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LUBRICANT CONTAINING COPOLYMER VISCOSITY INDEX IMPROVER

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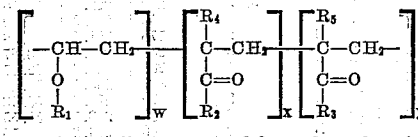
This invention relates to a superior new lubricant composition. More particularly, the invention is concerned with a novel polymer thickened lubricant composition having an improved viscosity index.

Lubricant compositions in many present-day applications contain viscosity index improvers in order to be more effective over a wide temperature range. At low temperatures such as normal starting temperatures of internal combustion engines, the lubricant compositions must be sufficiently fluid to circulate freely and provide a lubricating film between wearing surfaces such as bearings, piston rings, and cylinder walls. On the other hand, at high temperatures like the usual operating temperatures of internal combustion engines, the lubricant composition should be thick enough to give a similarly protective lubricating film.

It has now been found that surprisingly improved viscosity indexes are provided in a lubricant composition comprising a major proportion of an oil of lubricating viscosity and a minor proportion, sufficient to improve the viscosity index of said oil of the copolymer of (A) vinyl alkyl ether having from 2 to 6 carbon atoms in the alkyl group and (B) at least one ester of the class consisting of alkyl acrylates and alkyl methacrylates having from 4 to 12 carbon atoms in each of the alkyl groups, the total of carbon atoms in the alkyl group of (A) and the average alkyl group of (B) being from about 8 to about 12, the mol ratio of (A) to (B) being approximately 1:1 and the molecular weight of the copolymer being at least 50,000.

The lubricant composition of the invention containing the particular copolymer described above possesses an unusually high viscosity index compared to other lubricant compositions containing viscosity index improvers as previously suggested in the art. The particular balance of the carbon atoms in the alkyl groups of the copolymer of the lubricant composition as well as the ratio of monomers and the minimum molecular weight are all critical to the provision of viscosity index improved lubricant compositions of this unusual quality. Other, closely related copolymers of the vinyl alkyl ether type in lubricant compositions are remarkably less satisfactory by comparison.

The copolymers of the lubricant composition according to the invention have the following general formula:



in which R_1 is an alkyl group of from 2 to 6 carbon atoms and R_2 and R_3 are alkyl groups of from 4 to 12 carbon atoms each, all of which may be the same or different from one another, R_4 and R_5 are members of the class consisting of hydrogen and methyl groups, and w, x, and y being the relative occurrence of the (A) and (B) monomer units, as described above, in which relationship w is equal to 1 while x and y are fractional numbers, the sum of which is equal to 1, the total occurrence of the monomer units in the formula being equivalent to a molecular weight of at least 50,000 for the total co-

polymer, the ratio of w to $x+y$ being approximately 1:1 and the total carbon atoms of wR_1 and xR_2+yR_3 being from about 8 to about 12.

Suitable unsaturated alkyl ethers within the above description include vinyl isobutyl ether, vinyl n-butyl ether, vinyl 2-ethylhexyl ether, etc. For present purposes the vinyl alkyl ethers having 4 to 6 carbon atoms in the alkyl group are preferred.

Alkyl esters of methacrylic acid and acrylic acid in accordance with the above formula include n-octyl methacrylate, n-octadecyl acrylate, 2-ethylhexyl acrylate, "Oxy" decyl methacrylate, n-butyl methacrylate, etc. The alkyl methacrylates having 4 to 12 carbon atoms in the alkyl groups are presently preferred.

The copolymers are prepared by conventional bulk, solution or emulsion methods, in the presence of an addition-type polymerization initiator. Preferably, the copolymerization is effected in an inert organic solvent, such as benzene, toluene, xylene or petroleum naphtha, in the presence of a free radical-liberating type initiator such as a peroxy compound, for example, benzoyl peroxide, acetyl peroxide, tert. butyl hydroperoxide, di-tert. butyl peroxide, dibenzoyl peroxide, or di-tert. amyl peroxide, or an azo initiator such as 1,1'-azodicyclohexanecarbonitrile or α,α'-azodiisobutyronitrile, or a persulfate, such as potassium persulfate. The catalyst, or polymerization initiator, is employed in an amount of from about 0.1 to 10%, with a preferred range being from 0.10 to 2%. If desired, the catalyst can be added in increments as the reaction proceeds. Likewise, 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 copolymerization varies from about 100 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 duration of the reaction. Much the same conditions are employed when the copolymerization is effected in bulk rather than in the presence of an inert solvent.

