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COPOLYMER OF MIXED ALKYL ESTERS OF UNSATURATED CARBOXYLIC ACIDS

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This invention relates to a novel class of polymers. More particularly, the invention is directed to a novel class of polymers capable of imparting improved properties to lubricant compositions.

In their U.S. patent applications No. 340,378 filed March 4, 1953, and now abandoned, No. 400,757 filed December 28, 1953, and now abandoned, No. 400,758 filed December 28, 1953, and now abandoned, No. 400,759 filed December 28, 1953, and now abandoned, No. 574,635 filed March 29, 1956 and No. 574,636 filed March 29, 1956, Messrs. Frank A. Stuart, William T. Stewart, Warren Lowe and Frank W. Kavanagh have described a novel class of polymeric additives for lubricant compositions. Lubricant compositions containing these polymeric additives are capable of maintaining large amounts of decomposition products in solution and greatly reduce the wear of rubbing surfaces.

In order for a lubricant composition to function properly, it must be capable of flowing freely through oil lines and between moving parts at all the lower ranges of temperatures ordinarily encountered. The temperature at which a lubricant composition ceases to flow or pour is called its "pour point." If a lubricant composition does not have a suitably low pour point, the fact that it is a very effective detergent and wear inhibitor will make no difference since it will be unable to flow and penetrate between rubbing surfaces.

Practically all of the common base oils of lubricating viscosity which are employed in lubricant compositions have undesirably high pour points and are incapable of providing proper lubrication during low temperature operation of an engine such as is encountered during the starting up period. In such cases, it is necessary to modify the flowing properties of the base oil so as to lower its pour point. This is commonly done by the addition of agents which are termed "pour depressants" since they act in combination with the base oil to depress its pour point.

From the above description, it can be readily seen that proper lubrication presents many problems. Because of these problems, there is a constant demand for the continued improvement of lubricant compositions. So far there has been no single solution for the problem. One agent may be added to the lubricant composition to prevent deposition of solid products. Another may be employed simultaneously to reduce wear of rubbing metal parts. Still another additive is needed to render the composition soluble at lower temperatures of operation. Even though the polymeric additive of Stuart, Stewart, Lowe and Kavanagh, referred to above, is very effective in preventing solid deposits of combustion products and reducing wear of rubbing parts, it is still generally necessary to add a pour depressant in order that the lubricant composition may function properly.

It is therefore an object of this invention to provide a novel class of polymers.

It is a more particular object of the invention to provide a novel class of polymers capable of imparting improved properties to oils of lubricating viscosity.

Still other objects of the invention will be apparent from the disclosure which follows hereinafter.

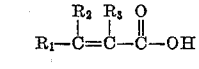
The multi-functional polymers of this invention are

polymers of at least the (A), (B) and (D) monomers of the following: (A) an alkyl ester of a lower aliphatic α,β-unsaturated monocarboxylic acid in which the alkyl group contains from 4 to 30 carbon atoms, (B) an alkyl ester of the same or another lower aliphatic α,β-unsaturated monocarboxylic acid in which the alkyl group contains a different number in the range of 4 to 30 carbon atoms, which is 4 to 16 carbon atoms more than the alkyl group of said (A) alkyl ester, (C) a lower aliphatic α,β-unsaturated monocarboxylic acid, and (D) an ester of a polyoxy-1,2-alkylene glycol and a lower aliphatic α,β-unsaturated monocarboxylic acid.

Lubricant compositions containing the polymers of the invention are capable of maintaining large amounts of combustion products in solution thus preventing the formation of solid deposits on surfaces in internal combustion engines. The wearing of rubbing parts of engines is also effectively reduced. No objectionable metal ash deposits are formed as decomposition products of the lubricant compositions. Compared to the base oil employed, these lubricant compositions are characterized by remarkably improved flowing properties at the lower temperatures of operation. It is indeed surprising that all of these improved properties are obtained solely by the use of the polymers of the invention in lubricant compositions.

