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Scope of the Invention

The invention relates to viscosity index (VI) improvers having a dispersing action, with good shear stability and a good dispersant/detergent activity in lubricating oils, particularly for diesel and otto engines.

Prior Art

Modern high performance engines make ever greater demands on the dispersant and detergent qualities of the engine lubricating oils.

In the field of otto engines, engine tests are used in the selected engines (DBM 102 E or sequence VE test) to assess the sludge dispersing action. As for diesel engines, the tendency to form deposits, which may result in ring sticking, among other things, is assessed in engine tests (VW-TD or MWM-B). As a rule, it is only possible to satisfy all the requirements by using multigrade oils which contain, in addition to correspondingly matched detergent inhibitor (DI) packages, VI improvers with an optimum dispersant/detergent activity.

US-A 3198739 claims mineral oil preparations which contain copolymers of C_{12-20} -alkylmethacrylate and the methacrylic acid ester of an α, ω - C_5 - C_7 -alkanediol. The good detergent and anti-sludge activity of the copolymer is emphasised. An effect which is improved by comparison with this US patent, particularly in relation to the undesirable increase in viscosity and gelatinization, is obtained by adding a low-molecular representative of a group of heterocyclic compounds having the structural element $-RN-C=O$.

(cf. US-A- 3 377 285)

FR-A-1 173 356 lays claim to a vast range of structural variations of oil additives, since it reserves the right to choose any type of monomer which can impart oil solubility. No interpretation is provided of the specific effects of functional groups with regard to the detergent effect, but it can be concluded from the specification, with reference to the Examples, that the presence of -OH and/or -NH groups is absolutely essential in order to achieve a specific detergent effect. This conclusion is confirmed not only by the specifications mentioned above but also by FR-A 2 069 681. In this latter publication, again, monomers with hydroxyl groups are copolymerised in addition to olefinically unsaturated esters with the $\geq C_8$ -alcohols.

It has long been known that a special dispersing action can be introduced into polymeric VI improvers by introducing polar monomers, particularly basic comonomers, for example N-vinylheterocyclic compounds or dialkylaminoalkyl(meth)-acrylates (cf. H. Rauch-Puntigam, Th. Völker, Acryl- und Methacrylverbindungen, p. 314-318, Springer-Verlag, Berlin 1967; Ullmanns Encyclopädie der technischen Chemie, 4th Edition, Vol. 20, pg 547-550, Verlag Chemie 1981).

It has proved particularly useful, from an industrial point of view, to graft base polymers of the olefin copolymer (OCP) and polyalkyl(meth)acrylate (PAMA) type with polar monomers having a dispersant activity, for which numerous alternative processes have been proposed in the course of time. (cf. DE-A 12 35 491, BE-A 592 880, US-A 4 281 081, US-A 4 338 418, US-A 4 290 025).

Objective and Solution

Experience has shown that N-vinylpyrrolidone as well as N-vinylimidazole are particularly suitable as monomers

with a dispersant activity. In particular, graft products onto OCP or PAMA as base polymers, or as components of concentrated polymer emulsion made up of both types of polymer (so called mixed polymers, cf. EP 14 746) have acquired practical importance.

Concentrated emulsions of olefin copolymers with a graft or block copolymer of olefin copolymer sequences and poly(meth)acrylate sequences as emulsifier in a carrier medium which essentially does not dissolve the olefin copolymers but does dissolve the poly(meth)acrylate sequences, the olefin copolymers being emulsified at 40-150°C in the carrier medium, with the use of shear forces, are described in EP 88 904.

On the other hand, it has been found that in numerous cases a sufficient dispersant/detergent effect can be achieved if the graft yield when grafting N-vinylpyrrolidone is increased from about 60% to about 75%. This increase in the graft yield can admittedly be achieved in an obvious manner by increasing the graft component from about 58% to about 70%, based on the PAMA base polymer, but this brings such serious disadvantages with it that this measure does not result in any genuine progress. Thus, the molecular weight is disproportionately increased by cross-linking side reactions of the base chains (so-called graft increase in the molecular weight) in the grafting stage with N-vinylpyrrolidone, with the result that the shear stability is dramatically reduced. The ratio of thickening action to shear stability then comes nowhere near satisfying present requirements. The objective was therefore to prepare polyalkyl(meth)acrylates, particularly in the form of highly concentrated polymer emulsions with an adequate dispersant action and detergent effect, the other properties of which, particularly the ratio of thickening effect to shear stability would satisfy modern requirements. It has now

been found that the additives according to the present invention meet the requirements of the art exceptionally well.

The invention relates to concentrated polymer emulsions of polyalkyl(meth)acrylates (PAMA) and olefin copolymers (OCP) and/or hydrogenated isoprene- or butadiene-styrene copolymers (HSD) and/or hydrogenated polyisoprene or polybutadiene in liquid carrier media (TM), suitable for improving the viscosity index, for use as oil additives with improved dispersant and detergent effects in diesel and otto engines, the polyalkyl(meth)acrylates (PAMA) being made up of 80-99.5 parts by weight of alkyl(meth)-acrylates of the formula

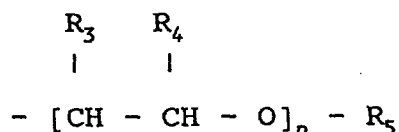


wherein R represents hydrogen or methyl and R₁ denotes a C₆₋₂₄-alkyl group, preferably a C₈₋₂₀-alkyl group,

together with 0.5 to 20 parts by weight of at least one functionalised alkylmethacrylate of formula II



wherein R' denotes hydrogen or methyl and R₂ denotes a C₂₋₆-alkyl group substituted by at least one OH group, or R₂ denotes a polyalkoxylated group



wherein R_3 and R_4 denote hydrogen or methyl, R_5 denotes a C_{1-40} -alkyl group and n is an integer from 1 to 60, and the sum of the monomers of formulae (I) and (II) is 100 parts by weight,

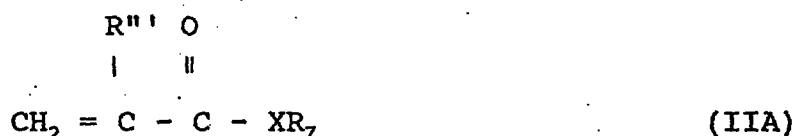
and optionally 0 to 20 parts by weight of one or more monomers of formula III



wherein R'' denotes hydrogen or methyl and R_6 denotes a C_{1-9} -alkyl group,

as comonomer.

