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LUBRICANT COMPOSITIONS

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10 Claims

ABSTRACT OF THE DISCLOSURE

Lubricant compositions containing oil-soluble copolymers of one or more alkyl esters of a C₃₋₅ alpha, beta-vinylidene monocarboxylic acid and one or more monohydroxy alkyl esters of a C₃₋₅ alpha, beta-vinylidene monocarboxylic acid, wherein the average number of the carbon atoms in the CH₃-(CH₂)_n- groups present in the alkyl side chains, *n* being at least 9, is from 12.5 to 14.3, have improved pour points, viscosity indices and dispersant properties.

This invention relates to improved lubricant compositions and to novel oil-soluble copolymers contained therein.

The suitability of a lubricating oil for use in internal combustion engines is dependent, among other properties, on its pour point, viscosimetric behavior, and dispersant ability. Since most lubricating base stocks do not inherently possess these properties to the extent required for use in present day internal combustion engines, it is customary to add one or more additives to the lubricating medium to improve these characteristics.

Numerous polymeric additives have been proposed in the literature which are capable of improving the pour point, viscosity index or dispersant ability of lubricating oils. A select few of these polymeric materials can be classified as multi-functional additives, i.e., capable of improving more than one of these properties, and fewer still capable of simultaneously improving all three of the aforementioned characteristics. The present invention relates to such a class of polymeric additives, which because of their unique structural configuration, have been unexpectedly found to significantly reduce the pour points of lubricating oils and also improve their viscosity indices and dispersant properties. The high activity of these polymeric materials is attributed to a combination of their side chain length, molecular weight and polarity.

It has now been found that lubricating compositions comprising a major amount of a lubricating oil and a minor amount, from 1 to 10% by weight, of an oil soluble copolymer of one or more alkyl esters of an alpha, beta-vinylidene monocarboxylic acid and one or more monohydroxy alkyl esters of an alpha, beta-vinylidene monocarboxylic acid, wherein the average number of carbon atoms in the CH₃-(CH₂)_n- alkyl side chain groups, *n* being at least 9, is from 12.5 to 14.3; the molar ratio of the units derived from alkyl esters to those derived from hydroxy alkyl esters is 10 to 0.25-5; and the molecular weight M_w of the copolymer is from 100,000 to 2,000,000, have improved pour point, viscosimetric, and dispersant properties. It was further found that the above-stated limitations, particularly the length of the alkyl side chains, was extremely critical in respect to the activity of the polymeric additives of the invention.

Comparison of the pour point depressing action in lubricating oil of polymers according to the invention with similar polymers in which the average number of carbon atoms of the CH₃-(CH₂)_n- groups present in the alkyl side chain, *n* being at least 9, is more than 14.3,

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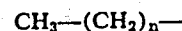
for example 14.6 or 15.0, or less than 12.5, for example 12.0, shows that the polymers according to the invention are capable of depressing the pour point of the lubricating oil to a much greater extent. Preferred polymers according to the invention are those in which the average number of carbon atoms of the CH₃-(CH₂)_n- groups present in the alkyl side chains, *n* being at least 9, is from 13.0 to 14.1.

The molecular weight of the present polymers may vary within wide limits. Often polymers are selected with a molecular weight M_w of at least 100,000 and at most 2,000,000, in particular polymers with a molecular weight M_w of at least 250,000 and at most 1,250,000. An important further aspect of polymeric lube oil additives is their resistance to degradation by shear in the engine. If polymeric lube oil additives have insufficient shear stability, one of the consequences is that the viscosity of the lubricating oil composition in which they are incorporated diminishes during use of the composition in the engine. It has been found that the molecular weight of the present polymers plays an important part as far as their shear stability is concerned. Polymers according to the invention have a high shear stability, especially if their molecular weight M_w is below 750,000.

The molar ratio of the units derived from the alkyl esters to those derived from the hydroxy alkyl esters may vary within wide limits. Generally, for every 10 units derived from alkyl esters, the copolymers should contain 0.25-5 units derived from the monohydroxy alkyl esters. To assure satisfactory pourability of concentrates of the present polymers in oil, preference is given to polymers which for every 10 units derived from the alkyl esters fewer than 3 units are derived from the monohydroxy alkyl esters. The use of the present polymers with low polarity is not only preferred from the standpoint of better pourability, but also for another reason. If the polarity is lowered, the thickening power of the polymers increases, which means that lower molecular weight polymers can be used to achieve the same viscosity level. As previously noted, reduction of the molecular weight of the present polymers results in an increase of shear stability. However, too large a reduction of polar groups in the present polymers results in a reduction of the dispersive power and the VI-improving action. In view of the foregoing, preference is given to polymers according to the invention which for every 10 units derived from alkyl esters at least 1 and at most 3 units are derived from the hydroxy alkyl esters.

