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LUBRICATING OIL COMPOSITIONS

Lyman E. Lorensen, Orinda, and Emmett R. Barnum and John Zachar, Berkeley, Calif., assignors to Shell Development Company, New York, N.Y., a corporation of Delaware

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This invention relates to new and improved mineral oil lubricating compositions containing a high molecular weight polymer which does not form ash, these lubricating compositions possessing particularly good pour point depressing properties.

Many lubricating oils, because of the nature of their source and/or methods of refining, contain greater or lesser amounts of wax. Lubricating oils of this type are less desirable for many types of operations, particularly under cold operating conditions, such as those encountered in cold climates, this because they readily congeal. In order to overcome this defect in wax-containing lubricating oils, pour point depressants have to be employed with such oils. Among the best known additives for this purpose are the polymeric esters of the acrylic or alkacrylic, e.g. methacrylic, acids. Other known polymeric materials used for this purpose are the polymerized olefins, alkylated naphthalene and the like.

Although the above-mentioned polymeric materials can effectively reduce the pour point of some oils, they are restricted in use to some particular base oils; otherwise they are ineffective and impart certain undesirable properties to the final composition because: (*a*) they are corrosive, (*b*) they have the tendency to form emulsions when water or steam is present, and (*c*) they possess the tendency to break down at elevated temperatures.

It has now been discovered that an excellent pour point depressant which is effective in all mineral oils comprises an oil-soluble polymeric compound of at least three polymerizable monomers one of them being a vinylpyridine and at least two dissimilar esters of acrylic acid and preferably methacrylic acid and dissimilar long chain aliphatic alcohols, these alcohols containing at least 10 and not more than 20 carbon atoms and wherein the average chain length of these alkyl side chains (straight or branch-chain) in the ester mixture is in the C_{10} to C_{16} range and preferably in the C_{12} to C_{14} range. The mole ratio of the vinylpyridine to the polymerizable esters can vary from 1:2 to 1:10 and the dissimilar acrylate esters can vary in the mole ratio of 1:4 to 4:1. The final polymer should have a molecular weight varying from about fifty thousand to about two and one-half million and preferably between 100,000 and 850,000 as determined by the light scattering method. More specifically, it has been found that terpolymers of a vinylpyridine and mixtures of esters of methacrylic acid and dissimilar aliphatic alcohols, as described above exhibit pour point depressant activity which is far greater than that of the corresponding copolymers of a vinylpyridine with a single ester of methacrylic acid and a long chain aliphatic alcohol.

The vinylpyridines used in making the polymers may be exemplified by 2-vinylpyridine, 3-vinylpyridine, 4-vinylpyridine, as well as the alkyl-substituted derivatives thereof, e.g. 2-methyl-5-vinylpyridine, 4-methyl-2-vinylpyridine, 5-ethyl-2-vinylpyridine and 2-butyl-5-vinylpyridine and the like.

The esters which can be polymerized with the vinylpyridines include at least two dissimilar esters of acrylic

or methacrylic acid and long chain aliphatic alcohols, e.g. decyl, dodecyl, tetradecyl, hexadecyl (or technical lauryl alcohol), octadecyl and eicosyl alcohols. Specific mixture combinations of these esters include dodecyl methacrylate/octadecyl methacrylate, tetradecyl acrylate/octadecyl methacrylate, decyl methacrylate/octadecyl methacrylate, tetradecyl methacrylate/hexadecyl methacrylate, technical lauryl methacrylate/octadecyl methacrylate, these ester mixtures being in a mole ratio of from 1:4 to 4:1, respectively, and so controlled that the average chain length of the alkyl radicals in the final polymer is in the range indicated above.

An ester of acrylic or methacrylic acid and technical lauryl alcohol, which is a mixture of straight chain alcohols should not be considered as a mixture of two or more esters or that using such an ester would result in a polymeric additive suitable for use in oil compositions of this invention since copolymers of lauryl (technical) methacrylate and a vinylpyridine will not have the required dissimilar alkyl chains or the average alkyl chain length which is an essential limitation that polymers of this invention should possess. Rather such copolymers function as simple copolymers and possess the limitations of such esters namely they function as pour point depressants only in specific oils, they tend to break down, form emulsion and cause corrosion. On the other hand, terpolymers derived from a vinylpyridine and a mixture of lauryl methacrylate (derived from technical lauryl alcohol) and octadecyl (stearyl) methacrylate form excellent pour point depressants of this invention.

Any suitable method may be employed to make polymers of the present invention. Factors which exert an influence on the molecular weight of the polymer include the method of polymerization (e.g., polymerization in emulsion, suspension, solvent solution or bulk), the nature and concentration of the catalyst employed, the temperature, and nature and amount of the monomers. When the polymerization is accomplished in solution, the molecular weight of the product will be lower when the dilution is stronger, i.e., when the concentration of solvent is greater. With the same catalyst, the higher polymerization temperature tends to give lower molecular weights.