In addition to the monomers of formula II or III, additionally 0-20 parts by weight, preferably 0.5 to 15 parts by weight of functionalised alkyl(meth)acrylates of formula IIA



wherein X denotes oxygen or $-NH$ or $-NR'_6$ and

R''' denotes hydrogen or methyl and R_7 denotes an optionally branched C_{2-20} -alkyl group, preferably a C_{2-6} -alkyl group, substituted by at least one group $-NR_8R_9$, wherein R_8 and R_9 independently of each other represent a C_{1-20} -alkyl group, preferably a C_{1-6} -alkyl group, or wherein R_8 and R_9 including the nitrogen atom and optionally another nitrogen or oxygen atom form a 5- or 6-membered ring which may optionally be substituted by C_{1-6} -alkyl and wherein R'_6 has the same meaning as R_6 ,

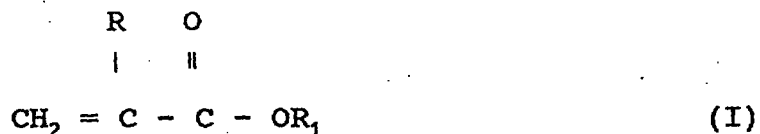
and/or a vinyl heterocyclic compound of formula IIB



wherein Bs denotes a 5- or 6-membered heterocyclic group, particularly an N-heterocyclic group, preferably selected from the group wherein Bs denotes a pyridine, carbazol, imidazol and particularly a pyrrolidone group, are copolymerised in the polyalkyl(meth)acrylates (PAMA).

In one particular embodiment of the invention, following the polymerisation of the monomers of formulae I, II, IIA, IIB and optionally III, a further 0.5 to 15 parts by weight of monomers of formula IIA and/or IIB, are added, optionally together with 1 to 30 parts by weight of monomers of formula I and III and are polymerised.

The present application further relates to a process for preparing concentrated polymer emulsions from poly(meth)acrylates and olefin copolymers in liquid carrier media, suitable for improving the viscosity index, for use as oil additives with an improved dispersant and detergent effect in diesel and otto engines, wherein the monomers polymerised are 80 to 99.5 parts by weight alkyl(meth)acrylates of formula I



together with 0.5 to 20 parts by weight of functionalised alkyl(meth)acrylates of formula II



wherein the sum of the monomers of formula I and II always amounts to 100 parts by weight and 0 to 20 parts by weight of one or more monomers of formula III



and 0 to 20 parts by weight of one or more monomers of formulae IIA and/or IIB, wherein the substituents occurring (R, R', R'', R''', X, R₁-R₉ and Bs) are as hereinbefore defined, in the presence of 1 to 30% by weight (based on all the monomers and polymers present in the mixture) of olefin copolymers (OCP) and/or hydrogenated isoprene- or butadiene-styrene copolymers (HSD) and/or hydrogenated poly-isoprene or polybutadiene.

In one particular embodiment of the process for preparing concentrated polymer emulsions, the polymerisation of monomers I, II, IIA, IIB and III may be carried out with the addition of 0.1 to 2.0% by weight of radical initiator and with the simultaneous presence of 0.05 to 0.5% by weight of molecular weight regulators, all based on all the monomers. The regulators used may be conventional sulphur regulators (cf. Th. Völker, H. Rauch-Puntigam, Acryl- und Methacrylverbindungen, Springer-Verlag 1968), as well as products such as terpinols and the derivatives thereof.

Preferably, the concentrations of the monomers and polymers are such that all the monomers and polymers present in the liquid carrier medium TM amount to 40 to 75% by weight, preferably 55 to 70% by weight, based on

the entire system. In another advantageous embodiment of the process, after polymerisation has ended, further olefin copolymer is added to the polymerisation mixture in quantities such that the olefin copolymer content of the entire polymer present amounts to 31 to 80% by weight. The olefin copolymer can advantageously be added just as it is, ie. in undiluted form, and is preferably emulsified in the mixture by the use of shear forces.

Alternatively, the additional olefin copolymer may also be added in the form of a solution, for example a 10 to 20% solution in the liquid carrier medium.

As has already been shown hereinbefore, known VI improvers, namely olefin copolymers (OCP), polyalkyl(meth)acrylates (PAMA) and the above mentioned mixed polymers, eg. according to EP 14 746, are used as base polymers for the process according to the invention.

The Polyalkyl(meth)acrylates

The polyalkyl(meth)acrylates are primarily those having alkyl groups with 6-24 carbon atoms which result in solubility in mineral oil. Shorter alkyl groups and those with polar substituents which do not impart any solubility in mineral oil may be present to a certain extent. The molecular weights Mw are between 5,000 and 1,000,000, preferably between 50,000 and 500,000. Products of this kind are described in the publications GB-C 1 068 938, US-A 3 732 334, US-A 4 149 984, US-A 4 229 331, US-A 4 281 081, US-A 4 338 418, US-A 4 290 925, DE-A 3 339 103, DE-A 3 607 444, DE-A 3 613 992, and US-A 4 677 151, US-A 4 622 358, US-A 822 508. The monomers to be used in the process according to the invention are described in detail hereinafter.

