to 5 carbon atoms,
R^2 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 5 carbon atoms or a cycloalkyl group with 3 to 5 carbon atoms,

(A2) 20% to 93.5% by weight of one or more ethylenically unsaturated ester compounds of formula (II)

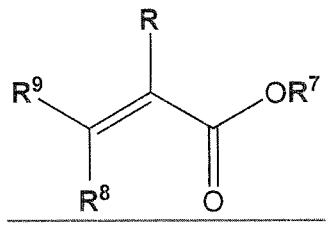


(II),

wherein

R is H or CH_3,
R^4 represents a linear or branched, saturated or unsaturated alkyl group with 6 to 15 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 6 to 15 carbon atoms,

(A3) 5% to 60% by weight of one or more ethylenically unsaturated ester compounds of formula (III)



(III),

wherein

R is H or CH_3,
R^7 represents a linear or branched, saturated or unsaturated alkyl group with 16 to 30 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 16 to 30 carbon atoms, and

(A4) 1% to 40% by weight of at least one N-dispersant monomer selected from the group consisting of vinyl pyridine, N-vinyl imidazole, N-vinyl pyrrolidone (NVP), morpholinoethyl methacrylate, N-vinyl caprolactam, N,N-dimethylaminoethyl methacrylate (DMAEMA), *tert*-butyl aminoethyl methacrylate, N,N-dimethylaminopropylmethacrylamide (DMAPMAm), dimethylaminopropylacrylamide and dimethylaminoethylacrylamide,

wherein components (A1) to (A4) add up to 100% by weight based on the total weight of the polymer backbone;

and

(A5) 0.5% to 10% by weight of a monomer unit, which is grafted on the polymer backbone, consisting of at least one N-dispersant monomer selected from the group consisting of vinyl pyridine, N-vinyl imidazole, N-vinyl pyrrolidone (NVP), morpholinoethyl methacrylate, N-vinyl caprolactam, N,N-dimethylaminoethyl methacrylate (DMAEMA), *tert*-butyl aminoethyl methacrylate, N,N-dimethylaminopropylmethacrylamide (DMAPMAm), dimethylaminopropylacrylamide and dimethylaminoethylacrylamide, based on the total weight of grafted polyalkyl(meth)acrylate copolymer (A),

the process comprising the steps of:

(a) charging a mineral oil to a reaction vessel;
(b) preparing a monomer mixture of monomer units (A1) to (A4) as hereinbefore described and a first reaction initiator;
(c) adding the mixture as prepared under step (b) to the mineral oil of step (a), preferably over the course of 1 to 5 hours, more preferably over the course of 2 to 3 hours;
(d) polymerizing the mixture as obtained under step (c), preferably in the absence of any chain transfer agent;
(e) optionally isolating the polymer as obtained under step (c);
(f) adding monomer units (A5) as hereinbefore described;

(g) adding a second reaction initiator;

(h) polymerizing the mixture as obtained under step (g);

(i) optionally isolating the polymer as obtained under step (h); and/or

(j) diluting the polymer mixture as obtained under step (h) or the isolated polymer obtained under step (i) with a mineral oil to achieve the desired concentration of polymer in oil.

In a second aspect, there is provided a grafted polyalkyl(meth)acrylate copolymer prepared by the process as defined above, characterized by a sulfur content of at most 50 ppm.

In a third aspect, there is provided the use of a grafted polyalkyl(meth)acrylate copolymer as defined above as a compatibilizer for additive packages, especially for additive packages for middle distillates.

In a fourth aspect, there is provided the use of a grafted polyalkyl(meth)acrylate copolymer as defined above as a component in additive packages to stabilize middle distillates.

In a fifth aspect, there is provided the use of a grafted polyalkyl(meth)acrylate copolymer as defined above for improving the cold flow properties of middle distillates.

In a sixth aspect, there is provided the use of a grafted polyalkyl(meth)acrylate copolymer as defined above for reducing n-Paraffin wax sedimentation in middle distillates, preferably in diesel fuels.

In a seventh aspect, there is provided a composition, comprising:

(A) 10% to 90% by weight of a grafted polyalkyl(meth)acrylate copolymer as defined above, and

(B) 10% to 90% by weight of a hydrocarbon solvent or an oil or a mixture of a hydrocarbon solvent and an oil,

wherein components (A) and (B) add up to 100% by weight.

In an eighth aspect, there is provided the use of a composition as defined above as a compatibilizer for additive packages for middle-distillates.

In a ninth aspect, there is provided the use of a composition as defined above as a component in additive packages to stabilize middle-distillates.

In a tenth aspect, there is provided the use of a composition as defined above for improving the cold flow properties of middle distillates.

In an eleventh aspect, there is provided the use of a composition as defined above for reducing n-Paraffin wax sedimentation in middle distillates, preferably in diesel fuels.

Detailed description of the invention

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.

Non-limiting examples of component (A1) include acrylates, methacrylates, 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,