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LUBRICATING OIL COMPOSITIONS

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This invention relates to lubricating oil compositions and more particularly to highly detergent mineral lubricating oil compositions.

It is known that polyvalent metal salts of sulfonic or naphthenic acids impart detergency and dispersancy to mineral lubricating oils. However their effectiveness is noted only when such lubricants are subjected to relatively high temperatures and pressures. At low temperatures such as encountered in engines operating under severe "stop-and-go" conditions, such lubricants are generally ineffective as detergent and dispersant compositions.

As obviating some of the shortcomings of the metallic detergents, oil-soluble non-ash polymers have been used, such as Du Pont's ashless detergent sold under the trade name of LOA–564 and 565 which are copolymers of polymerizable basic amino nitrogen-containing compounds and alkyl methacrylates, e.g. diethylaminoethyl methacrylate/lauryl methacrylate copolymers and Rohm and Haas' ashless detergents sold under the tradenames of Acryloid 917 and 966, which are copolymers of N-vinyl pyrrolidone and an alkyl methacrylate such as lauryl methacrylate.

Although polymers of the type mentioned above are excellent for low temperature detergents, they are drawbacks to their use in combination with high temperature metallic detergents such as metal sulfonates and naphthenates; one drawback is the tendency of such additive combinations to complex and form sludge.

It has now been discovered that a combination of minor amounts of particular classes of oil additives is unexpectedly effective in improving the detergent and dispersant properties of mineral oils over a wide temperature range such as from starting engine temperature of from below 0° C. to temperatures above 500 or 600° C. The two types of additives are: (I) an oil-soluble chromium salt of an alkyl salicylic acid and (II) an oil-soluble copolymer of (1) a vinylpyridine, (2) a mixture of at least two dissimilar esters of an acrylic acid and two different aliphatic alcohols one of which is a long chain aliphatic alcohol containing at least 10 carbon atoms, and the other alcohol being a lower aliphatic alcohol of not more than 6 carbon atoms, said copolymers having the vinylpyridine and the acrylate esters in the mol ratio of from 2:1 to 1:10. A preferred copolymer is one in which the acrylates comprise a mixture of at least two dissimilar acrylates of different long chain alcohols and also an acrylate of a C_{1-4} alcohol, total acrylic ester being in a mol ratio varying from 1:10 to 2:1, the acrylate of the lower aliphatic alcohol making up not more than 60 mol percent of the total ester, and the molecular weight of the copolymer varying from 5×10^4 to 2.5×10^8, as determined by the light scattering method.

The chromium salts may be oil-soluble neutral and basic chromium salts of alkyl salicylic acid in which the alkyl group contains from 8 to 30, preferably 14 to 22 carbon atoms. Exemplary compounds are neutral and basic chromium C_{8-12} alkyl, C_{12-14} alkyl, and C_{14-18} alkyl salicylates.

The chromium compounds are readily prepared by the double decomposition of the sodium salt of the salicylic acid with an inorganic chromium salt, e.g., chromium nitrate, in water or aqueous alcohol. To avoid partial hydrolysis of the organic chromium salt, immediately upon double decomposition and before the separation of

water, the reaction may be carried out in the presence of alcohol under distillation conditions, the chromium salt solution being added to an alcohol/water mixture of the sodium compound as the alcohol distills from the mixture.

The vinylpyridines used in making the special copolymers (II) are exemplified by 2-vinylpyridine, 3-vinylpyridine, 4-vinylpyridine, 2-methyl-5-vinylpyridine, 4-methyl-2-vinylpyridine, 5-ethyl-2-vinylpyridine and 2-butyl-5-vinylpyridine, and the like. Particularly preferred groups comprise 2-, 3- and 4-vinylpyridine and the lower alkyl-substituted derivatives thereof.