The Alkyl(meth)acrylates

According to the invention, it is obligatory to include in the polymerisation alkyl(meth)acrylates of formula I in amounts of from 80 to 99.5, preferably 90 to 98.5 parts by weight. Examples of monomers of formula I include (meth)acrylic acid esters of stearic alcohols (for example with a carbon number ranging from 14-20, on average about 17.3), coconut oil alcohols (carbon number ranging from 10-16, on average about 12.6) or synthetic alcohols such as Dobanol 25° (C-number ranging from 11-16, on average 13.5).

Examples of functionalised monomers of formula II include, on the one hand, those having an OH group in the alkyl moiety, particularly in the ω position of the alkyl moiety, eg. 2-hydroxyethylmethacrylate and acrylate, 3-hydroxypropylmethacrylate and acrylate, and the derivatives which are mono- or di-methyl substituted in the 2-position, 4-hydroxybutylmethacrylate and acrylate, as well as 2-hydroxypropylmethacrylate and acrylate.

There is particular interest in the monomers of formula II wherein R_2 represents a polyalkoxylated, more particularly ethoxylated group, eg. 2-(2-ethoxy-ethoxy)-ethyl-methacrylate and acrylate and including (meth)-acrylic acid esters of C_{1-18} -fatty alcohol mixtures with average ethoxylation levels of 1 to 60, eg. with an average ethoxylation level of 11 or 25, starting from corresponding industrial products, because of their low aggressiveness under practice conditions in engine tests. Mention may be made of (meth)acrylic acid esters of Carbowax 550°, Marlipal 1618/11°, Marlipal 1618/25°, Carbowax 2000° and Carbowax 750°.

Mention should also be made of the functionalised monomers of formula IIA wherein R_7 denotes an alkylene-dialkylamino group, particularly 2-dimethylamino- and 2-diethylaminoethylmethacrylate and acrylate, 3-dimethylaminopropylmethacrylate and acrylate and the corresponding diethylamino compounds, as well as the corresponding amides, particularly N-(3-dimethylaminopropylmethacrylamide. These comonomers may be included in polymerisation, for example by copolymerisation with compounds of formula II, or else at a later stage. Formula IIA also includes heterocyclically substituted monomers such as 2-(1-imidazolyl)ethylmethacrylate and acrylate, 2-(4-morpholinyl)-ethylmethacrylate and acrylate and 1-(2-methylacryloyloxyethyl)-2-pyrrolidone, as well as the corresponding amides. The monomers of formula IIB are also of particular significance, especially N-vinylpyrrolidone-2.

The Olefin Copolymers OCP

The olefin copolymers to be used according to the invention are known per se. They are primarily polymers consisting of ethylene, propylene, butylene and/or other α -olefins having 5 to 20 carbon atoms, such as those which have already been recommended as VI improvers. The molecular weight Mw is generally from 10,000 to 300,000, preferably from 50,000 to 150,000. Olefin copolymers of this kind are described for example in German Patent Application publications DE-A 16 44 941, DE-A 17 69 834, DE-A 19 39 037, DE-A 19 63 039 and DE-A 20 59 981. If the base copolymer consists of a hydrogenated polyisoprene or copolymer with styrene, commercially obtainable hydrogenated products (eg. the commercial products SHELLVIS 50, 200 or 250 °) are preferred. Particularly suitable are ethylene-propylene copolymers and also terpolymers with the known ter components, such as ethylidene-norbornene (cf.

Macromolecular Reviews, Vol. 10 (1975)) are possible, but their tendency to cross-link during the ageing process must be taken into account. The distribution may be substantially statistical, but sequence polymers with ethylene blocks may also be used to advantage. The ratio of the monomers ethylene and propylene is variable within certain limits, which may be set at about 75% for ethylene and about 80% for propylene as the upper limit. Because of its reduced tendency to dissolve in oil, polypropylene is less suitable than ethylene-propylene copolymers.

The Polymerisation Process

The solvent or carrier medium TM used is conveniently an inert solvent compatible with the subsequent application, having a boiling point of at least 300°C at 760 mm Hg, preferably a mineral oil. The solvents therefore come under the group of the hydrocarbons such as kerosene (boiling range 180 to 210°C), the naphthene-based oils, the paraffin-based oils or the gas oils, for example. (Cf. Ullmanns Enzyklopädie der Techn. Chemie, 4th Edition, Vol. 10, p. 641-714). When preparing concentrated polymer emulsions it is advantageous to use carrier media which dissolve OCP only to a limited extent or which are only swelling agents, as described in detail in US-P 4 677 151 and US-P 4 622 358. These are, in particular, phthalic acid esters such as dibutylphthalate and esters of 2,2,4-trimethyladipic acid, eg. with a mixture of octanol and decanol. The mono- or multifunctional alcohols themselves are also possible, eg. hexadecanol, octadecanol, diethylene-glycol, tetraethyleneglycol and methoxypolyethylene-glycols with ethoxylation levels of about 2 to 50.

The polymerisation of the alkyl(meth)acrylates is generally carried out by monomer feed polymerisation at

80-100°C in the liquid carrier medium with the addition of peroxide initiators such as t-butylperoctoate. When preparing concentrated polymer emulsions this is carried out in the presence of a small amount of dissolved OCP. Polymerisation is usually complete after about 8 hours. Then further monomers may be grafted on by polymerisation at 130°C with the addition of t-butylperbenzoate. Finally, the desired end composition is achieved by the addition of further OCP and if necessary solvent or carrier medium.