In principle the present copolymers can be prepared by two routes. It is possible to prepare these copolymers directly by copolymerization of a mixture of monomers consisting of one or more alkyl esters of unsaturated monocarboxylic acids and one or more monohydroxy alkyl esters of unsaturated monocarboxylic acids. The copolymers are preferably prepared via an indirect route by copolymerization of a mixture of monomers consisting of one or more unsaturated monocarboxylic acids and one or more alkyl esters of unsaturated monocarboxylic acids and after treatment of the acid copolymers, in which the carboxylic groups are converted to COOR groups, in which R represents a monohydroxy alkyl group.

The alkyl esters of monocarboxylic acids suitable for use as monomers in the preparation of the present copolymers should consist of at least 60 mole percent of alkyl esters having an alkyl chain which contains a



group, *n* being at least 9. Moreover, these alkyl esters should have such a chain length and be present in the monomer mixture in such relative proportions that the average number of carbon atoms of the CH₃-(CH₂)_n- groups present in the alkyl chains, *n* being at least 9, is at

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least 12.5 and at most 14.3. Examples of such monomers are alkyl esters of unsaturated monocarboxylic acids in which an unbranched saturated hydrocarbon chain with at least 10 carbon atoms such as n-decyl, n-dodecyl, n-tetradecyl, n-hexadecyl, and n-octadecyl esters of unsaturated monocarboxylic acids. Alkyl esters of unsaturated monocarboxylic acids in which a branched hydrocarbon chain occurs are also suitable provided this branched hydrocarbon chain contains a $\text{CH}_3-(\text{CH}_2)_n-$ group, in which n is at least 9.

In addition to the aforesaid alkyl esters which must be present in the monomer mixture to be polymerized, the monomer mixture can contain other alkyl esters of unsaturated monocarboxylic acids such as alkyl esters with fewer than 10 carbon atoms in the alkyl chain or alkyl esters with 10 or more carbon atoms in the alkyl chain, in which, however, a $\text{CH}_3-(\text{CH}_2)_n-$ group, with n being at least 9, is absent. Examples of such monomers are methyl, ethyl, n-butyl, iso-octyl, and 2-methyldecyl esters of unsaturated monocarboxylic acids. Polymers prepared by using a mixture of alkylmethacrylates consisting at least in part of alkylmethacrylates which contain the group $\text{CH}_3-(\text{CH}_2)_n-$, wherein n is 11-17 have been found to be very advantageous. The present copolymers can be conveniently prepared from a mixture of alkylmethacrylates which consists at least in part of alkylmethacrylates derived from alcohols obtained by a special hydroformulation process. The alcohols in question can be prepared by reacting olefins with carbon monoxide and hydrogen in the presence of a complex catalyst which contains in the molecule a transition metal with an atomic number of 23 to 85 and at least one molecule of a biphyllic ligand which contains trivalent phosphorus, arsine or antimony as catalyst. In this context a biphyllic ligand is understood to mean a compound containing an element with an electron pair which is capable of forming a coordination bond with a metal atom and which element is at the same time capable of accepting electrons from the metal, as a result of which the stability of the complex is increased. Highly favorable results may be obtained by using a complex which contains cobalt, carbon monoxide and one or more phosphorus compounds.

Unsaturated monocarboxylic acids which are particularly suitable for use in preparing alkyl ester and hydroxy alkyl ester monomers are those having 3 to 5 carbon atoms and alpha,beta-vinylidene unsaturation. Examples of such acids are acrylic acid, methacrylic acid, itaconic acid and crotonic acid. Esters of methacrylic acid have been found to be particularly advantageous in forming the copolymeric additives of the invention.