In components (A) and (B) the alkyl esters of a lower aliphatic α,β-unsaturated monocarboxylic acid having from 4 to 30 carbon atoms in the alkyl group constitute a definite class of materials. They include such esters as butyl acrylate, dodecyl methacrylate or lauryl methacrylate, hexadecyl methacrylate, isooctyl α-chloroacylate, hexadecyl α-methylcrotonate, octacosyl methacrylate, tricosyl α-ethylcrotonate, triacontyl tiglate, pentadecyl angelate, etc. A preferred group of esters are the alkyl esters of acrylic and methacrylic acid in which the alkyl group contains from 4 to 20 carbon atoms.

The optional (C) monomer component of the present polymers is an α,β-unsaturated monocarboxylic acid, preferably one of the type having the general formula



where R_1, R_2 and R_3, which can be the same as or different from one another, are selected from the group consisting of hydrogen atoms and alkyl groups of from 1 to 4 carbon atoms. Representative acids of this type, any one or more of which can be employed in forming the copolymers hereof, are acrylic, methacrylic, crotonic, tiglic, angelic, α-ethylacrylic, α-methylcrotonic, α-ethylcrotonic, β-ethylcrotonic, α-butylcrotonic acids, and the like. A more preferred group of acids for use in the present invention comprises those of the type indicated by the above structural formula which contain a total of from about 3 to 8 carbon atoms in the molecule, as represented by the acids listed above. A still more preferred group of acids is made up of acrylic and methacrylic acids.

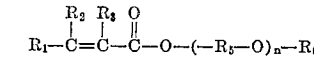
The (D) component of the polymers is an ester of a lower aliphatic α,β-unsaturated monocarboyxlic acid (of the type defined in the preceding paragraph) and a polyoxy-1,2-alkylene glycol. The polyglycols which can be used in forming said esters have molecular weights between 106 and 10,000, or higher, preferably between about 134 and 30,000. These polyglycols are of the type obtained by polymerizing one or more 1,2-alkylene oxides in the presence of a catalyst and suitable reaction initiator, e.g., water, a monohydric alcohol, a glycol, an acid, amine, mercaptan, or the like. The resulting polymer materials are polyoxyalkylene glycols, or polyoxyalkylene glycols wherein one or both of the terminal —OH groups are replaced (either during the polymerization

reaction or subsequently thereto) by alkoxy, acyloxy, or other end groups. Methods for synthesizing said polyglycol compounds are well known in the art and need not further be described here, reference being made to U.S. Patents Nos. 2,448,664 and 2,457,139, for example, for a description of such methods.

The preferred polyglycol materials for employment in the present invention are those which are formed from ethylene oxide, from 1,2-propylene oxide, or from mixtures of said oxides, and which have molecular weights between about 200 and 2,000, or higher, preferably between about 400 and 10,000.

The polymeric glycols employed in forming the ester component (D) of the polymers can be a single compound of relatively pure nature such as triethylene glycol, pentaethylene glycol, nonaethylene glycol, tetra-1,2-propylene glycol, monobutyl ether of heptaethylene glycol, or the like, though as a general rule the polyglycol material employed (and hence the (D) monomer component itself) will be a mixture of polymeric molecules of varying chain length, structure, and molecular weight. Accordingly, in referring herein to the molecular weight of the polyglycol material, reference is had to either a relatively pure compound, or to the average molecular weight of a mixture of such compounds.

The ester, or (D) component of the polymer can be described as one of the type (or a mixture of compounds, each of the type) having the general structural formula



where R_1, R_2 and R_3, as indicated above in connection with the definition of the (C) component, are preferably hydrogen atoms or C_1–C_4 alkyl radicals, the R_5's are 1,2-alkylene radicals, n is an integer greater than 1, and R_6 is a hydrogen atom or a substituted or unsubstituted hydrocarbon group, the substituent groups here contemplated being the polar groups —COOH,