The Additives

The VI-improving additives according to the invention with a dispersant/detergent effect are generally available as relatively concentrated polymer solutions in the carrier media. Generally, the content of polymer in the concentrates ranges from 30 to 75% by weight, preferably 40 to 70%. It is advantageously added to the oils or fractions whose viscosity indices are to be improved in quantities such that they preferably contain 1 to 10% by weight of the polymer additives according to the present invention.

The advantage of the additives according to the invention is the outstanding dispersant and detergent effect in otto and diesel engines and at the same time a totally neutral behaviour in the presence of sealing materials such as Viton®.

Test Methods

Testing is carried out in accordance with

1. CCMC European Oil Sequence for Service - Fill Oils for Gasoline Engines, Classes G4 and G5:
Low Temperature Sludge according to ASTM 315 H,

Part III, Seq. VE.

Black Sludge M 102 E: according to CEC L-41-T-88.

2. CCMC European Oil Sequence for Service - Fill Oils for Diesel Engines, Classes D4, D5 and PD2:
Ring Sticking and Piston Cleanliness VW 1.6 TC Diesel according to CEC L-35-T-84.
3. Screening Test for Bore Polishing and Piston Cleanliness for Diesel Engines:
MWM B according to CEC L-12-A-76.
4. VW-Elastomer Test TL-VW 521 of 07.10.1988, FKM-E-281.
5. Viscosity Measurement according to DIN 51562 (Ubbelohde-Viscometer).

The following Examples serve to illustrate the invention.

SSI = Shear stability index: Loss of thickening effect in % during shear stability test according DIN 51382

In addition, the following abbreviations have been used:

"DI Package A" is a standard commercial DI package of API Performance Class SF/CC.

"DI Package B" is a standard commercial DI package of API Performance Class SF/CD.

EXAMPLES

A. Preparation of the Viscosity Index Improvers

a) Additive 1

The following mixture is placed in a 2 litre 4-necked round flask with stirrer, thermometer, reflux condenser and metering line:

400.00 g Mineral oil (η 100°C = 3.9 mm²/s)
4.44 g 2-Hydroxyethylmethacrylate
39.96 g Methacrylic acid ester of a C₁₂₋₁₈-
alcohol mixture
0.35 g Dodecylmercaptane
1.00 g tert.-Butylperoctoate

After the components have dissolved, the following mixture is evenly metered in over a period of 3.5 hours at 90°C:

55.56 g 2-Hydroxyethylmethacrylate
500.04 g Methacrylic acid ester of a C₁₂₋₁₈-
alcohol mixture
4.44 g Dodecylmercaptane
1.67 g tert.-Butylperoctoate

Two hours after the mixture has been added a further 1.2g of tert.-butylperoctoate are added. Total polymerisation time 8 hours. A clear viscous solution is obtained.

Polymer content = 60% by weight

Viscosity (100°C, 60% by weight) = 1300 mm²/s

Viscosity (100°C, 6% by weight in mineral oil with η
100°C = 5.4 mm²/s) = 9.7 mm²/s

SSI (6% by weight in mineral oil with η 100°C = 6.4

$\text{mm}^2/\text{s}) = 3.6$

b) Additive 2

Apparatus and method as in Example 1;
the following are put in:

400.0 g Mineral oil (η 100°C = 3.9 mm^2/s)
5.73 g Methacrylic acid ester of an ethoxylated
C₁₆₋₁₈-fatty alcohol mixture, average
ethoxylation level = 25
3.86 g Methylmethacrylate
34.81 g Methacrylic acid ester of a C₁₂₋₁₅
alcohol mixture
0.35 g Dodecylmercaptane
1.00 g tert.-Butylperoctoate

the following are added:

71.67 g Methacrylic acid ester of an ethoxylated
C₁₆₋₁₈-fatty alcohol mixture, average
ethoxylation level = 25
48.33 g Methylmethacrylate
435.60 g Methacrylic acid ester of a C₁₂₋₁₅
alcohol mixture
4.44 g Dodecylmercaptane
1.67 g tert.-Butylperoctoate

Two hours after all of the above has been added, 1.2g of
tert.-butylperoctoate are added. Total polymerisation
time 8 hours. A clear viscous solution is obtained.

Polymer content = 60% by weight

Viscosity (100°C, 60% by weight) = 270 mm^2/s

Viscosity (100°C, 6% by weight in mineral oil with η
100°C = 5.4 mm^2/s) = 9.7 mm^2/s

SSI (6% by weight in mineral oil with η 100°C = 5.4

$$\text{mm}^2/\text{s}) = 3.6$$

c) Additive 3

Apparatus and method as in Example 1;
the following are put in:

- 360.0 g Mineral oil (η 100°C = 5.4 mm²/s)
- 42.0 g Ethylene-propylene copolymer (50% by weight ethylene; SSI (1% in mineral oil η 100°C = 5.4 mm²/s) = 24)
- 5.5 g Methacrylic acid ester of an ethoxylated C₁₆₋₁₈-fatty alcohol mixture; average ethoxylation level = 25
- 2.5 g Methylmethacrylate
- 36.7 g Methacrylic acid ester of a C₁₂₋₁₅ alcohol mixture
- 0.05 g Terpinolene
- 0.61 g tert.-Butylperoctoate

the following are added:

- 92.7 g Methacrylic acid ester of an ethoxylated C₁₆₋₁₈-fatty alcohol mixture, average ethoxylation level = 25
- 42.2 g Methylmethacrylate
- 618.6 g Methacrylic acid ester of a C₁₂₋₁₅ alcohol mixture
- 0.75 g Terpinolene
- 3.39 g tert.-Butylperoctoate

Two hours after the above has all been added, 1.6g of tert.-butylperoctoate are put in. Total polymerisation time 8 hours. A slightly cloudy, viscous solution is obtained.