The monohydroxy alkyl esters are generally formed from the aforementioned unsaturated monocarboxylic acids and dihydric alcohols or aliphatic ethers. Preferably, the monohydroxy alkyl group of the ester should contain from two to five carbon atoms. Thus, suitable monohydroxy alkyl ester monomers include partial esters of dihydric alcohols such as ethylene glycol with unsaturated monocarboxylic acids such as acrylic acid and methacrylic acid. Examples of such esters further include reaction products of cyclic ethers which in addition to an oxygen atom contain two or three carbon atoms in the ring, such as ethylene oxide and trimethylene oxide with unsaturated monocarboxylic acids such as acrylic acid and methacrylic acid. Preference is given to copolymers of β -hydroxyethyl methacrylate. If the preparation of the present copolymers is effected via an indirect route, by copolymerization of a mixture of monomers consisting of one or more unsaturated monocarboxylic acids and by after-treatment of the copolymers thus obtained, it is preferred to use methacrylic acid as the unsaturated monocarboxylic acid. The aftertreatment of the copolymers with free carboxyl groups as a result of which these groups are converted into $-\text{COOR}$ groups, wherein R represents a monohydroxy alkyl group, can be carried out in various ways.

It is possible, for example, to react the copolymers

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having free carboxyl groups with dihydric alcohols such as ethylene glycol. The after-treatment is preferably carried out by reacting the copolymers having free carboxyl groups with cyclic ethers which in addition to an oxygen atom contain two or three carbon atoms in the ring, such as ethylene oxide and trimethylene oxide, in particular ethylene oxide.

The preparation of the acid copolymers is preferably carried out in solution in the presence of a radical initiator such as an azo compound or a peroxide. As is known, the relative proportion in which the monomers are incorporated into a growing copolymer molecule is dependent on the reactivity of the monomers in question. If these reactivities differ, the molar ratio of the monomers in the mixture to be polymerized will change considerably as the copolymerization proceeds, since the more reactive monomer is incorporated more rapidly. The effect of this is that the composition of the copolymer likewise changes continually. In general, it may be said that if no special measures are taken in the polymerization of monomers which differ strongly in reactivity, products with an extremely heterogeneous composition are obtained. A case in point occurs in the co-polymerization of unsaturated monocarboxylic acids and alkyl esters of unsaturated monocarboxylic acids. It has been found, however, that the rates of incorporation of these monomers can be made equal by carrying out the subject copolymerization in the presence of a substance which associates with the unsaturated monocarboxylic acid. As a result of the equal rate of incorporation of the monomers the molar ratio of the incorporated monomers becomes the same as that of the monomers in the starting mixture. Eligible associating substances are, inter alia, aliphatic compounds containing an oxygen atom linked to carbon such as alcohols, ethers, ketones and carboxylic acids. Preference is given to aliphatic alcohols such as methanol, ethanol, isopropanol and tert-butanol, in particular methanol. Suitable solvents in which the copolymerizations can be carried out are, for example, benzene, toluene, or xylene, in particular toluene.

In general, the polymerization of unsaturated monocarboxylic acids with alkyl esters of unsaturated monocarboxylic acids proceeds rapidly until a conversion of approximately 90% has been reached. However, continued polymerization to a conversion of 95-100% is rather time-consuming. It was found that the polymerization rate can be considerably increased if, after the conversion is approximately 90% complete, an additional quantity of initiator varying from 10-100% by weight based on the quantity of initiator used at the beginning of the polymerization is added to the reaction mixture.

The after-treatment of the copolymers with free carboxyl groups in which the carboxyl groups are converted into $-\text{COOR}$ groups wherein R represents a monohydroxy alkyl group, is preferably carried out by means of a cyclic ether, in particular ethylene oxide. This conversion can take place under the influence of a basic reacting substance as catalyst. Examples of suitable basic reacting substances include alkali metals, alkali metal oxides, alkali metal hydroxides, alkaline earth metals, alkaline earth metal oxides, alkaline earth metal hydroxides and organic compounds such as trimethylamine, N-methyl morpholine, pyridine, quinoline and β -picoline. It is preferred to use a lithium compound as catalyst. Examples of suitable lithium compounds are, inter alia, lithium hydroxide, lithium hydride, lithium alkoxides, lithium carbonate, and lithium acetate. Very favorable results may be obtained by using lithium hydroxide as catalyst.

A variant of the after-treatment described above is one in which contrary to the usual practice, the reaction of the acid copolymer with the cyclic ether is not carried out in the presence of a basic reacting substance as catalyst, but instead this catalyst is incorporated into the acid polymer at the outset of the reaction. The incorporation of the catalyst into the acid polymer can be effected by including

in the mixture of monomers from which the acid polymer is prepared; one or more salts of basic reacting substances and unsaturated monocarboxylic acids. The acid copolymer resulting from the polymerization of this mixture of monomers can subsequently be reacted with a cyclic ether without using any additional catalyst. Here again preference is given to lithium salts.