The long chain acrylate esters used in the preparation of the copolymers (II) include the ester of acrylic acid and the alpha-substituted acrylic acids such as methacrylic acid, ethacrylic acid, alpha-phenyl acrylic acid, alpha-cyclohexyl acrylic acid and chloroacrylic acid. The long-chain aliphatic alcohols used in the esterification of these acids may be exemplified by decyl, lauryl, cetyl, stearyl, eicosanyl, nonadecanyl, and the like alcohols and mixtures thereof. Particularly preferred esters to be used are the acrylic acid and methacrylic acid esters of aliphatic monohydric alcohols, and especially alkyl alcohols, containing from 14 to 20 carbon atoms.

Specific examples of these long chain acrylic acid esters include, among others, decyl acrylate, lauryl acrylate, stearyl acrylate, decyl methacrylate, lauryl methacrylate, cetyl methacrylate, stearyl methacrylate, eicosanyl acrylate, docosanyl acrylate and the like, and mixtures thereof.

As noted, in addition to the short chain acrylate, one and preferably a mixture of two or more of the long chain acrylate esters is used in making the copolymers. Illustrative examples of these esters and mixtures thereof include, among other, dodecyl methacrylate/octadecyl methacrylate, tetradecyl acrylate/octadecyl methacrylate; decylmethacrylate/octadecyl methacrylate; tetradecyl methacrylate/hexadecyl methacrylate; tetradecyl acrylate/octadecyl methacrylate; dodecyl methacrylate/eicosanyl acrylate, and the like.

When mixture of two long chain acrylates are used it is highly desirable to have a substantial difference in the number of carbon atoms of the alcohol portion. Particularly superior results are obtained when one of the acrylate esters is a C_{10} to C_{14} acrylate ester and the other is a C_{16} to C_{20} acrylate ester.

In the mixture, the different long chain acrylate esters are employed in mol ratios from 1:4 to 4:1. The superior copolymers are obtained when the higher ester, e.g., those having from 10 to 20 carbon atoms in the alcohol portion, and the lower esters, e.g., those having from 10 to 14 carbon atoms in the alcohol portion are combined in a mol ratio varying from 1:1 to 1:3.

In considering the above mixtures, it should be noted that an ester of acrylic acid 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 of group (2) 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 vinylpyridine will not have the required ratio of dissimilar alkyl chains or the average alkyl chain length which is required of polymers of this invention. 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, the claimed polymers form excellent pour point depressants, detergents and viscosity index improving additives for use in lubricating oil compositions.

The short chain acrylate used in making the copolymers

is an ester of an acrylic acid and a lower aliphatic alcohol of not more than 6 carbon atoms. Examples of these lower acrylates include, among others, the acrylic acid and methacrylic acid esters of methanol, ethanol, butanol, hexanol, isobutyl alcohol and propanol.

The ester of the acrylic acids and the aliphatic alcohol containing not more than 6 carbon atoms should be employed in less than 60 mol percent of the total of the acrylate esters. Preferably the lower acrylate ester is employed in amounts varying from 10% to 30% by weight of the total of the acrylate esters.

As the vinylpyridines and the acrylic esters have different polymerization rates, the proportions in which they enter the copolymer molecule will differ from the proportions in which they occur in the reaction mixture. It will be necessary, therefore, to determine beforehand the ratio of proportions of monomers needed to give copolymers having the two monomers in the necessary ratio. This can be easily accomplished by conducting a few routine runs and examining the composition of the resulting copolymer. The initial concentration of monomers can then be adjusted so as to give the copolymer of the desired composition.

As the reaction progresses, the monomer concentration ratios change due to the difference in the rate of polymerization, in some cases, the ratio will change so that it will not be producing copolymers having the monomers in the desired ratio. The superior products are, therefore, obtained by employing some steps during the copolymerization which will insure that the ratio of concentrations of monomers does not vary during the reaction period from the above described limits. This may be accomplished in a variety of ways. One way, for example, comprises stopping the copolymerization after the ratio of the monomer concentrations has reached the limiting value. This method is of particular value if the change in the ratio between the monomer concentrations during copolymerization is slow and a considerable yield of copolymer has been obtained before the limiting values have been attained.

Another method is to adjust the ratio between the monomer concentrations by adding monomer during the course of the polymerization. In this case, it is usually sufficient to add the monomer which is consumed the fastest. Such additions may be periodic or continuous.

