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COPOLYMERS AND LUBRICANTS
CONTAINING THE SAMEWillard E. Catlin, Wilmington, Del., assignor to
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mington, Del., a corporation of DelawareNo Drawing. Application December 7, 1950,
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4 Claims. (Cl. 252—51.5)

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This invention relates to copolymers and lubricants containing the same and, more particularly, to new copolymers adapted for use as additives to lubricating oils to minimize their change in viscosity with change in temperature.

Lubricating oils have the undesirable characteristic of decreasing in viscosity as the temperature of the oil is increased. Oils with a low rate of change of viscosity with temperature are desired for lubrication purposes, especially in applications where widely varying temperature conditions are encountered. Consequently, numerous materials have been proposed as additives to oils to minimize their change in viscosity with temperature. Many of the additives which hitherto have been proposed for decreasing the rate of change of viscosity with temperature have been quite satisfactory from this standpoint. However, some of the most effective additives, which are polymeric materials, have too great a thickening effect on the oil. In these cases the oils may have a satisfactory rate of change of viscosity with temperature but they are too viscous for satisfactory lubrication at low temperature. Consequently, the most desirable lubricating oil compositions are those which have a low enough viscosity to permit ready flow at low temperature together with the characteristic of a small decrease in viscosity with increase in temperature.

An object of this invention is to provide new copolymers. A further object is to provide new copolymers particularly adapted for use as additives to lubricating oils. A still further object is to provide an improved lubricating oil having a low enough viscosity to permit ready flow at low temperatures together with the characteristic of a small decrease in viscosity with increase in temperature. Other objects will be apparent from the description of the invention given hereinafter.

The above objects are accomplished according to the present invention by providing a small class of copolymers, these being the copolymers of acrylonitrile or methacrylonitrile and alkyl esters in which the alkyl group contains from 10 to 18 carbon atoms, inclusive, of acrylic or methacrylic acids, the acrylonitrile or methacrylonitrile amounting to 2% to 20% by weight of the copolymer. The invention further comprises a lubricating oil in which a small proportion of such copolymer has been dissolved.

It has been found that the class of copolymers as defined above may be readily formed and that when dissolved in small proportion in lubricating oil, they give a lubricant having extremely desirable temperature viscosity characteristics.

The lubricant compositions of this invention contain the copolymers defined above in rela-

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tively small amounts, i. e., in amounts ranging from 0.1% to 10% by weight of the oil. Amounts ranging from 1% to 5% by weight of the oil are preferred, the precise optimum amount of any specific copolymer being dependent on the particular alkyl group in the ester component and the proportion of the nitrile group in the copolymer, the particular type of oil being treated, and the specific degree of change in viscosity characteristics desired in the oil. Copolymers having the best solubility in lubricating oils are those of the above defined class in which the acrylonitrile or methacrylonitrile amounts to not more than 11% by weight of the copolymer. For convenience in storage and handling, more concentrated solutions of the copolymers in lubricating oils may be prepared than would normally be used. For example, lubricating oil solutions containing 50% copolymer can be prepared and then diluted to the desired concentration at the time of use.

The copolymers of this invention are effective additives to lubricating oils of all types obtained from petroleum, i. e., the paraffin base, the naphthenic base, and the mixed base oils, and also the ester type lubricants such as the alkyl esters of aliphatic dicarboxylic acids, e. g., diethylhexyl sebacate. The lubricating oils may also contain in solution or suspension conventional lubricating oil modifiers which impart other desirable characteristics to the oil, e. g., antioxidants.

The lubricating compositions of this invention can be prepared by incorporating the copolymer in the lubricating oil by simply blending with stirring at ordinary temperatures or, if desired, a mixture of oil and copolymer may be heated to elevated temperature, e. g., 100° C. to 130° C., with agitation to form a uniform dispersion.

The copolymers of this invention can be prepared by conventional bulk or solution methods of addition polymerization using conventional addition polymerization initiators. The polymerization is conveniently carried out by contacting a mixture of from slightly more than 2% to 30% by weight of acrylonitrile or methacrylonitrile and from slightly less than 98% to 70% of an alkyl ester of acrylic or methacrylic acid in which the alkyl groups contain from 10 to 18 carbon atoms, inclusive, with from 0.1% to 10%, preferably 0.2% to 2%, of a free radical-liberating type of initiator such as a peroxy compound, e. g., benzoyl peroxide or di(tertiaryamyl) peroxide, or an azo initiator, e. g., 1,1'-azodicyclohexanecarbonitrile or alpha, alpha'-azodiisobutyronitrile, in the presence or absence of an inert solvent such as a hydrocarbon, e. g., benzene, mineral oil or lubricating oil, and preferably in an

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inert atmosphere, e. g., under a blanket of nitrogen or carbon dioxide. The mixture is then agitated and maintained at a temperature at which the polymerization initiator generates free radicals rapidly. The exact temperature selected depends on the particular initiator being used. Temperatures ranging from room temperature or lower to 150° C. or higher are suitable.