The reaction of the acid copolymer with the cyclic ether can be carried out at room temperature, but is preferably carried out at an elevated temperature, for example at a temperature between 95° and 130° C. If the final product is liquid, the reaction can take place without the use of a solvent. If a solvent is used it can be either a polar or a non-polar solvent. The polymer with free carboxylic acid groups shows a tendency, especially in a non-polar solvent, to form intermolecular hydrogen bonds as a result of which the viscosity increases sharply. For this reason it is preferred to carry out the reaction with the cyclic ether in the presence of a polar substance which inhibits the formation of intermolecular hydrogen bonds. A low-boiling aliphatic alcohol is very convenient for this purpose. A highly suitable medium for carrying out the reaction is a mixture of a low-boiling aliphatic alcohol and an aromatic hydrocarbon.

In the preparation of the present polymeric compounds by copolymerization of acid polymers followed by after-treatment with a cyclic ether, it is not necessary to isolate the acid polymers before reacting these with the cyclic ether. The cyclic ether may be added directly to the reaction mixture obtained in the copolymerization. If in the preparation of the acid polymer, use was made of an alcohol as associating substance, this one-step process offers the additional advantage that the alcohol present in the reaction mixture also inhibits the formation of intermolecular hydrogen bonds in the acid polymer.

The lubricants in which the polymers according to this invention can be incorporated as additives may be mineral lubricating oils of varying viscosity, synthetic lubricating oils or lubricating oils containing fatty oils. The polymers can also be employed in greases. The present polymers are of special importance for the improvement of mineral lubricating oils or mixtures thereof. The polymers can be added to the lubricant as such or in the form of a concentrate obtained for example by mixing the polymers with a minor quantity of oil. The concentration of the present polymers in the lubricants may vary within wide limits, for example from 0.1 to 10% by weight, more specifically 0.5 to 5% by weight.

In addition to the present polymers, the lubricating compositions may contain other additives such as antioxidants, anti-foaming agents, anti-corrosive agents, means for improving the lubricating action and other substances which are generally added to lubricants.

erization of a mixture of alkyl methacrylates and methacrylic acid followed by ethoxylation of the acid copolymers. For comparison three related copolymers (Polymers A-C) were also prepared by copolymerization of a mixture of alkyl methacrylates and methacrylic acid followed by ethoxylation of the acid copolymers; however, these three polymers did not meet the criterion laid down in the main claim in respect of the alkyl side chains. For illustrative purposes, the preparation of Polymer 12 is described below. The preparation of the other polymers was effected in the same manner.

Preparation of Polymer 12

42.5% by weight of a mixture of alkyl methacrylates and methacrylic acid in the ratio desired in the ultimate copolymer, were mixed with 12% by weight of methanol, 45.5% by weight of toluene and 0.165% by weight of benzoyl peroxide. The mixture was heated to 80° C. and the polymerization was carried out with the exclusion of oxygen. To the reaction mixture were subsequently added 0.045% by weight of lithium hydroxide and 2 moles of ethylene oxide per equivalent of acid present in the acid copolymers. The temperature was increased in 110° C. and the ethoxylation carried out over 15 hours. To the reaction mixture such a quantity of a thin mineral lubricating oil was subsequently added that after removal of methanol and toluene in a film evaporator a 30%-concentrate of the desired polymers in the oil was obtained. The molar composition of the various polymers is given in Table I.

In this table use is made of the following abbreviations:

$C_{7-9}MA$ = mixture of alkyl methacrylates with 7-9 carbon atoms in the alkyl group.

$C_{12-15}MA$ = mixture of alkyl methacrylates with 12-15 carbon atoms in the alkyl group. These alkyl methacrylates were derived from an alcohol mixture prepared by reacting olefins having 11-14 carbon atoms with carbon monoxide and hydrogen in the presence of a complex which contained cobalt and organically bound trivalent phosphorus. The average number of carbon atoms of the $CH_3-(CH_2)_n-$ groups present in the alkyl chains, n being at least 9, was 12.9 for this mixture.

$n-C_{10}MA$, $n-C_{12}MA$, $n-C_{14}MA$, $n-C_{16}MA$ and $n-C_{18}MA$ = alkyl methacrylates with an unbranched saturated alkyl chain having 10, 12, 14, 16 and 18 carbon atoms respectively.

HEMA = hydroxyethylmethacrylate.