This solution is poured into a 4 litre 3-necked flask with stirrer, thermometer and reflux condenser and heated to 100°C.

The following are then added:

384.5 g Ethylene-propylene copolymer (50% by weight of ethylene; SSI (1% in mineral oil η 100°C = 5.4 mm²/s) = 24)
1,476.7 g Mineral oil (η 100°C = 5.4 mm²/s)

After dissolving at 100°C within 8 hours a cloudy viscous emulsion is obtained.

Polymer content = 40% by weight

Viscosity (100°C, 40% by weight) = 2,800 mm²/s

Viscosity (100°C, 3% by weight in mineral oil with η 100°C = 5.4 mm²/s) = 14.1 mm²/s

SSI (3% by weight in mineral oil with η 100°C = 5.4 mm²/s) = 24

d) Additive 4

Apparatus and method as in Example 1;
the following are put in:

360.0 g Mineral oil (η 100°C = 5.4 mm²/s)
42.0 g Ethylene-propylene copolymer (50% by weight ethylene; SSI (1% in mineral oil η 100°C = 5.4 mm²/s) = 24)
2.24 g 2-Hydroxyethylmethacrylate
42.46 g Methacrylic acid ester of a C₁₂₋₁₈ alcohol mixture
0.05 g Terpinolene
2.10 g tert.-Butylperoctoate

the following are added:

37.7 g 2-Hydroxyethylmethacrylate
715.8 g Methacrylic acid ester of a C₁₂₋₁₈ alcohol
mixture
0.75 g Terpinolene
3.39 g tert.-Butylperoctoate

Two hours after the above has been added, a further 1.6g of tert.-butylperoctoate are put in. Total polymerisation time 8 hours. A slightly cloudy, highly viscous solution is obtained.

This solution is poured into a 4 litre 3-necked flask with stirrer, thermometer and reflux condenser and heated to 100°C.

The following are then added:

384.5 g Ethylene-propylene copolymer (50% by weight of ethylene; SSI (1% in mineral oil η 100°C = 5.4 mm²/s) = 24)
1,476.7 g Mineral oil (η 100°C = 5.4 mm²/s)

After dissolving at 100°C within 8 hours a cloudy, viscous emulsion is obtained.

Polymer content = 40% by weight

Viscosity (100°C, 40% by weight) = 2,800 mm²/s

Viscosity (100°C, 3% by weight in mineral oil with η 100°C = 5.4 mm²/s) = 14.1 mm²/s

SSI (3% by weight in mineral oil with η 100°C = 5.4 mm²/s) = 24

e) Additive 5

Apparatus and method as in Example 1;
the following are put in:

360.0 g Mineral oil. (η 100°C = 5.4 mm²/s)
42.0 g Ethylene-propylene copolymer (50% by
weight ethylene; SSI (1% in mineral oil
 η 100°C = 5.4 mm²/s) = 24)
0.22 g 2-Dimethylaminoethylmethacrylate
2.60 g Methylmethacrylate
41.88 g Methacrylic acid ester of a C₁₂₋₁₈ alcohol
mixture
0.05 g Terpinolene
2.40 g tert.-Butylperoctoate

the following are added:

3.77 g 2-Dimethylaminoethylmethacrylate
43.70 g Methylmethacrylate
706.03 g Methacrylic acid ester of a C₁₂₋₁₈ alcohol
mixture
0.75 g Terpinolene
7.50 g tert.-Butylperoctoate

Two hours after the addition has ended a further 1.6g of
tert.-butylperoctoate are put in. Total polymerisation
time 8 hours.

The following are then added:

26.0 g N-Vinylpyrrolidone-2
11.0 g Mineral oil (η 100°C = 5.4 mm²/s)

and the mixture is heated to 130°C.

After the temperature has been reached, 1.95g of tert.-
butylperbenzoate are added and a further 0.94g of tert.-
butylperbenzoate are fed in after 1 and 2 hours. Total
duration of grafting 6 hours. A slightly cloudy,
viscous solution is obtained. This solution is placed
in a 1 litre 3-necked flask with stirrer, thermometer

and reflux condenser and heated to 100°C.

The following are then added:

384.5 g Ethylene-propylene copolymer (50% by
weight of ethylene; SSI (1% in mineral
oil η 100°C = 5.4 mm²/s) = 24)
1,476.7 g Mineral oil (η 100°C = 5.4 mm²/s)

After dissolving at 100°C within 8 hours a cloudy
viscous emulsion is obtained.

Polymer content = 40% by weight

Viscosity (100°C, 40% by weight) = 2,800 mm²/s

Viscosity (100°C, 3% by weight in mineral oil with η
100°C = 5.4 mm²/s) = 14.1 mm²/s

SSI (3% by weight in mineral oil with η 100°C = 5.4
mm²/s) = 24

f) Additive 6

Apparatus and method as in Example 1;
the following are put in:

417.0 g Mineral oil (η 100°C = 5.4 mm²/s)
29.15 g Ethylene-propylene copolymer (50% by
weight ethylene; SSI (1% in mineral oil
 η 100°C = 5.4 mm²/s) = 24)
2.87 g Methylmethacrylate
46.70 g Methacrylic acid ester of a C₁₂₋₁₈ alcohol
mixture
3.0 g tert.-Butylperoctoate

the following are added:

29.25 g Methylmethacrylate
475.13 g Methacrylic acid ester of a C₁₂₋₁₈ alcohol

mixture

5.00 g tert.-Butylperoctoate

Two hours after all has been added, a further 1.1g of tert.-butylperoctoate are put in. Total polymerisation time 8 hours.