Polymerization initiators that are particularly suited for use in preparing the claimed copolymers include various free radical yielding catalysts as peroxide catalysts, such as, for example benzoyl peroxide, lauroyl peroxide, tertiary butyl hydroperoxide, 2,2-bis(tertiary butyl peroxy) butane, di(tertiary butyl) peroxide, tertiary butyl perlargonate, hydrogen peroxide, sodium or potassium persulfate, percarbonate, peracetic acid and the like. Other suitable catalysts include sodium bisulfite, diethyl sulfoxide, azo compounds, such as alpha,alpha-azodiisobutyronitrile and the like. The amount of the initiator added may vary over a considerable range. In general, the amount of initiator added will vary from 0.1% to 5% by weight of the material being polymerized. Preferred amounts vary from 0.1% to 2% by weight.

The temperature selected will vary depending chiefly on the type of initiator selected, the desired rate of reaction and the molecular weight desired. Generally, the temperature will range from about 50° C. to 150° C., and more preferably from 60° to 150° C.

The polymerization may be conducted in the presence or absence of air. In most cases, however, it has been found desirable to conduct the polymerization in the absence of air, e.g., in the presence of an inert gas such as nitrogen. Atmospheric, reduced or superatmospheric pressure may be employed.

At the end of the polymerization, any unreacted monomer or monomers and/or solvents may be removed, preferably by distillation or by precipitation with appropriate solvents.

The mineral lubricating oils used in compositions of this invention can be obtained from any paraffinic, naphthenic, asphaltic or mixed base crude, and/or mixtures thereof. The viscosity of these oils may vary over a wide range, such as from 100 SUS at 100° F. to 100 SUS at 210° F. The hydrocarbon oils may be blended with fixed oils such as castor oil, lard oil and the like and/or with synthetic lubricants such as polymerized olefins, copolymers of alkylene glycols and alkylene oxides, organic esters, e.g., 2-ethylhexyl sebacate, dioctyl polymers, e.g., dimethyl silicone polymers and the like.

Mineral lubricating oils which are particularly desirable for use in compositions of this invention can be obtained from West Texas Ellenburger crudes, East Texas crudes, Oklahoma crudes, California crudes. A useful refined East Texas mineral lubricating oil had the following properties:

Pour point, ° F.	+20
Viscosity, cs. at 100° F.	57.2
Viscosity index	90

The novel polymer additives are effective in the lubricating compositions in ranges varying from about 0.01% to about 10% and preferably from about 0.1% to 5% by weight of the oil.

The following examples illustrate polymer additives which can be used in compositions of this invention:

Example I

A mixture of 2.5 mole of stearyl methacrylate, 5.3 mole of lauryl methacrylate and 1 mole of 2-methyl-5-vinylpyridine and 0.2% w. of alpha,alpha'-azodi-isobutyronitrile dissolved in a minor amount for solubility of acetone were placed in a reaction vessel and reacted for about 24–48 hours at 65° C. with stirring in a nitrogen atmosphere. The polymer was then dispersed in equal volumes of benzene and thereafter precipitated with 5–10 volumes of a mixture of acetone and methanol. This was repeated and a terpolymer of stearyl methacrylate/lauryl methacrylate/2-methyl-5-vinylpyridine having a nitrogen content of 0.64% by weight and a molecular weight in excess of 750,000 was recovered. The polymer contained the monomer units in the ratio 2.3/5.0/1 respectively.

Example II

The procedure of Example I was followed except that the monomers stearyl methacrylate, lauryl methacrylate and 2-methyl-5-vinylpyridine were reacted in the mole ratio of 2.9, 1.3 and 1, respectively. The average side chain length of the end product was around 13.1.

Example III

The procedure of Example I was followed except that the monomers stearyl methacrylate, lauryl methacrylate and 2-methyl-5-vinylpyridine were reacted in the mole ratio of 1.3, 2.9 and 1 respectively. The average side chain length of the end product was around 12.

Example IV

The procedure of Example I was followed except that the monomers stearyl methacrylate, lauryl methacrylate and 2-methyl-5-vinylpyridine were reacted in the mole ratio of 2.2, 2.2, and 1 respectively. The average side chain length of the end product was around 12.5.

Example V

The procedure of Example I was followed except that the monomers stearyl methacrylate, lauryl methacrylate and 2-methyl-5-vinylpyridine were reacted in the mole ratio of 2, 6 and 1, respectively. The average side chain length of the end product was around 12.7.

Other examples of polymeric additives which can be used in compositions of this invention include, dodecyl acrylate/stearyl acrylate/vinylpyridine, hexadecyl methacrylate/stearyl methacrylate/2-methyl-5-vinylpyridine, lauryl methacrylate/stearyl methacrylate/2-ethyl-5-vinylpyridine and decyl methacrylate/octadecyl methacrylate/vinylpyridine.