—OH, —NO_2, —SH, —NR_7R_8, or

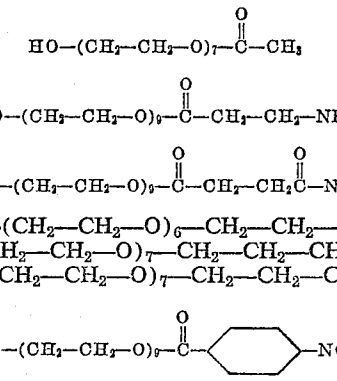
where the R_7's and the R_8's are hydrogen atoms or hydrocarbon groups. Preferably, however, a still more preferred group of (D) monomer components is made up of those compounds wherein, in the above structural formula, R_1 and R_2 represent hydrogen atoms, R_3 represents hydrogen or a methyl group, the R_5's are ethylene or propylene groups, and R_6 is hydrogen or an alkyl group of from 1 to 18 carbon atoms. Representative (D) monomer component esters coming within this more preferred grouping are esters of acrylic or methacrylic acid with the following glycol polymers:

HO—(CH_2—CH_2—O)$_2$—H
HO—(CH_2—CH_2—O)$_3$—H
HO—(CH_2—CH_2—O)$_7$—H
HO—(CH_2—CH_2—O)$_9$—H
HO—(C_3H_6O)$_3$—H
HO—(C_3H_6O)$_7$—H
HO—(CH_2—CH_2—O—C_3H_6O)$_5$—H
HO—(CH_2—CH_2—O)$_9$—CH_3
HO—(CH_2—CH_2—O)$_{13}$—C_8H_{17}
HO—(CH_2—CH_2—O)$_{13}$—$C_{12}H_{25}$
HO—(CH_2—CH_2—O)$_{13}$—$C_{18}H_{37}$

Polyethylene glycol mixtures having average molecular weights of 200, 400, 1000, 1540 or 2000.

Poly-1,2-propylene glycol mixtures having average molecular weights of 425 or 1025.

In addition to the above exemplary (D) monomer components, it should also be noted that good results can be obtained with acrylates and methacrylates of polyglycols such as the following wherein the terminal, or R_6, group is a polar-substituted radical:



In preparing the polymers of this invention, it is important that the ratio of the (A), (B), (C) and (D) components to one another be such as to ensure that the finished polymeric material will be soluble in the petroleum or other lubricating oil employed to the extent of at least 0.5% by weight and preferably 2% or more, in addition to imparting the desired antiwear, detergent and pour depressant characteristics to the oil. Since the various (A) and (B) components differ somewhat in their oil-solubilizing characteristics, and since the (D) component (and to a lesser extent the (C) component) tends to exert an oil-insolubilizing effect of greater or lesser magnitude on the polymer, the optimum monomer component ratios in a polymer will depend on the particular components. Accordingly, as a general rule, preliminary tests are preferably made with the contemplated polymeric additive to determine whether the ratio of (A) and (B) to (C) and (D) components is high enough to give the desired degree of oil solubility. In general, however, satisfactory oil-solubility, antiwear and detergency properties are obtained with polymers wherein the (A) and (B), or oil-solubilizing components constitute from about 75 to 97 mole percent or more, for example, 99.9 mole percent of the over-all polymer composition, with the (C) and (D), or polar monomer components representing a total of from 25 to 3 mole percent or less, for example, 0.1 mole percent of the polymer composition, there being in all cases at least one and usually several monomer units of each of said (D) polyglycol ester monomer component in the copolymer. Expressed percentagewise, of the total polar monomer content of the copolymer, the (C) or acid component constitutes from 0 to 97 mole percent, while the (D), or polyglycol ester component, constitutes from 100 to 3 mole percent. Preferred ranges can be established within the aforesaid ranges for particular polymers and classes of polymers coming within the scope of this invention. Thus, with copolymers of (A) and (B), a higher alkyl methacrylate (e.g., lauryl methacrylate), (C) acrylic or methacrylic acids, and (D) an acrylate or methacrylate of a polyethylene glycol or a polypropylene glycol, or a monoalkyl ether of said glycols, or mixture of said glycols or glycol ethers, or a polyglycol monoether, there preferably is employed from 80 to 92 mole percent of the oil-solubilizing, (A) and (B) components, while the balance of the polymer is made up of from 65 to 90 mole percent of the (C) component and 35 to 10 mole percent of the (D) component.