The copolymers have molecular weights of at least about 50,000, as already mentioned. The molecular weight may run as high as several million or more. Polymers having molecular weights of from about 200,000 to about 1,000,000 are preferred. The aforementioned molecular weights are based on standard viscosity determinations.

The following specific example illustrates the preparation of the copolymer of vinyl isobutyl ether, n-butyl acrylate and n-octyl acrylate.

Into a 2-liter, 3-necked flask equipped with water condenser, addition funnel, thermometer, stirring unit and heating means, is charged 9 grams of sodium lauryl sulfate and 420 ml. of distilled water. After stirring at room temperature for 1½ hours, 1½ grams of sodium pyrophosphate, 1½ grams of potassium persulfate, and 350 cc. vinyl isobutyl ether are added with stirring. Stirring is continued for 1½ hours and from an addition funnel a mixture is slowly introduced containing 135 grams polymerization inhibitor-free n-octyl acrylate and 32 grams of inhibitor-free n-butyl acrylate. The time of addition is 1½ hours. Temperature of the reaction mixture during reaction is 110 to 120° F.

The total mixture is vigorously stirred at 150 to 160° F. for 4 hours. After heating slowly to 170° F., an exothermic reaction takes place. A cold water bath is used to cool the reaction mixture. The thickened mixture is stirred at 140 to 150° F. for 4 hours. The resulting polymer is coagulated by the addition of 20 grams of hydrated aluminum sulfate, $Al_2(SO_4)_3 \cdot 18H_2O$. After stirring at 140° F. for 2 hours, the lower layer is decanted. A total of 700 ml. distilled water is added to the reaction

flask and stirring is continued for 2 hours at 140° F. The polymer is dissolved in 300 ml. of benzene and reprecipitated with 750 ml. of methanol. The solvents are removed from the reaction mixture by distillation under reduced pressure. The copolymer product obtained after the removal of the solvents is the ternary copolymer of vinyl isobutyl ether, n-butyl acrylate and n-octyl acrylate having a mole ratio of 1 to 0.25 to 0.75. The copolymer has a molecular weight of approximately 200,000.

In general, excellent viscosity indexes can be imparted to lubricating oils by dissolving in them a quantity of from about 0.1 to 10% by weight of the polymers of the type described above, although a preferred range is from about 1 to 5% weight. On the other hand, since the polymers of this invention are unusually compatible with mineral and other lubricating oils in substantially all proportions, as much as 75% of the present polymeric additives can be dissolved in a suitable lubricating oil for the purpose of preparing a concentrate capable of dilution with lubricating oils and the like to prepare the final lubricant composition. Such concentrates, which may also contain other additives in desired amounts, and which normally contain at least 10% of the polymer, comprise a convenient method for handling the polymer and may be used as a compounding agent for lubricants in general.

The polymeric additives of this invention can be used with good effect in the case of any one of a wide variety of oils of lubricating viscosity, or of blends of such oils. Thus, the base oil can be a refined Pennsylvania or other paraffin base oil, a refined naphthenic base oil, or a synthetic hydrocarbon or nonhydrocarbon oil of lubricating viscosity. As synthetic oils there can be alkylated waxes and similar alkylated hydrocarbons of relatively high molecular weight, hydrogenated polymers of hydrocarbons, and the condensation products of chlorinated alkyl hydrocarbons with aryl compounds. Other suitable oils are those which are obtained by polymerization of lower molecular weight alkylene oxides such as propylene and/or ethylene oxide. Still other synthetic oils are obtained by etherification and/or esterification of the hydroxy groups in alkylene oxide polymers such as, for example, the acetate of the 2-ethylhexanol-initiated polymer of propylene oxide. Other important classes of synthetic oils include the various esters as, for example, di-(2-ethylhexyl) sebacate, tricresyl phosphate, and silicate esters such as hexa (2-ethyl butoxy) disiloxane. If desired, the oil can be a mixture of mineral and synthetic oils.