Control over the change of ratio can be made by periodic withdrawal of samples and analyzing the product, or can be made in a homogeneous system by simply observing a physical property of the mixture which varies with the ratio of concentrations of monomers, such as boiling point, refractive index, vapor pressure, specific gravity and the like, and adding the monomer or monomers so as to bring the value up to the predetermined level for the desired product.

Copolymers of the present invention which have the superior properties noted above are those having molecular weights between 50,000 and 2,500,000 as determined by the light scattering technique described in Chem. Rev., vol. 40, page 319 (1948). Preferably, the molecular weights range from about 75,000 to 1,000,000 and more preferably from 100,000 to 650,000.

Any suitable conditions may be employed to maintain the molecular weight within the desired range. 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 greater, 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-azodiisobutylonitrile 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 is important relative to the viscosity temperature (VT) properties desired. For a given lower acrylate content, the higher temperatures give lower VT values. Preferred temperatures range from 40° C. to 90° C. As shown in Example XVI temperatures up to 120° C. or even up to 160° C. may be used but give lower VT values.

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 recovered, preferably by distillation or by precipitation with appropriate solvents.

The following examples illustrate the preparation of suitable polymers for use in oil compositions in accordance with the invention. Unless otherwise specified, parts disclosed in the examples are parts by weight.

In the examples, the molecular weights were determined by light scattering method and the ratio of vinylpyridines to alkyl ester was determined by analysis for nitrogen.

EXAMPLE I

A mixture of 2.52 mols of stearyl methacrylate, 5.04 mols of lauryl methacrylate, 0.83 mol of methyl methacrylate and 1 mol of 2-methyl-5-vinylpyridine and 0.2% wt. of alpha,alpha'-azodiisobutyronitrile dissolved in a minor amount of acetone for solubility was 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 stearyl methacrylate/lauryl methacrylate/methyl methacrylate/2-methyl-5-vinylpyridine polymer having a nitrogen content of 0.60% by weight and a molecular weight in excess of 750,000 was recovered.

Following essentially the procedure of Example I, other polymers are prepared from monomer mixtures in the molar proportions as shown in Table I.

Table I

Example	SMA*	LMA	MMA	BMA	MVP	EVP
II	2.24	4.48	1.86		1	
III	2.24	4.48		1.86	1	
IV	2.05	3.92	2.43		1	
V	2.05	3.92		2.43	1	
VI	1.68	3.36	3.36		1	
VII	1.68	3.36		3.36	1	
VIII	1.40	2.80	4.2		1	
IX	1.40	2.80		4.2	1	
X	1.12	2.24	5.04	5.04	1	
XI	1.12	2.24			1	
XII	2.52	5.04	0.83			1
XIII	2.24	4.48		1.86		1
XIV	2.05	3.92	2.43			1
XV	2.05	3.92		2.43		1

*SMA=Stearyl methacrylate; LMA=Lauryl methacrylate; MMA=Methyl methacrylate; BMA=Butyl methacrylate; MVP=2-Methyl-5-vinylpyridine; EVP=5-Ethyl-2-vinylpyridine.

Other examples of useful polymers for the purpose of the invention include: dodecyl acrylate/stearyl acrylate/ethyl methacrylate/vinylpyridine; hexadecyl methacrylate/stearyl methacrylate/propyl methacrylate/2-methyl-5-vinylpyridine, lauryl methacrylate/stearyl methacrylate/ethyl methacrylate/5-ethyl-2-vinylpyridine and decyl methacrylate/octadecyl methacrylate/butyl methacrylate/vinylpyridine in which the mol ratios of the total ester mixture to the vinylpyridine are ratios of from 1:2 to 10:1, respectively, and in which the amounts of methyl, ethyl, propyl or butyl acrylate or methacrylate in the ester mixtures are amounts of from 10 to 60 and preferably from 15 to 45 mol percent of the total ester mixture.

EXAMPLE XVI

29.3% stearyl methacrylate, 49.7% lauryl methacrylate, 16% methyl methacrylate and 5.0% methyl vinylpyridine were charged to a 300-gallon stainless steel autoclave. A 50/50 mixture of benzene and neutral petroleum oil was then added to the autoclave so as to furnish 1 part of the mixture per 3 parts of the total monomer. 0.25% of di-tertbutyl peroxide was then added and the mixture heated at 120° C. for about seven hours.