Any mixtures of the alkyl radicals containing from 4 to 30 carbon atoms and preferably from 4 to 20 carbon atoms will effect a desirable reduction in the pour point of lubricant compositions containing the polymeric additives of this invention. The alkyl radicals may vary widely in chain length, as in the case when n-butyl meth-

acrylate and stearyl methacrylate are employed. Preferably the alkyl radicals will not differ by more than 16 carbon atoms or less than 4 carbon atoms. In these cases, it is preferred to employ from 50 to 80 mole percent of the shorter alkyl ester with 20 to 50 mole percent of the longer to obtain the greatest reduction in pour point.

The polymers of this invention can be prepared by several methods. Thus, one may polymerize a mixture of (A), (B), (C) optionally, and (D) monomer components to form the desired polymer. It is also possible to form the desired polymer by first preparing a suitable polymer intermediate and then subjecting the latter material to an appropriate treatment to form the finished polymer. Thus, one may polymerize given oil-solubilizing (A) and (B) compounds such as the alkyl methacrylates with a suitable (C) component acid such as acrylic or methacrylic acid; the resulting polymer is then reacted with a polyglycol whereby a portion or all of the free —COOH groups in the polymer intermediate becomes ester-linked to the polyglycol. Instead of forming an intermediate polymer by thus reacting the (A), (B) and (C) components, one may start with a homopolymer such, for example, as poly(dodecyl methacrylate), this homopolymer being first partially hydrolyzed to free the desired portion of its —COOH groups, after which the correction portion or all of the latter is then esterified with a suitable different alkyl alcohol and a suitable polyglycol material. Other possible variations in the nature of the reactants and in the selection of a suitable reaction path would also suggest themselves to those skilled in the art.

When the polymers of this invention, or a suitable polymeric intermediate, is to be prepared by reaction of monomeric components, said polymers can be prepared by conventional bulk, solution or emulsion methods in the presence of an addition polymerization initiator such as benzoyl peroxide, acetyl peroxide, tert. butyl hydroperoxide, di-tert.butyl peroxide, or di-tert.amyl peroxide, or an azo initiator such as 1,1'-azodicyclohexanecarbonitrile or α,α'-azodiisobuteronitrile. The catalyst, or polymerization initiator, can be employed in an amount of from about 0.1 to 10%, with a preferred range being from about 0.25 to 2%. If desired, the catalyst can be added in increments as the reaction proceeds. An inert solvent can be employed if desired, and, as is the case with the catalyst, additional portions of the solvent can also be added from time to time in order to maintain the solution in a homogeneous condition. The temperature of polymerization varies from about 150 to 300° F., with the optimum temperature for any given preparation depending on the nature of the solvent, the concentration of monomers present in the solvent, the catalyst, and the time of the reaction. The polymers formed by such methods have an apparent molecular weight of at least 2,000, and preferably of at least 8,000. In the main, however, they have apparent molecular weights of 20,000 or more. For practical purposes, molecular weights of from 100,000 to 1,000,000 are most suitable from the standpoint of viscosity and other physical characteristics of the polymeric additives.

The following examples of the preparation of the novel polymers of the invention and proofs of their unusual effectiveness are submitted as additional illustrations. Unless otherwise specified, the proportions given are on a weight basis.

EXAMPLE 1

The following reactants were charged to a 3-liter resin jar equipped with a thermometer, a reflux condenser and a stirrer: 150 grams of oxotridecyl methacrylate, 124 grams of tallow methacrylate, 8.05 grams of 91% active methacrylic acid, 27.4 grams of decaethylene glycol tridecyl ether methacrylate, 1.99 grams of benzoyl peroxide, and 309 milliliters mixed hexanes.

The resin jar was partially immersed in an oil bath maintained at 190° F. and the reactants stirred at the reflux temperature for 8 hours. At the end of this reaction period, 383 grams of a low viscosity mineral lubricating oil were added as a diluent. The mixed hexanes were stripped from the resulting oil solution to provide a finished concentrate containing 40% of polymeric additives.