The table also shows the molecular weight M_w of the polymers as well as the average number of carbon atoms of the groups $CH_3-(CH_2)_n-$ present in the alkyl side chains, wherein n is at least 9. This average number of carbon atoms is designated in the table with C_n .

TABLE I

Pol. No.	Molar composition of the copolymers							HEMA	M _w	C _n
	C ₇₋₉ MA	C ₁₂₋₁₅ MA	C ₁₀ MA	C ₁₂ MA	C ₁₄ MA	C ₁₆ MA	C ₁₈ MA			
A				98	2			30	1,000,000	12.
B				50			50	30	1,200,000	15.
C			1	37	17	18	26	30	250,000	14.0
1			2	52	19	11	16	30	1,200,000	13.6
2				55	24	13	8	30	1,200,000	12.2
3			2	59	22	11	16	30	1,200,000	13.5
4		20		46	16	11	16	30	1,000,000	13.6
5		20		38	14	11	16	30	1,200,000	14.9
6		70				2	11	30	1,000,000	14.1
7		50		1	22	10	11	20	900,000	13.1
8			2	52	19	11	16	28	1,000,000	13.8
9			2	52	19	11	10	27	900,000	13.7
10			2	52	19	11	10	27	960,000	13.7
11			2	52	19	11	10	27	870,000	13.7
12			2	52	19	11	10	18	470,000	13.7
13			2	52	19	11	16	18	260,000	13.7

The invention will now be demonstrated by means of the following examples.

EXAMPLE I

Thirteen copolymers according to the invention (Polymers 1-13 shown in Table I) were prepared by copoly-

EXAMPLE II

The effect of the present polymers on the pour point and the viscosimetric properties of a lubricating oil were examined by incorporating the polymers in various concentrations into a distillate lubricating oil. The pour point

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was determined by ASTM method D 97. The results are shown in the following table.

TABLE II

Composition of the oil	V _k 38° C., cs.	V _k 100° C., cs.	Pour point, °C.
Base oil.....	47.2	6.64	-9
Base oil plus—			
1.5% by weight of polymer A.....			-9
1.5% by weight of polymer B.....	62.0	10.0	-15
4.0% by weight of polymer C.....			-23
1.5% by weight of polymer 1.....	62.3	9.8	-32
1.5% by weight of polymer 2.....	62.0	9.8	-32
1.5% by weight of polymer 3.....	61.9	9.7	-32
1.5% by weight of polymer 4.....	62.0	9.6	-32
1.5% by weight of polymer 5.....	62.3	9.8	-21
1.5% by weight of polymer 6.....	62.1	10.0	-21
1.5% by weight of polymer 7.....	63.2	10.0	-32
1.5% by weight of polymer 8.....	63.0	10.0	-32
1.5% by weight of polymer 9.....	62.7	9.9	-32
4.0% by weight of polymer 9.....			-40

EXAMPLE III

The pourability of 20%-concentrates of the present polymers in a mineral lubricating oil with a V_k 100° C.=4.5 cs. was examined by means of the tar viscometer. This instrument is described in IP method 72/58. The cross-section of the outflow opening was 10 mm. The flow-out time in seconds at 15° C. of some polymer concentrates is given in Table III.

TABLE III

Concentrate of polymer:	Flow-out time, sec.
8	164
9	143
1	328

EXAMPLE IV

The shear stability of the present polymers was determined in an Opel pump test. To this end they were incorporated in various concentrations into mineral lubricating oil with a V_k 100° C.=5.5 cs., to which had been added 8% by weight of a commercial additive package with detergent, anti-rust, anti-oxidant and EP-action. The conditions of the shear test in the Opel pump were as follows:

Shear time: 24 hours
Temperature: 50° C.
Speed: 1500 r.p.m.
Quantity of oil: 800 g.

The results of the shear tests are shown in Table IV.

TABLE IV

	V _k , 100° C.		Pour point, °C.
	Before shear, cs.	After shear, cs.	
Base oil plus—			
3.1% by weight of polymer 10.....	16.8	12.8	-34
4.4% by weight of polymer 11.....	16.8	14.0	-37
4.3% by weight of polymer 12.....	16.7	14.3	-34
5.0% by weight of polymer 13.....	15.0	13.7	-37

EXAMPLE V

The behavior of the present polymers as dispersants was examined in a one-cylinder CLR engine. Lubricating oil compositions consisting of a mineral lubricating oil with a V_k 100° C.=6.3 cs., which in addition to one of the present polymers contained 0.75% by weight of 4,4'-methylene-bis-2,6-ditert-butylphenol and 1.0% by weight of triphenyl phosphate, were subjected to a CLR MS Sequence V-A test. For comparison, a test was also carried out with a lubricating oil composition which contained a commercial dispersant (a copolymer of alkyl methacrylates and N-vinyl pyrrolidone) instead of one of the present polymers.