The following are then added:

18.03 g N-Vinylpyrrolidone-2

12.90 g Mineral oil (η 100°C = 5.4 mm²/s)

and the mixture is heated to 130°C.

After the temperature has been reached, 1.5g of tert.-butylperbenzoate are added, with a further 0.72g of tert.-butylperbenzoate being added after 1 and 2 hours. Total duration of grafting 6 hours. A slightly cloudy, viscous solution is obtained.

This solution is placed in a 4 litre 3-necked flask with stirrer, thermometer and reflux condenser and heated to 100°C.

The following are then added:

266.88 g Ethylene-propylene copolymer (50% by weight of ethylene; SSI (1% in mineral oil η 100°C = 5.4 mm²/s) = 24)

857.90 g Mineral oil (η 100°C = 5.4 mm²/s)

After dissolving at 100°C within 8 hours a cloudy, viscous emulsion is obtained.

Polymer content = 40% by weight

Viscosity (100°C, 40% by weight) = 2,800 mm²/s

Viscosity (100°C, 3% by weight in mineral oil with η

$$100^{\circ}\text{C} = 5.4 \text{ mm}^2/\text{s}) = 24$$

g) Additive 7

Apparatus and method as in Example 1;
the following are put in first:

400.00 g Mineral oil (η $100^{\circ}\text{C} = 3.9 \text{ mm}^2/\text{s}$)
1.55 g N-Dimethylaminopropylmethacrylamide
4.44 g Methylmethacrylate
38.45 g Methacrylic acid ester of a C_{12-18} alcohol
mixture
0.35 g Dodecylmercaptane
1.00 g tert.-Butylperoctoate

the following are then added:

19.44 g N-Dimethylaminopropylmethacrylamide
55.56 g Methylmethacrylate
480.56 g Methacrylic acid ester of a C_{12-18} alcohol
mixture
4.44 g Dodecylmercaptane
1.67 g tert.-Butylperoctoate

Two hours after the ingredients have all been added,
1.2g of tert.-butylperoctoate are added. Total
polymerisation time 8 hours. A clear viscous solution
is obtained.

Polymer content = 60% by weight

Viscosity (100°C , 60% by weight) = $500 \text{ mm}^2/\text{s}$

Viscosity (100°C , 6% by weight in mineral oil with η
 $100^{\circ}\text{C} = 5.4 \text{ mm}^2/\text{s}$) = $9.8 \text{ mm}^2/\text{s}$

SSI (6% by weight in mineral oil with η $100^{\circ}\text{C} = 5.4$
 mm^2/s) = 3.6

h) Additive 8

Apparatus and method as in Example 1;
the following are put in first:

400.0 g Mineral oil (η 100°C = 3.9 mm²/s)
2.0 g N-Vinylpyrrolidone-2
4.44 g Methylmethacrylate
38.00 g Methacrylic acid ester of a C₁₂₋₁₈ alcohol
mixture
0.35 g Dodecylmercaptane
1.00 g tert.-Butylperoctoate

the following are added:

25.00 g N-Vinylpyrrolidone-2
55.56 g Methylmethacrylate
475.00 g Methacrylic acid ester of a C₁₂₋₁₈ alcohol
mixture
4.44 g Dodecylmercaptane
1.67 g tert.-Butylperoctoate

Two hours after the ingredients have been added, a
further 1.2g of tert.-butylperoctoate are put in. Total
polymerisation time 8 hours. A clear viscous solution
is obtained.

Polymer content = 60% by weight

Viscosity (100°C, 60% by weight) = 980 mm²/s

Viscosity (100°C, 6% by weight in mineral oil with η
100°C = 5.4 mm²/s) = 9.8 mm²/s

SSI (6% by weight in mineral oil with η 100°C = 5.4
mm²/s) = 3.6

B. Use of the Viscosity Index Improvers as Additives

Example 1

In a 20 litre VA container provided with heating means, stirrer and thermometer, the following components are mixed at 65°C to form a 10 W-30 multigrade oil:

- 331.5 g Additive 1
- 975.0 g Ethylene-propylene copolymer (50% by weight of ethylene; SSI (1% in mineral oil η 100°C = 5.4 mm²/s) = 24)
The copolymer was present as an 11% solution in mineral oil (η 100°C = 5.4 mm²/s)
- 1 280.0 g DI package A
- 1 300.0 g Poly- α -olefin (η 100°C = 4 mm²/s)
- 4 550.0 g Mineral oil (η 100°C = 3.9 mm²/s)
- 4 563.0 g Mineral oil (η 100°C = 6.2 mm²/s)

Example 2

Apparatus and method as in Example 1. The following components are mixed together to form a 10 W-30 multigrade oil:

- 331.5 g Additive 2
- 975.0 g Ethylene-propylene copolymer (50% by weight of ethylene; SSI (1% in mineral oil η 100°C = 5.4 mm²/s) = 24)
The copolymer was present as an 11% solution in mineral oil (η 100°C = 5.4 mm²/s)
- 1 280.5 g DI package A
- 1 399.9 g Poly- α -olefin (η 100°C = 4 mm²/s)
- 4 550.0 g Mineral oil (η 100°C = 3.9 mm²/s)
- 4 563.0 g Mineral oil (η 100°C = 6.2 mm²/s)

Example 3

Apparatus and method as in Example 1. The following components are mixed together to form a 10 W-30 multigrade oil:

- 762.8 g Additive 3
- 1 280.5 g DI package A
- 1 300.0 g Poly- α -olefin (η 100°C = 4 mm²/s)
- 407.2 g Mineral oil (η 100°C = 5.4 mm²/s)
- 4 550.0 g Mineral oil (η 100°C = 3.9 mm²/s)
- 4 699.5 g Mineral oil (η 100°C = 6.2 mm²/s)