While satisfactory lubricant compositions can be obtained by adding to the base oil employed only one or more of the polymeric additives of the type described above, it also falls within the purview of this invention to provide lubricant compositions which contain not only such polymers, but also other additives such as oiliness and extreme pressure agents, anti-oxidants, corrosion inhibiting agents, blooming agents, the temperature-viscosity characteristics of the oil. The present invention also contemplates the addition to the lubricant composition (particularly when the amount of copolymer employed is relatively small) of detergents and/or anti-wear agents.

Illustrative lubricant compositions of the above type containing the copolymeric additives of the invention in combination with other agents may include, for example, from about 0.1 to 10% by weight of alkaline earth metal higher alkylphenate and sulfonate detergents, such as calcium alkylphenates having an average of approximately 14 carbon atoms in the alkyl group and basic calcium petroleum sulfonate, as well as organic thiophosphate corrosion and high temperature oxidation inhibitors such as the reaction product of pinene and P_2S_5 and the bivalent metal dihydrocarbyl dithiophosphates, zinc butyl hexyl dithiophosphate and zinc tetradecylphenyl dithiophosphate in amounts of from about 0.1 to 10% by weight of the composition.

The efficacy of polymeric additives of the type described above as viscosity index improving agents in lubricating oils is illustrated by data from a number of tests. Various amounts of the polymeric additives are incorporated in the oil as noted in the following table in terms of percent by weight.

Oil A is a solvent refined mineral lubricating oil base containing 45 millimoles per kilogram of basic calcium petroleum sulfonate, 10 millimoles per kilogram of zinc di(alkylphenyl) dithiophosphate, and 0.25% by weight of diparaffin polysulfide. The viscosity of Oil A at 100° F. is 179.5 SSU (Saybolt seconds Universal) and the viscosity at 210° F. is 45.07 SSU, giving a viscosity index of 96.

Oil B is a solvent refined mineral lubricating oil containing 40 millimoles per kilogram of basic calium petroleum sulfonate, 6 millimoles per kilogram of zinc di(alkylphenyl) dithiophosphate, 0.25% by weight diparaffin polysulfide and 0.001% by weight of silicone foam inhibitor. The base oil has a viscosity index of 96.

Oil C is a typical 140 neutral mineral lubricating oil. The base oil has a viscosity index of 90.

Oil D is a typical 150 neutral mineral lubricating oil. The base oil has a viscosity of 90.

Table

Example No.	R_1	R_2	R_3	R_4	R_5	w	x	y	Total $wR_1+xR_2+yR_3$	Oil	Percent Polymer	Approx. Mol. Wt. (Thousands)	Vis SSU 100° F.	Vis SSU 210° F.	V.I.
1	i-Butyl	n-Butyl	n-Octyl	H	H	1	0.25	0.75	11	A	3.75	385	476.4	80.85	139
2	n-Butyl	do	do	H	H	1	0.75	0.25	9	A	3.75	260	222.4	70.10	167
3	do	do	do	H	H	1	0.75	0.25	9	A	4	455	261.9	88.9	164
4	do	do	do	H	H	1	0.75	0.25	9	B	2	175	191.4	54.8	158
5	do	do	do	H	H	1	0.75	0.25	9	B	3	230	210.9	63.27	165
6	do	do	do	H	H	1	0.75	0.25	9	B	4	265	226.9	72.47	167
7	do	do	do	H	H	1	0.75	0.25	9	C	4	300	203.5	71.11	170
8	i-Butyl	do	n-Octadecyl	CH_3	CH_3	1	0.5	0.5	15	B	2	70	216.6	50.33	125
9	do	do	do	CH_3	CH_3	1	0.75	0.25	11.5	B	2	80	203.1	50.55	135
10	do	2-Et. hexyl	do	CH_3	CH_3	1	0.5	0.5	17	B	2	60	213.2	49.75	124
11	do	"OxO" decyl.	do	CH_3	CH_3	1	0.5	0.5	18	B	2	80	219.6	50.45	126
12	do	2-Et. hexyl		H		1	1		12	B	2	140	244.7	53.10	129
13	do	n-Octyl		H		1	1		12	B	2	140	245.4	53.10	129
14	do	2-Et. hexyl		H		1	1		12	B	2	175	259	54.89	131
15	do	n-Butyl	2-Et. hexyl	H	H	1	0.5	0.5	10	E	4	240	313.6	66.92	142
16	do	do	do	H	H	1	0.25	0.75	11	A	4	285	437.4	74.32	136
17	do	2-Et. hexyl		H		1	1		12	C	4	480	507	86.83	140
18	do	n-Octyl	n-Butyl	H	H	1	0.5	0.5	10	C	4	260	318.4	67.85	147
19	do	n-Hexyl		CH_3		1	1		10	B	2	385	304.1	64.14	145
20	n-Butyl	n-Octyl	n-Butyl	H	H	1	0.25	0.75	9	A	4	310	326.8	76.39	154
21	do	do	do	H	H	1	0.4	0.6	9.6	A	4	395	434.7	83.81	146
22	do	n-Decyl	do	H	H	1	0.25	0.75	9.5	A	4	295	297.7	74.84	157
23	Ethyl	2-Et. hexyl		H		1	1		10	A	3.75	1,225	611	149.5	147
24	2-Et. hexyl	do		H		1	1		16	A	3.75	115	308.6	58.18	128
25	Ethyl	Decyl		H		1	1		12	A	3.75	360	462.5	78.28	138