The actual nitrile content of the copolymers obtained may be somewhat less than indicated by the proportions of the reactants because of loss of acrylonitrile or methacrylonitrile. The nitrile monomers are relatively volatile and, hence, may be lost to a greater or lesser extent depending upon temperature of polymerization and the precautions taken to avoid escape of volatilized monomers.

The following examples wherein all proportions are by weight unless otherwise stated, illustrate specific embodiments of the invention.

EXAMPLE 1

A mixture of 18 parts of lauryl methacrylate (prepared from technical lauryl alcohol obtained by reduction of coconut oil acids and containing approximately 3% decyl alcohol, 61% dodecyl alcohol, 23% tetradecyl alcohol, 11% hexadecyl alcohol and 2% octadecyl alcohol) containing 0.05% by weight of hydroquinone stabilizer, two parts of acrylonitrile, and 0.1 part of alpha, alpha'-azodiisobutyronitrile is placed in a reaction vessel fitted with an inlet tube reaching almost to the bottom and having an opening for the escape of gas. The reaction vessel is placed in a water bath held at 55°-60° C. and stirring is effected, and an inert atmosphere maintained, by passing carbon dioxide gas through the inlet tube. Heating is continued for a period of 24 hours after which any remaining unreacted acrylonitrile is removed by vacuum drying. The resulting polymer is clear and homogenous in appearance and is soluble in lubricating oils of both the naphthenic and paraffinic types. This copolymer of lauryl methacrylate and acrylonitrile contains 1.06% nitrogen. The combined acrylonitrile content, calculated from nitrogen analysis, is 4.0%.

Additional copolymers of alkyl acrylates or methacrylates and acrylonitrile or methacrylonitrile containing from 2% to 20% of the nitrile components are prepared in a manner similar to that of Example 1. The various copolymers, the particular proportions of the component monomers, and the proportion of alpha, alpha'-azodiisobutyronitrile catalyst used in the polymerizations are listed in Table I.

Table I

ACRYLATE/NITRILE COPOLYMERS

Ex. No.	Copolymer (Monomer Proportions)	Catalyst (Percent of Monomers)	Approx. Nitrile Content (Percent)
2	Lauryl methacrylate/acrylonitrile (80:20)	1.0	10.25
3	Lauryl methacrylate/acrylonitrile (90:10)	0.7	2.7
4	Lauryl methacrylate/acrylonitrile (75:25)	0.7	8.04
5	n-Decyl acrylate/acrylonitrile (90:10)	0.7	6.0
6	do	0.7	5.5
7	n-Decyl methacrylate/acrylonitrile (90:10)	0.7	4.4
8	Lauryl methacrylate/methacrylonitrile (95:5)	0.7	2.5
9	Lauryl methacrylate/methacrylonitrile (90:10)	0.7	6.1

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A significant measure of the suitability of a lubricating oil for use over a wide range of operating temperatures is afforded by the "slope" of the oil. This is the calculated slope of the line joining the points of intersection of the viscosities of the oil at 100° F. plotted as ordinates with the viscosities at 210° F. plotted as abscissas for different concentrations of additive. For practical purposes, the slope of the line may be determined with sufficient accuracy from the viscosity data of the oil at one concentration of the additive and the viscosity data of the unmodified oil (the oil containing 0% concentration of the additive). In this calculation oils having the lowest values of slope exhibit the least change in viscosity with changes of temperature and, hence, are the most favorable. The slope value is a particularly valuable criterion of the suitability of a lubricating oil because it is influenced to such a slight degree by the thickening effect of the additive. An advantageous feature of the instant copolymers is that they have such a relatively small thickening effect on the lubricating oil; this feature is not shown by the slope values but, of course, is readily apparent from the viscosity measurement of the oil.