Example 4

Apparatus and method as in Example 1. The following components are mixed together to form a 10 W-30 multigrade oil:

- 762.8 g Additive 5
- 1 280.5 g DI package A
- 1 300.0 g Poly- α -olefin (η 100°C = 4 mm²/s)
- 407.2 g Mineral oil (η 100°C = 5.4 mm²/s)
- 4 550.0 g Mineral oil (η 100°C = 3.9 mm²/s)
- 4 699.5 g Mineral oil (η 100°C = 6.2 mm²/s)

Example 5

Apparatus and method as in Example 1. The following components are mixed together to form a 10 W-30 multigrade oil:

- 688.5 g Additive 4
- 1 447.5 g DI package A
- 5 250.0 g Mineral oil (η 100°C = 10.5 mm²/s)
- 7 584.0 g Mineral oil (η 100°C = 5.4 mm²/s)

Example 6

Apparatus and method as in Example 1. The following components are mixed together to form a 15 W-40 multigrade oil:

688.5 g Additive 5
1 477.5 g DI package A
5 250.0 g Mineral oil (η 100°C = 10.5 mm²/s)
7 584.0 g Mineral oil (η 100°C = 5.4 mm²/s)

Example 7

Apparatus and method as in Example 1. The following components are mixed together to form a 15 W-30 multigrade oil:

130.0 g Additive 2
539.5 g DI package B
975.0 g Mineral oil (η 100°C = 10.5 mm²/s)
4 855.5 g Mineral oil (η 100°C = 5.4 mm²/s)

Example 8

Apparatus and method as in Example 1. The following components are mixed together to form a 15 W-30 multigrade oil:

130.0 g Additive 2
539.5 g DI package B
975.0 g Mineral oil (η 100°C = 10.5 mm²/s)
4 855.5 g Mineral oil (η 100°C = 5.4 mm²/s)

Comparison Example 1

Apparatus and method as in Example 1. The following components are mixed together to form a 10 W-30

multigrade oil:

762.8 g Additive 6
1 280.5 g DI package A
467.2 g Mineral oil (η 100°C = 5.4 mm²/s)
1 300.0 g Poly- α -olefin (η 100°C = 4 mm²/s)
4 550.0 g Mineral oil (η 100°C = 3.9 mm²/s)
4 639.5 g Mineral oil (η 100°C = 6.2 mm²/s)

Comparison Example 2

Apparatus and method as in Example 1. The following components are mixed together to form a 15 W-30 multigrade oil:

130.0 g Additive 7
539.5 g DI package B
975.0 g Mineral oil (η 100°C = 10.5 mm²/s)
4 855.5 g Mineral oil (η 100°C = 5.4 mm²/s)

Comparison Example 3

Apparatus and method as in Example 1. The following components are mixed together to form a 15 W-30 multigrade oil:

130.0 g Additive 8
539.5 g DI package B
975.0 g Mineral oil (η 100°C = 10.5 mm²/s)
4 855.5 g Mineral oil (η 100°C = 5.4 mm²/s)

In Table 1 which follows, the following conventional abbreviations are used:

AS = Average Sludge
RCS = Rocker Cover Sludge
PSV = Piston Skirt Varnish

AV = Average Varnish
 CW = Cam Wear [10^{-3} inches]

For the evaluation in the Table, 10 = clean.

TABLE 1

Sequence VE Test Results
 (ASTM 315 H, Part III)

Example	Additive	AS	RCS	PSV	AV	Cw max	CW ϕ
Limits		9.0	7.0	6.7	5.0	15.5	4.0
1	1	9.19	7.98	7.14	5.81	8.90	3.30
2	2	9.17	7.83	6.72	5.84	9.30	1.88
3	3	9.27	8.39	6.52	5.76	7.90	2.89
4	5	8.52	7.63	6.78	5.85	12.50	12.50
Comparison Example 1	6	8.01	6.85	6.01	9.7	6.32	7.10

TABLE 2

M 102-E Test Run Results
 (CEC-L-41-T-88)

Example	Additive	Cylinder Head	Valve Cover	Oil Sump	Oil distrib- utor pipe	Control Cover	ϕ Value
5	4	9.26	9.14	9.39	9.34	9.25	9.27
6	5	7.33	8.45	6.31	8.42	8.13	7.72

TABLE 3

MWMB Test Run Results
(CEC-L-12-A-76)

VW Elastomer Test TL-VW-521
of 07.10.1988 FKM-E-281

Example	Additive	Piston Evaluation (Points)	Delta tear strength %	Delta elongation at break %	Cracks
			Limit ± 20	± 25	None
7	2	65	- 9	- 13	None
8	1	68	- 7	- 10	None
Comparison	7	63	- 30	- 29	None
Example 2					
Comparison	8	63	- 16	- 25	None
Example 3					

Result of Examples 1-8:

Special Effects

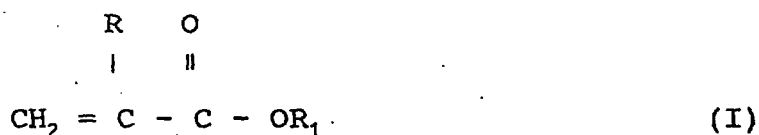
Table 1 (see the Examples) shows that both additives with OH groups (Example 1) and additives with ether groups (Examples 2 and 3) lead to an improved sludge and varnish evaluation in the Seq. VE test. A comparison is made with the prior art, represented by an additive with vinylpyrrolidone (Comparison Example 1). Example 4 shows that an additive according to the invention which is present as a concentrated polymer emulsion and has been produced in the presence of regulators (see claim) is somewhere in between in the evaluation.