From the tests in the foregoing table, it will be seen that each of the illustrative compositions containing the copolymeric thickeners according to the invention possesses surprisingly improved viscosity-temperature properties compared to base oils alone. Furthermore, the particular copolymers of vinyl alkyl ethers and alkyl methacrylates having the appropriate balance of carbon atoms in the alkyl groups are much superior to other closely related copolymers without this proper balance.

The above results are even more surprising when compared to viscosity indexes obtained with homopolymers of either vinyl alkyl ether or alkyl acrylates or alkyl methacrylates alone. Although the viscosity index obtained with the alkyl esters in similar compositions is about 140 and that with vinyl ether is about 130, the viscosity index with the preferred coplymers of the invention is as high as 170, which is surprisingly better than would be expected from the average of the two types.

We claim:

1. A lubricant composition comprising a major proportion of an oil of lubricating viscosity and a minor proportion sufficient to improve the viscosity index of said oil of the copolymer of (A) vinyl alkyl ether having from 2 to 6 carbon atoms in the alkyl group and (B) at least one ester of the class consisting of alkyl acrylates and alkyl methacrylates having from 4 to 12 carbon atoms in each of the alkyl groups, the total of carbon atoms in the alkyl group of the (A) and the average alkyl group of the (B) monomers being from about 8 to about 12, the mol ratio of (A) to (B) being approximately 1:1 and the molecular weight of the copolymer being at least about 50,000.

2. A lubricant composition comprising a major proportion of mineral lubricating oil and a minor proportion sufficient to improve the viscosity index of said oil of the copolymer of (A) vinylisobutyl ether and (B) a mixture of n-butylacrylate and n-octylarcrylate, the mol ratio of

(A) to (B) being approximately 1:1 and the molecular weight of the copolymer being at least about 50,000.

3. A lubricant composition comprising a major proportion of mineral lubricating oil and a minor proportion sufficient to improve the viscosity index of said oil of the copolymer of (A) vinyl 2-ethylhexyl ether and (B) n-butylacrylate, the mol ratio of (A) to (B) being approximately 1:1 and the molecular weight of the copolymer being at least about 50,000.

4. A lubricant composition comprising a major proportion of mineral lubricating oil and a minor proportion sufficient to improve the viscosity index of said oil of the copolymer of (A) vinyl n-butyl ether and (B) a mixture of n-butylacrylate and n-octylacrylate, the mol ratio of (A) to (B) being approximately 1:1 and the molecular weight of the coplymer being at least about 50,000.

5. A concentrate for the preparation of lubricant compositions comprising from 25 to 90 percent by weight of mineral lubricating oil and from 10 to 75 percent by weight of the copolymer of (A) vinyl alkyl ether having from 2 to 6 carbon atoms in the alkyl group and (B) at least one ester of the class consisting of alkyl acrylates and alkyl methacrylates having from 4 to 12 carbon atoms in each of the alkyl groups, the total of carbon atoms in the alkyl group of the (A) and the average alkyl group of the (B) monomers being from about 8 to about 12, the mol ratio of (A) to (B) being approximately 1:1 and the molecular weight of the copolymer being at least about 50,000.

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