EXAMPLE 2

To a 3-liter resin jar of the type described in Example 1 were charged 75 grams of oxotridecyl methacrylate, 62 grams of tallow methacrylate, 4.03 grams of 91% active methacrylic acid, 13.7 grams of decaethylene glycol tridecyl ether methacrylate, 1.0 gram of benzoyl peroxide and 155 milliliters of mixed hexanes. The materials were reacted for 8 hours at a temperature of 190° F. under refluxing conditions as described in the above example. 383 grams of 140 neutral mineral lubricating oil were added as a diluent and the mixed hexanes stripped from the resulting oil solution to give a concentrate containing approximately 20% of the polymeric additive.

The remarkable ability of the polymers of this invention to enable lubricating oil compositions to flow at low temperatures is effectively illustrated by evaluating them in the "Pour Point Test." In these tests there is employed a variety of the polymers containing different proportions of mixed alkyl methacrylates (A) and (B). For the purpose of comparison, a synthetic mixture of polymers obtained by simply mixing the polymer of (A) oxotridecyl methacrylate, (C) methacrylic acid, and (D) decaethylene glycol tridecyl ether methacrylate with the polymer of (B) tallow methacrylate, (C) methacrylic acid, and (D) decaethylene glycol tridecyl ether methacrylate in different proportions is also tested. In both cases, the molar ratio of alkyl methacrylate, methacrylic acid and decaethylene glycol tridecyl ether methacrylate was maintained at 8.3/0.8/0.2.

The "oxotridecyl" group referred to above and hereinafter is one obtained from a primary branched-chain alcohol of 13 carbon atoms produced by the Oxo process. The "tallow" group is one obtained from a predominantly straight chain alcohol of 18 carbon atoms produced by hydrogenation and hydrolysis of tallow, also referred to as a "stearyl" group.

The pour point tests are performed in accordance with ASTM method D–97. In this test, the sample is maintained at a temperature of 115° F. or lower for at least 24 hours prior to the test. The sample is then cooled systematically under quiescent conditions and observed at intervals of 5° F. The pour point is the lowest temperature at which the oil flows when the container is tilted. Illustrative test results are given in the following table:

Table I

Mole Percent A	Mole Percent B	Pour Point, °F.	
		Synthetic Mixture	Mixed Alkyl Polymer
0	100	+18	+18
10	90	+15	+12
25	75	+10	0
35	65	+5	−10
50	50	+3	−30
65	35	+3	−40
100	0	+3	+3

Additional tests illustrate the Pour Point depressing ability of the neutral copolymers of the invention which contain only the (A), (B) and (D) monomers, as described above, without the free acid (C) monomer. In these tests, the "Pour Point Test" is again employed, as described above. The (A) monomers are dodecyl methacrylate and mixtures of dodecyl methacrylate with oxotri-

decyl methacrylate. The (B) monomer is tallow methacrylate, and the (D) monomer is polyethylene glycol tridecyl ether methacrylate in which the polyethylene glycol group has an average molecular weight of about 1800. In each test, 0.3% of the copolymer is employed in SAE 10W solvent refined paraffinic type mineral lubricating oil. The ASTM method Pour Point, as described above, is then obtained. Illustrative test results are given in the following table.

Table II

Mole Percent A		Mole Percent B	Pour Point, °F.
Dodecyl Methacrylate	Tridecyl Methacrylate	Octadecyl Methacrylate	
100	0	0	+15
67	0	33	−20
27	44	29	−15
11	54	35	−15
36	64	0	+15
26	74	0	+15

The above tests results show that the neutral type copolymers of the invention in lubricating oils possess the same sort of improved lower pour points already shown as characteristic of the free acid-containing copolymers of the invention. When the afore-described percentages of mixed alkyl esters, including the higher octadecyl methacrylate, are used, pour point improvements amounting to decreases of as much as 35° F. are obtained. This is surprising since the octadecyl methacrylate copolymers themselves have higher pour points and would be expected to increase rather than decrease the pour point of the dodecyl and tridecyl methacrylate copolymers when incorporated therein.

As shown by the test results of the above tables, the lubricating oil compositions with the polymers of this invention possess improved pour points compared to similar compositions containing polymeric additives characterized by a single type alkyl ester. It is further evident from the above data that this improvement is a particular or peculiar effect of the mixed alkyl ester polymers of the invention since comparable amounts of simple mixtures of polymers of varying alkyl groups do not provide the same degree of enhancement.