Table II below illustrates lubricating oils of this invention containing copolymers of lauryl methacrylate and acrylonitrile in 1.5% concentration in a mixed base lubricating oil. In each instance, 0.75 part of the selected copolymer is blended with 49 parts of a low viscosity Mid-Continent pale oil. For purposes of comparison, there are also included (Examples A and B) lubricating oil compositions in which the copolymers contain a proportion of acrylonitrile outside the limits of the invention, as well as a control containing no additive and a further composition containing lauryl methacrylate homopolymer.

Table II

LAURYL METHACRYLATE/ACRYLONITRILE COPOLYMERS (1.5%) IN MIXED BASE LUBRICATING OIL

Ex. No.	Approx. Acrylonitrile Content (Percent)	Viscosity of Oil in Centistokes		
		at 100° F.	at 210° F.	Slope
Control	No additive	12.53	2.88	-----
Lauryl methacrylate homopolymer		21.38	4.96	4.26
10	4.0	17.12	4.06	3.9
11	10.25	14.60	3.47	3.6
A	1.7	21.05	4.89	4.25
B	34.5	(¹)	(¹)	(¹)

¹ Insoluble in the oil.

Table III below illustrates lubricating oil compositions of this invention containing various copolymers of acrylonitrile or methacrylonitrile with alkyl acrylates or methacrylates in concentrations of 1.5% and 3.0% in solvent extracted paraffin base lubricating oils. The concentration of additive in the oil is 1.5% down through Example 17 and 3.0% in the remaining examples, the lubricating oils used in the two instances being substantially identical as the two controls show. For purposes of comparison, the viscosity data are given, for each concentration of additive, of the lubricating oil containing a lauryl methacrylate homopolymer and, with respect to the 1.5% concentration of additive, Examples C and D have been included to illustrate lubricating oil compositions comprising copolymers falling outside the scope of this invention, the alkyl

group of the ester component not containing the required number of carbon atoms.

nitrile as some of the nitrile component may be lost during the polymerization.

Table III

COPOLYMERS IN PARAFFIN BASE LUBRICATING OIL

Ex. No.	Copolymer (Monomer Proportions)	Approx. Nitrile Content (Percent)	Viscosity of Oil in Centistokes		
			at 100° F.	at 210° F.	Slope
Control.....	No additive.....		46.83	6.52	-----
Lauryl methacrylate homopolymer.			62.92	9.04	6.4
C.....	Octyl methacrylate/acrylonitrile (90:10).	6.9	(¹)	(¹)	(¹)
D.....	Octyl acrylate/acrylonitrile (90:10).	7.0	(¹)	(¹)	(¹)
12.....	n-Decyl acrylate/acrylonitrile (90:10).	6.0	50.85	7.52	4.14
13.....	Lauryl methacrylate/acrylonitrile (90:10).	2.7	59.94	8.79	5.78
14.....	Lauryl methacrylate/acrylonitrile (75:25).	8.04	51.54	9.06	1.85
15.....	n-Decyl methacrylate/acrylonitrile (90:10).	4.4	57.90	8.7	4.25
16.....	Lauryl methacrylate/methacrylonitrile (95:5).	2.5	54.86	7.98	5.6
17.....	Lauryl methacrylate/methacrylonitrile (90:10).	6.1	49.13	7.16	3.78

(Concentration of additive in oil—1.5% in the above)

Control.....	No additive.....		46.5	6.53	-----
Lauryl methacrylate homopolymer.			62.7	9.20	6.12
18.....	Lauryl methacrylate/methacrylonitrile (90:10).	5.8	51.96	7.89	3.84
19.....	Lauryl methacrylate/acrylonitrile (92.5:7.5).	7.0	74.5	12.15	4.92
20.....	Lauryl methacrylate/acrylonitrile (89:11).	8.0	74.7	12.61	4.65
21.....	Lauryl methacrylate/acrylonitrile (87.5:12.5).	7.5	86.7	14.63	4.90

(Concentration of additive in oil—3.0% in above)

¹ Insoluble in oil.

It will be understood that the above examples are merely illustrative and that the present invention broadly comprises copolymers of acrylonitrile or methacrylonitrile and an alkyl ester in which the alkyl group contains from 10 to 18 carbon atoms, inclusive, of acrylic or methacrylic acids, the nitrile component amounting to 2% to 20% by weight of the copolymer, and a lubricating oil containing a small amount, usually from 0.1% to 10% by weight thereof, of such a copolymer soluble therein.