At the completion of the reaction, the benzene was stripped off to final conditions of 120° C. and 10 mm. Hg with nitrogen sparging. The benzene-free product was then diluted with neutral oil to a polymer content of about 30% by weight and filtered at 100–120° C.

EXAMPLE XVII

Example XVI was repeated with the exception that the proportion of methyl methacrylate in the feed mixture was varied from 16% to 30%. The resulting copolymers were then added to the base oil as in the preceding example.

EXAMPLE XVIII

Example XVII was repeated with the exception that the catalyst was as in Example I and the temperature was 65° C. The resulting copolymers were then added to the base oil as in the preceding example.

EXAMPLE XIX

Example XVI repeated with the exception that the methyl methacrylate is replaced by hexyl acrylate.

EXAMPLE XX

Example XVI was repeated with the exception that the methyl methacrylate was used in an amount of 14% and the lauryl methacrylate and stearyl methacrylate were present in the mol ratios of 1.8 to 1, respectively, a mounting to 81% of the total polymer mixture and the end product rod a molocular weight of 5×10^5 and a nitrogen content of 0.60%.

The two additives are each used in amounts ranging from 0.001% to 10%, preferably from 0.01% to 2% by weight.

The foregoing combination of polymer and chromium salicylate appears to co-act with certain phosphorus compounds to give unexpected improvement in anti-wear and anti-scuffing inhibition. This desirable improvement can be imparted to lubricants of this invention by incorporating a small amount (0.01–2%, preferably 0.1–1%) of a partial or full ester of an organic phosphorus compound. Phosphorus compounds of this type include alkyl, cycloalkyl, alkaryl, aralkyl, and aryl phosphites, phosphates, phosphonates, and their thio-derivatives, such as C_{3-18} alkyl phosphites, e.g., di and tributyl, octyl, lauryl, stearyl, cyclohexyl, benzyl, cresyl, phenyl phosphites or phosphates, as well as their thio-derivatives; P_2S_5-terpene reaction product, P_2S_5-pine oil reaction product and metal salts thereof such as Na, K, Ca or Ba salts of P_2S_5-terpene reaction product; dibutyl methanephosphonate, dibutyl trichloromethanephosphonate, dibutyl

monochloromethanephosphonate, dibutyl chlorobenzene phosphonate, dibutyl monochloromethanephosphonate, dibutyl chlorobenzenephosphonate, and the like. The esters of pentavalent phosphorus acids such as diphenyl, dicresyl, triphenyl, tricresyl, trilauryl and tristearyl ortho phosphates, P_2S_5-terpene reaction products and mixtures thereof are preferred. Also the oxidative stability of such compositions is greately enhanced and the overall properties of such compositions substantially improved by addition thereto of a small amount (0.01–2% by weight, preferably 0.1–1% by weight) of a phenolic antioxidant compound such as mono or bisphenols, preferably phenols which contain at least one tertiary alkyl radical. Alkyl phenols of this type include 2,4,6-triethyl-, tributyl-, trioctyl-, 2,4-ditert-butyl-6-methyl-, 2,6-ditert-butyl-4-methyl-, 2,4,6-tritert-butyl-, 2,6-dicyclohexyl-4-methyl-, 2,6-dimethyl-4-cyclohexyl-phenols, 2,6-ditert-butyl, 2,2-ditertbutyl, 2,6-tertbutylcyclohexyl, 2-methyl-6-tertbutyl-4-methylphenols. The alkyl bisphenols include 1,1-bis(2-hydroxy-3-t-butyl-5-methylphenyl)-methane; bis(2-hydroxy-3-t-butyl-5-methylphenyl)ethane; 1,1-bis(2-hydroxy-3-t-butyl-5-methylphenyl)propane; bis(2-hydroxy-3-t-butyl-5-methylphenyl)butane; bis(2-hydroxy-3-t-butyl-5-methylphenyl)isobutane; 1,1-bis(6-hydroxy-5-t-butyl-3-methylphenyl)methane; bis(2-hydroxy-5-t-butyl-3-methylphenyl)ethane; 1,1-bis(2-hydroxy-5-t-butyl-3-methylphenyl)propane; 1,1-bis(2-hydroxy-5-t-amyl-3-methylphenyl)butane; etc. The 2,4,6-trialkyl phenols containing two tertiaryalkyl groups in the 2,4- or 2,6-positions are preferred, such as 2,4-ditert-butyl-6-methyl-, 2,6-ditert-butyl-4-methylphenol or 2,6-ditert-butyl-4-methylolphenol or 4,4'-methylene bis(2,6-dibutylphenol).