The effectiveness of the polymers of the invention as detergents and wear inhibitors is evaluated in a series of engine tests. The method employed in these tests is that described for the "FL–2 Engine Test" in the June 21, 1948, Report of the Coordinating Research Council. In accordance with this method, the compounded oil is employed as the crankcase lubricant in a 6-cylinder Chevrolet engine operated with a low grade gasoline especially prone to cause engine deposits. A jacket temperature of 95° F. and a crankcase oil temperature of 155° F. are maintained. The engine is operated at 2,500 r.p.m. under a load of 45 brake horsepower for 40 hours. "Cold" engine conditions normally experienced in city driving are thus closely simulated. At the end of each test, the engine is dismantled and the amount of engine deposits on the piston determined and expressed as the Average Piston Varnish Rating. This value is obtained by visually rating the amount of deposit on each piston and averaging the individual ratings so obtained for the various pistons on a scale of 0 to 10 representing the absence of any deposits.

The lubricant compositions which are used for the purpose of illustration in the test comprise a solvent refined SAE 30 mineral lubricating oil as the base oil with 2% by weight of an alpha-pinene-P_2S_5 oxidation inhibitor. The polymeric additive of the invention in these illustrative examples is present in the amount of 1.6% by weight dry polymer based on the total composition.

Table III

Polymeric Additive	Molar Proportions of A, B, C and D Components in Polymeric Additive	Average Piston Varnish Rating	Piston Ring Wear (mgs./hour)
None (base oil alone)		3.5	5.0
Oxotridecyl methacrylate/tallow methacrylate/methacrylic acid/decaethylene glycol tridecyl ether methacrylate	3.70/2.40/0.70/0.30	6.5	2.7
Oxotridecyl methacrylate/tallow methacrylate/methacrylic acid/decaethylene glycol tridecyl ether methacrylate	4.31/2.88/0.70/0.30	6.6	2.9
Octadecyl methacrylate/stearyl methacrylate/methacrylic acid/decaethylene glycol propyl ether methacrylate	4.20/2.80/0.70/0.30	7.1	3.1
Butyl methacrylate/stearyl acrylate/acrylic acid/methacrylate of lauryl monoether of polyethylene glycol (avg. molecular weight—440)	2.30/1.31/0.70/0.30	6.7	2.8

The effectiveness of the polymers of the invention as detergents and wear inhibitors is readily apparent from the illustrative test data of the above table. The base oil containing only the conventional oxidation inhibitor gives an average piston varnish rating and piston ring wear of 3.5 and 5.0, respectively, whereas the improved compositions containing the polymers illustrative of the invention give results in the order of 7 and 3, respectively.

As indicated in the foregoing examples, the polymers of this invention possess a relatively high molecular weight and are normally of a solid or semi-solid (gel-like) character. They are soluble in a wide variety of hydrocarbon liquids including benzene, toluene, xylene, petroleum ether and various petroleum fractions. They are soluble with difficulty in lower molecular weight paraffinic hydrocarbons such as pentane, hexane and the like. They are substantially insoluble in oxygenated solvents such as acetone and the various alcohols. The present polymers have good detergent, emulsifying and peptizing qualities and are adapted to be used in a wide variety of applications where such qualities are desired. Thus, when added in small amounts (e.g., 0.1–10%) to lubricating oils, they impart improved detergency, antiwear and low pour characteristics to the resulting lubricant composition. They may also be employed in special grease compositions to give an improved low pour lubricant of high detergency and wear inhibiting properties. Asphalt emulsions and plastic compositions may also be improved by their addition.