The ester component of the instant copolymers can be an ester of either acrylic or methacrylic acid but must be an alkyl ester in which the alkyl group contains from 10 to 18 carbon atoms, inclusive. Thus the decyl, dodecyl, tetradecyl, hexadecyl and octadecyl acrylates and methacrylates are all suitable. It is not necessary that the alkyl radical be derived from a pure alcohol. Technical grades of alcohol having an average carbon content within the range of 10 to 18 carbon atoms are suitable for use in the preparation of the ester component of these copolymers. The commercially available alcohols such as technical lauryl alcohol obtained by reduction of the fatty acids in coconut oil and the analogous products made by hydrogenation of carbon monoxide are especially suitable as sources from which the alkyl radical of the esters can be derived.

The nitrile component of the instant copolymers can be either acrylonitrile or methacrylonitrile. This nitrile component must be present in the copolymer in an amount from 2% to 20% by weight of the copolymer and it should be realized that having the two monomers in proportions within this range in the mixture to be polymerized, does not necessarily mean the resulting copolymer will have the requisite proportion of

The acrylic and methacrylic esters employed as comonomers in making the polymers of this invention may contain a small amount, e. g., about 0.05% by weight, of stabilizers such as hydroquinone or m-dinitrobenzene as illustrated by Example 1. However, higher molecular weight copolymers can be obtained by the use of unstabilized alkyl acrylate or methacrylate monomers. Furthermore, the polymerization rate is more rapid when such stabilizers are not present in the polymerization mixture. When unstabilized alkyl acrylates or methacrylates are employed in combination with acrylonitrile or methacrylonitrile of high purity, substantially complete polymerization takes place in periods of three to five hours.

The copolymers of this invention are, in general, soluble in lubricating oils. There are some exceptions to this in that all of the copolymers are not soluble in all types of lubricating oils although each one is soluble in at least one type. The copolymers containing a proportion of acrylonitrile or methacrylonitrile toward the upper limit of the permitted range and at the same time a short chain alkyl group, i. e., one of only 10 carbon atoms, in the acrylate or methacrylate, are less soluble in the paraffinic type of oil than they are in the naphthenic or mixed base types of oils. Obviously, a copolymer soluble therein will be selected as an additive to any given type of oil.

The copolymers of this invention are also useful for converting a base oil to an oil having viscosities and a viscosity index in the range acceptable for power transmission oils used in automotive transmissions. The present requirements for torque converter fluids in automotive transmissions and the like are a viscosity index of at least 150 and a Saybolt Universal viscosity

at 210° F. of 54-56 seconds. Some of the copolymers of this invention are particularly effective in such oils.

As many apparently widely different embodiments of this invention may be made without departing from the spirit and scope thereof, it is to be understood that the invention is not limited to the specific embodiments thereof except as defined in the appended claims.

The invention claimed is:

1. A lubricating oil containing from 0.1% to 10% by weight thereof of an oil-soluble copolymer of a nitrile from the group consisting of acrylonitrile and methacrylonitrile, and an alkyl ester in which the alkyl group contains from 10 to 18 carbon atoms, inclusive, of an unsaturated acid from the group consisting of acrylic and methacrylic acids, said nitrile amounting to 2% to 20% by weight of said copolymer.

2. A lubricating oil containing from 0.1% to 10% by weight thereof of an oil-soluble copolymer of a nitrile from the group consisting of acrylonitrile and methacrylonitrile, and an alkyl ester in which the alkyl group contains from 10 to 18 carbon atoms, inclusive, of an unsaturated acid from the group consisting of acrylic and methacrylic acids, said nitrile amounting to 2% to 11% by weight of said copolymer.

3. A lubricating oil containing from 1% to 5%

by weight thereof of an oil-soluble copolymer of a nitrile from the group consisting of acrylonitrile and methacrylonitrile, and an alkyl ester in which the alkyl group contains from 10 to 18 carbon atoms, inclusive, of an unsaturated acid from the group consisting of acrylic and methacrylic acids, said nitrile amounting to 2% to 20% by weight of said copolymer.

4. A lubricating oil containing from 1% to 5% by weight thereof of an oil-soluble copolymer of a nitrile from the group consisting of acrylonitrile and methacrylonitrile, and an alkyl ester in which the alkyl group contains from 10 to 18 carbon atoms, inclusive, of an unsaturated acid from the group consisting of acrylic and methacrylic acids, said nitrile amounting to 2% to 11% by weight of said copolymer.

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