The results of the engine tests are reported in Table V.

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Table V

Composition of the oil:	Engine sludge rating (50=clean)
Base oil+1.5% of polymer 10	37.2
Base oil+2.1% of polymer 11	35.4
Base oil+1.5% commercial additive	27.5

EXAMPLE VI

The effect of the addition of extra initiator towards the end of the polymerization in the preparation of the acid copolymers is represented in the following table.

TABLE VI

	Polymer 10	Polymer 3
Monomer concentration, percent by weight.....	42.5	42.5
Initial benzoyl peroxide concentration, percent by weight.....	0.08	0.065
Temperature, °C.....	78	77
Benzoyl peroxide added extra, percent by weight.....	¹ None	² None
	Conversion, percent	
Time, hours:		
1/2.....	23	15
2.....	68	49
4.....	80	69
6.....	80	
7.....		92
8 1/2.....		90
9.....	92	96
10.....	98	94
12.....	93	96
13.....		97
18.....	96	96

¹ 0.05 after 6 hrs.
² 0.04 after 8 1/2 hrs.

It should be noted that the physical constants stated for the base oils in the tests listed above have already been corrected with a view to the fact that the present polymers were not added to these base oils as such but in the form of a 30%-concentrate in oil.

The foregoing data clearly demonstrate the improved properties of the compositions of the invention. The pour point test results shown in Table II indicate that while copolymers having side chains with a C_n of 12.0 (Polymer B) did not reduce the pour point of the base oil at all, and Polymer B having a C_n value of 15.0 decreased the pour point by only 6° C., the polymers of the invention having C_n numbers ranging from 13.2 to 14.1 decreased the pour point 20° C. or more. In view of the relatively poor performance of polymers A and B which are similar to those of the invention but have different C_n values, it was quite remarkable that polymers made in accordance with the invention should prove to be so highly effective.

The results shown in Table IV and V indicate that in addition to having improved pour points, the compositions of the invention also have good shear stability and have dispersant properties superior to those of a comparable commercial additive.

We claim as our invention:

1. A lubricant composition consisting essentially of a major amount of a lubricating oil and a minor amount, from 1 to 10% by weight, of an oil-soluble copolymer of one or more alkyl esters of a C₃₋₅ alpha, beta-vinylidene monocarboxylic acid and one or more monohydroxy C₂₋₅ alkyl esters of C₃₋₅ alpha, beta-vinylidene monocarboxylic acid; wherein at least 60 mole percent of the alkyl esters have CH₃-(CH₂)_n- groups, n being at least 9, and the average number of carbon atoms of said groups is from 12.5 to 14.3; the molar ratio of the units derived from alkyl esters to those derived from hydroxy alkyl esters is 10 to 0.25-5; and the molecular weight M_w of the copolymer is from 100,000 to 2,000,000.

2. The composition of claim 1 wherein the molecular weight M_w of the copolymer is from 250,000 to 1,250,000.

3. The composition of claim 2 wherein the molar ratio of the units derived from alkyl esters to those derived from hydroxy alkyl esters is 10 to 1-3.

4. The composition of claim 2 wherein the average number of carbon atoms in the $\text{CH}_3-(\text{CH}_2)_n-$ groups, n being at least 9, is from 13.0 to 14.1.
5. The composition of claim 3 wherein the monocarboxylic acid used to form the alkyl and monohydroxy alkyl esters is selected from the group consisting of methacrylic acid, acrylic acid and mixtures thereof.
6. The composition of claim 1 wherein the lubricating oil is a mineral lubricating oil.
7. The composition of claim 5 wherein the monocarboxylic acid is methacrylic acid.
8. The composition of claim 7 wherein the average number of carbon atoms in the $\text{CH}_3-(\text{CH}_2)_n-$ groups, n being at least 9, is from 13.0 to 14.1.
9. The composition of claim 8 wherein the hydroxyalkyl ester is a β -hydroxyethyl ester.

10. The composition of claim 9 wherein the lubricating oil is a mineral lubricating oil.

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