We claim:

1. An oil-soluble linear polymer of monomers comprising (A) an alkyl ester of a lower aliphatic α,β-unsaturated monocarboxylic acid of from 3 to 8 carbon atoms in which the alkyl group contains from 4 to 30 carbon atoms, (B) an alkyl ester of a lower aliphatic α,β-unsaturated monocarboxylic acid of from 3 to 8 carbon atoms in which the alkyl group contains a different number in the range of 4 to 30 carbon atoms, which is from 4 to 16 more than the number of carbon atoms in the alkyl group of the (A) component, (C) a lower aliphatic α,β-unsaturated monocarboxylic acid of from 3 to 8 carbon atoms, and (D) a monoester of a polyalkylene glycol and a lower aliphatic α,β-unsaturated monocarboxylic acid of from 3 to 8 carbon atoms, said (A) and (B) components representing a total of from 75 to 97 mole percent of the polymer, while the (C) component represents 65 to 90 mole percent and the (D) component represents 35 to 10 mole percent of the balance of the polymer, said polymer having a solubility in mineral lubricating oil of at least 0.5% by weight.

2. An oil-soluble linear polymer of monomers comprising (A) an alkyl ester of a lower aliphatic α,β-unsaturated monocarboxylic acid of from 3 to 8 carbon atoms in which the alkyl group contains from 10 to 20 carbon atoms, (B) an alkyl ester of a lower aliphatic

α,β-unsaturated monocarboxylic acid of from 3 to 8 carbon atoms in which the alkyl group contains a different number in the range of 10 to 20 carbon atoms, which is from 4 to 16 more than the number of carbon atoms in the alkyl group of the (A) component, (C) a lower aliphatic α,β-unsaturated monocarboxylic acid of from 3 to 8 carbon atoms, and (D) a monoester of a polyalkylene glycol and a lower aliphatic α,β-unsaturated monocarboxylic acid of from 3 to 8 carbon atoms, said (A) and (B) components representing a total of from 75 to 97 mole percent of the polymer, while the (C) component represents 65 to 90 mole percent and the (D) component represents 35 to 10 mole percent of the balance of the polymer, said polymer having a solubility in mineral lubricating oil of at least 0.5% by weight.

3. An oil-soluble linear polymer of monomers comprising (A) an alkyl ester of the group consisting of alkyl acrylates and alkyl methacrylates in which the alkyl group contains from 4 to 30 carbon atoms, (B) an alkyl ester of the same acid in which the alkyl group contains a different number in the range of 4 to 30 carbon atoms, which is from 4 to 16 more than the number of carbon atoms in the alkyl group of the (A) component, (C) methacrylic acid, and (D) monomethacrylates of polypropylene glycols and the monoalkyl ether derivatives of said glycols, which glycols have average molecular weights of between 200 and 2000, said (A) and (B) components representing a total of from 75 to 97 mole percent of the polymer, while the (C) component represents 65 to 90 mole percent and the (D) component represents 35 to 10 mole percent of the balance of the polymer, said polymer having a solubility in mineral lubricating oil of at least 0.5% by weight.

4. An oil-soluble linear polymer of monomers comprising (A) an alkyl ester of the group consisting of alkyl acrylates and alkyl methacrylates in which the alkyl group contains from 4 to 30 carbon atoms, (B) an alkyl ester of the same acid in which the alkyl group contains a different number in the range of 4 to 30 carbon atoms, which is from 4 to 16 more than the number of carbon atoms in the alkyl group of the (A) component, (C) methacrylic acid, and (D) a mixture of mono-methacrylates of polyethylene glycol monoalkyl ethers in which the glycols have an average molecular weight of between 200 and 2000, said (A) and (B) components representing a total of from 75 to 97 mole percent of the polymer, while the (C) component represents 65 to 90 mole percent and the (D) component represents 35 to 10 mole percent of the balance of the polymer, said polymer having a solubility in mineral lubricating oil of at least 0.5% by weight.

5. An oil-soluble linear polymer of monomers comprising (A) an alkyl ester of the group consisting of alkyl acrylates and alkyl methacrylates in which the alkyl group contains from 4 to 30 carbon atoms, (B) an alkyl ester of the same acid in which the alkyl group contains a different number in the range of 4 to 30 carbon atoms, which is from 4 to 16 more than the number of carbon atoms in the alkyl group of the (A) component, (C) methacrylic acid, and (D) a mixture of monomethacrylates of polyethylene glycols which have an average molecular weight of between 200 and 2000 and a terminal hydroxy group, said (A) and (B) components representing a total of from 75 to 97 mole percent of the polymer, while the (C) component represents 65 to 90 mole percent and the (D) component represents 35 to 10 mole percent of the balance of the polymer, said polymer having a solubility in mineral lubricating oil of at least 0.5% by weight.