Table 2 shows the results of the M-102-E black sludge test. The Additive 4 containing OH groups (Example 5) has a significantly better mark than Additive 5 with vinylpyrrolidone (Example 6). Both additives occur as concentrated polymer emulsions.

In Table 3, the ether group-containing additive 2 (Example 7) and the OH group-Additive 1 (Example 8) is compared with Additives 7 and 8 which are not according to the invention (Comparison Examples 2 and 3), the dimethylamino groups (Comparison Example 2) and pyrrolidone groups (Comparison Example 3). Whereas in the MWMB Screening Motor test there is no markedly different carbon evaluation, there are significant differences in the VW Elastomer test. Additives 2 and 1 according to the invention have the better performance, Additive 1 (OH groups) even being superior to Additive 2 (ether groups).

Patent Claims

1. Viscosity index improvers having a dispersing action, containing polyalkyl(meth)acrylate copolymers consisting of 80 to 99.5 parts by weight of alkyl(meth)acrylates of the formula

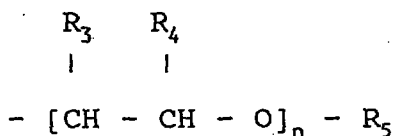


wherein R represents hydrogen or methyl and R₁ denotes a C₆₋₂₄-alkyl group, preferably a C₈₋₂₀-alkyl group,

together with 0.5 to 20 parts by weight of at least one functionalised alkylmethacrylate of formula II



wherein R' denotes hydrogen or methyl and R₂ denotes a C₂₋₆-alkyl group substituted by at least one OH group, or R₂ denotes a polyalkoxylated group



wherein R₃ and R₄ denote hydrogen or methyl, R₅ denotes a C₁₋₄₀-alkyl group and n is an integer from 1 to 60, and the sum of the monomers of formulae (I) and (II) is 100 parts by weight,



and optionally 0 to 20 parts by weight of one or more monomers of formula III



wherein R'' denotes hydrogen or methyl and R₆ denotes a C₁₋₉-alkyl group,

characterised in that the polyalkyl(meth)acrylates are present in combination with olefin copolymers (OCP) and/or hydrogenated isoprene- or butadiene-styrene copolymers (HSD) and/or hydrogenated polyisoprene or polybutadiene in the form of concentrated polymer emulsions.

2. Viscosity index improvers having a dispersing effect according to claim 1, characterised in that additionally 0 to 20 parts by weight of functionalised alkyl(meth)acrylates of formula IIA



wherein X denotes oxygen or -NH or -NR'₆ and

R''' denotes hydrogen or methyl and R₇ denotes an optionally branched C₂₋₂₀-alkyl group substituted by at least one group -RN₈-R₉, wherein R₈ and R₉ independently of each other represent a C₁₋₂₀-alkyl group, or wherein R₈ and R₉ including the nitrogen atom and optionally another nitrogen or oxygen atom form a 5- or 6-membered ring which may optionally



be substituted by C₁₋₆-alkyl and wherein R'₆ has the same meaning as R₆,

and/or vinyl heterocyclic compounds of formula IIB



wherein Bs denotes a 5- or 6-membered heterocyclic group, have been copolymerised as monomers in the polyalkyl(meth)acrylate copolymers.

3. Viscosity index improvers having a dispersing action, according to claims 1 and 2, characterised in that, when preparing the polyalkyl(meth)acrylate copolymers, following the polymerisation of the monomers of formulae I, II and III, a further 0.5 to 15 parts by weight of monomers of formula IIA and/or IIB have been added, optionally together with 1 to 30 parts by weight of monomers of formula I and II (based on the total polymer) and have been polymerised.

4. Process for preparing concentrated polymer emulsions from polyalkyl(meth)acrylates and olefin copolymers, suitable for improving the viscosity index, in liquid carrier media, characterised in that the monomers polymerised are 80 to 99.5 parts by weight alkyl(meth)acrylates of formula I



together with 0.5 to 20 parts by weight of



functionalised alkyl(meth)acrylates of formula II



and 0 to 20 parts by weight of one or more monomers of formula III



and 0 to 20% by weight of one or more monomers of formula IIA and/or IIB, wherein R, R', R'', R''', X, R₁ to R₆ and Bs have the meanings given in claims 1, 2 and 3, in the presence of 1 to 30 parts by weight (based on all the monomers and polymers present in the mixture) of olefin copolymers (OCP) and/or hydrogenated isoprene- or butadiene-styrene copolymers (HSD) and/or hydrogenated poly-isoprene or polybutadiene.

5. Process according to claim 4, characterised in that the polymerisation is carried out with the addition of 0.1 to 2.0 parts by weight of radical initiator and with the simultaneous presence of 0.05 to 0.5 parts by weight of molecular weight regulators, in each case referring to the total monomers.

6. Process according to claims 4 and 5, characterised in that, following the polymerisation of the monomers of formulae I, II, IIA and III, a further 0.5 to 15 parts by weight of monomers of formula IIA and/or IIB (based on the total polymer) are added and polymerised.



7. Process according to claims 4, 5 and 6, characterised in that the total quantity of monomers and polymers present in the liquid carrier medium is 40 to 75% by weight, preferably 55 to 70% by weight, based on the total system.

8. Process according to claims 4 to 7, characterised in that, finally, further olefin copolymer is added to the polymerisation mixture which has been fully polymerised, so that the content of olefin copolymer is increased to 31 to 80% by weight, based on the total polymer.

9. Process according to claim 8, characterised in that the olefin copolymer is added in the form of a 10 to 20% solution in the liquid carrier medium.

10. Process according to claim 8, characterised in that the olefin copolymer is added in undiluted form and is emulsified by the application of shearing forces.

11. Use of the viscosity index improvers having a dispersing action according to claims 1 to 3 for adding to mineral oils which contain DI packages.