The above mixture of copolymer and oil-soluble chromium salicylate, with or without the added presence of an organic phosphorus compound and/or phenolic antioxidant as defined, when added to a hydrocarbon lubricating oil exhibits a beneficial influence by imparting to the oil or co-acting with it so that the final composition has improved oxidation stability, detergency and wear-inhibiting properties. Hydrocarbon oils thus improved can be natural or synthetic oils having lubricating properties.

The following non-ash forming compositions are representative of the invention:

COMPOSITION A

	Percent wt.
Example XX copolymer	0.001
Cr C_{14-18} alkyl salicylate	0.2
1010 mineral oil	Balance

COMPOSITION B

Example XX copolymer	0.1
Cr C_{14-18} alkyl salicylate	0.1
Tricresyl phosphate	0.8
1010 mineral oil	Balance

COMPOSITION C

Example XIX copolymer	5.5
Cr diisopropyl salicylate	3
Tricresyl phosphate	0.8
4,4'-methylene bis(2,6-ditertbutylphenol)	0.5
Mineral lubricating oil (SAE 10)	Balance

COMPOSITION D

Example I copolymer	4
Cr C_{12-14} alkyl silacylate	2
2,6-ditertbutyl-4-methylolphenol	0.5
Mineral lubricating oil (SAE 10)	Balance

COMPOSITION E

Example I copolymer	4.5
Cr diisobutyl salicylate	1
Mineral lubricating oil (SAE 90)	Balance

Compositions of this invention were tested for their detergency and dispersancy by adding 0.2% carbon black to a test composition and shaking it in a shaking machine for 5 minutes and thereafter noting the time required for the first appearance of agglomeration of the carbon black particles. The test results show that neat mineral oil or mineral oil containing only the polymer or the chromium salt causes agglomeration of the carbon black particles in from 3 to 19 minutes whereas Composition A of the present invention which contains both the polymer and chromium salt shows no sign of carbon settling even after 12 days.

Composition	Settling Time 25° C. (composition containing 0.2% carbon black)
(1) 1010 mineral oil	3 min.
(2) (1)+.001% polymer Example XX	5 min.
(3) (1)+.002% Cr C_{14-18} alkyl salicylate	19 min.
(4) Composition A present invention	12 days.

The additive combinations of this invention are effective in lubricating oils which contain minor amount of other agents which are non-reactive with this combination, such as silicone antifoaming agents, polyacrylate ester viscosity index improvers, and the like.

I claim as my invention:

1. An improved mineral lubricating oil composition

comprising a major amount of mineral lubricating oil and from about 1% to 10% of a copolymer of 2-methyl-5-vinylpyridine, and a mixture of lauryl methacrylate, stearyl methacrylate, and methyl methacrylate, the said copolymer having the vinylpyridine and total acrylate esters in a mol ratio of about 1:10 to 2:1, the amount of the methyl methacrylate being 10 to 45 mol percent of the total acrylate esters, and the copolymer having a molecular weight varying from about 100,000 to 2,000,000 as determined by the light scattering method; and from about .01% to about 5% of oil-soluble chromium C_{8-30} alkyl salicylate.

2. The lubricating oil composition of claim 1 containing a minor amount of an aryl phosphate and an alkyl phenol.

3. The lubricating oil composition of claim 1 containing a minor amount of tricresyl phosphate and 4,4'-methylene bis(2,6-ditert. butyl phenol).

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