6. An oil-soluble linear polymer of monomers consisting essentially of (A) tridecyl methacrylate, (B) tallow methacrylate, (C) methacrylic acid, and (D) decaethylene glycol tridecyl ether monomethacrylate, said (A) and (B) components representing a total of from 80 to 92 mole percent of the polymer, while the (C) component represents 65 to 90 mole percent and the (D) component represents 35 to 10 mole percent of the balance of the polymer, said polymer having a solubility in mineral lubricating oil of at least 0.5% by weight.

7. An oil-soluble linear polymer of monomers consisting essentially of (A) tridecyl methacrylate, (B) stearyl methacrylate, (C) methacrylic acid, and (D) decaethylene glycol propylether monomethacrylate, said (A) and (B) components representing a total of from 80 to 92 mole percent of the polymer, while the (C) component represents 65 to 90 mole percent and the (D) component represents 35 to 10 mole percent of the balance of the polymer, said polymer having a solubility in mineral lubricating oil of at least 0.5% by weight.

8. An oil-soluble linear polymer of monomers consisting essentially of (A) butyl methacrylate, (B) stearyl acrylate, (C) acrylic acid, and (D) monomethacrylate of lauryl monoether of polyethylene glycol, which glycol has an average molecular weight of about 440, said (A) and (B) components representing a total of from 80 to 92 mole percent of the polymer, while the (C) component represents 65 to 90 mole percent and the (D) component represents 35 to 10 mole percent of the balance of the polymer, said polymer having a solubility in mineral lubricating oil of at least 0.5% by weight.

9. An oil-soluble linear polymer of monomers consisting essentially of (A) tridecyl methacrylate in which the tridecyl group is a primary branched-chain group of 13 carbon atoms, (B) stearyl methacrylate, and (D) polyethylene glycol tridecyl ether methacrylate in which the polyethylene glycol group has an average molecular weight of about 1800, said (A) and (B) components being present in the ratio of from 50 to 80 mole percent of (A) to 20 to 50 mole percent of (B) and amounting to a total of from 80 to 92 mole percent of the polymer, while the (D) component amounts to 20 to 8 mole percent of the polymer, said polymer having a solubility in mineral lubricating oil of at least 0.5% by weight.

10. An oil-soluble linear polymer of monomers comprising at least the (A), (B) and (D) monomers of the following: (A) an alkyl ester of a lower aliphatic α,β-unsaturated monocarboxylic acid of from 3 to 8 carbon atoms, said alkyl ester being characterized by an alkyl group of from 4 to 30 carbon atoms, (B) an alkyl ester of a lower aliphatic α,β-unsaturated monocarboxylic acid of from 3 to 8 carbon atoms, said alkyl ester being characterized by an alkyl group of from 4 to 30 carbon atoms, which is from 4 to 16 carbon atoms more than the alkyl group of said (A) alkyl ester, (C) a lower aliphatic α,β-unsaturated monocarboxylic acid of from 3 to 8 carbon atoms, and (D) a monoester of a polyoxy-1,2-alkylene glycol and a lower aliphatic α,β-unsaturated monocarboxylic acid of from 3 to 8 carbon atoms, in which the polyoxy-1,2-alkylene glycol is selected from the group consisting of polyethylene glycols, poly-1,2-propylene glycols and alkyl ethers thereof having a molecular weight between 106 and 10,000, said (A) and (B) components being present in the ratio of from 50 to 80 mole percent of (A) to 20 to 50 mole percent of (B) and amounting to a total of from 75 to 99.9 mole percent and the (C) and (D) components represent a total of from 0.1 to 25 mole percent of the polymer there being at least one unit of said (D) component in the polymer, said polymer having a solubility in mineral lubricating oil of at least 0.5% by weight.

References Cited in the file of this patent

UNITED STATES PATENTS

2,189,734 Kistler et al. ---------- Feb. 6, 1940