The pour point effects which additives of this invention impart to mineral oil is evidenced from the data presented below:

[Base-East Texas 250 neutral, pour point +20° F.]

Additive	Am't, percent wt.	ASTM (D-97-47) Pour Point, ° F.
Example I	0.5	−30
Example II	0.5	−10
Example III	0.5	−25
Example IV	0.5	−15
Example V	0.5	−15
Example A (Copolymer of stearyl methacrylate/2-methyl-5-vinyl-pyridine (4.3/1)): Average chain length 14.1	0.5	+15
Example B (Copolymer of lauryl methacrylate/2-methyl-5-vinyl-pyridine (1.7/1)): Average chain length 8.7	0.5	+20
Example C (Copolymer of stearyl methcrylate/2-methyl-5-vinyl-pyridine (8/1)): Average chain length 15.3	0.5	+20

Compositions of this invention can be modified by addition thereto of minor amounts (0.01–2%) of pour point depressants, viscosity index improvers, corrosion inhibitors, extreme pressure effects, anti-oxidants and the like. Among such materials are VI and pour point agent, e.g., high molecular weight polymers, e.g., "Acryloids;" wax naphthalene condensation products, isobutylene polymers, alkylstyrene polymers; corrosion inhibitors, e.g., inorganic and organic nitrites such as $NaNO_2$ or $LiNO_2$ and diisopropylammonium nitrite or dicyclohexyl ammonium nitrite, metal organic phosphates, e.g., Ca or Zn dicyclohexylthiophosphate or methylcyclohexylthiophosphate; extreme pressure agents such as organic phosphites, phosphates and phosphonates, e.g. trichloroethyl phosphite, tricresyl phosphate, dilorol phosphate, phosphorus sulfide-olefin reaction products such as P_2S_5-terpene reaction products, organic sulfides, e.g., wax disulfide, ethylene bistolyl sulfide; anti-wear agents such as sulfonates and phenates, e.g. calcium petroleum sulfonate and/or calcium salt of octyl phenol formaldehyde condensation product, anti-oxidants such as phenols and amines, e.g., octadecylamine, 2,6-dietertbutyl-4-methylphenol and the like.

This application is a continuation-in-part of our applications Serial No. 389,840, filed November 2, 1953, now abandoned, and Serial No. 553,731, filed December 12, 1955.

We claim as our invention:

1. A mineral lubricating oil composition comprising a major amount of a mineral lubricating oil and a minor amount sufficient to effectively depress the pour point of the oil and improve its detergent properties, of an oil-soluble copolymer of (1) a monovinyl-substituted pyridine of the group consisting of pyridines substituted on one of the ring carbon atoms with, as the sole substituted substituent, a vinyl group, and derivatives of the afore-described vinyl pyridines having a lower alkyl group substituted on a ring carbon atom and (2) a mixture of a C_{16} to C_{20} alkyl ester of an acrylic acid of the group consisting of acrylic acid and methacrylic acid and a C_{10} to C_{14} alkyl ester of an acrylic acid of the group consisting of acrylic acid and methacrylic acid in mole ratios varying from 1:4 to 4:1, said copolymer having the monovinyl pyridine and the combined acrylic acid esters in a mole ratio varying from 1:2 to 1:10, respectively, and a molecular weight from 5×10^4 to 2.5×10^6.

2. The composition of claim 1 wherein in the oil-soluble copolymer the pyridine is 4-vinylpyridine.

3. The composition of claim 1 wherein in the oil-soluble copolymer the pyridine is 2-methyl-5-vinylpyridine.

4. A mineral lubricating oil composition comprising

a major amount of a mineral lubricating oil and from about 0.1% to about 5% of an oil-soluble copolymer of (1) monovinyl-substituted pyridine of the group consisting of pyridines substituted on one of the ring carbon atoms with, as the sole substituted substituent, a vinyl group, and derivatives of the aforedescribed vinylpyridines having a lower alkyl group substituted on a ring carbon atom and (2) a mixture of a C_{16} to C_{20} alkyl ester of an acrylic acid of the group consisting of acrylic acid and methacrylic acid and a C_{10} to C_{14} alkyl ester of an acrylic acid of the group consisting of acrylic acid and methacrylic acid in mole ratios varying from 1:4 to 4:1, said copolymer having the vinylpyridine and the combined acrylic esters in a mole ratio varying from 1:2 to 1:10 and a molecular weight from 100,000 to 850,000.

5. The composition of claim 4 wherein in the oil-soluble copolymer the vinylpyridine is 2-methyl-5-vinylpyridine and the acrylic ester is a mixture of stearyl methacrylate and lauryl methacrylate.

6. The composition of claim 4 wherein the oil-soluble copolymer is a 2-methyl-5-vinylpyridine/stearyl methacrylate/lauryl methacrylate polymer in the mole ratio of 1:5:2.5, respectively, having a molecular weight of about 800,000.

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