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COPOLYMER CONCENTRATE AND OIL COMPOSITION

Charles R. Bearden, Lake Jackson, Tex., assignor to The Dow Chemical Company, Midland, Mich., a corporation of Delaware

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This invention relates to copolymers useful in improving lubricating oils and to lubricating oils containing such copolymers.

The principal use for lubricating oils is in internal combustion engines, the efficiency of which depends to a large degree upon the quality of the crankcase oils employed. A major problem in the operation of internal combustion engines, which may be broadly classified as spark ignition and diesel types, results from the tendency of conventional crankcase oils to undergo oxidation and other chemical changes that lead to the formation of carbon, resins, and insoluble varnish-like gums which deposit on moving engine parts and separate as sludge that markedly impairs the lubricating properties of the oil. Another source of sludge is the decomposition of the fuel and this source is particularly damaging since the deposits occur on piston surfaces and around piston rings. Sludge formation and gum deposition are most severe in light duty engine operation as exemplified by intermittent use of passenger automobiles and light trucks.

Many materials have been added to lubricating oils to improve them and considerable knowledge of such adjuvants has been gained. Some of the specific additives used to improve the properties of lubricating oils are pour point depressants, the viscosity index improvers (VI improvers), and the sludge dispersants and detergents. Lubricating oils have thus been formulated to improve performance with respect to one of these properties, i.e., improved viscosity index or better sludge dispersing or detergent action, and in some cases, lubricating oil additives have been prepared which, when blended with a lubricating oil, provide improvement with respect to two of these properties. For example, certain high molecular weight polymethacrylic copolymers are useful as both pour-point depressants and VI-improvers. Other copolymers, such as those prepared from alkyl methacrylates with N-vinyl-alkyl-oxazolidinone or N-vinylpyrrolidinone are of similar utility. However, among the known lubricating oil additives, there is not one that will improve all the properties of a lubricating oil equally at the same time. No detergent or sludge-dispersant additive for lubricating oils has heretofore been proposed that provides more than a partial answer to the problem of preventing sludge formation and varnish deposition in engines. In fact, known oil detergents in many cases increase the rate of accumulation of inorganic deposits within the combustion chambers of engines.

It is an object of the present invention to provide a copolymer suitable for mixing with lubricating oils.

Another object is to provide a copolymer which, when added to a lubricating oil, greatly improves the dispersant and detergent properties, improves the VI, reduces the pour point, and induces prolonged resistance to sludge and varnish formation. Other objects will appear hereinafter.

It is understood that the term "lubricating oil," as used herein, is to be interpreted broadly as referring to natural and synthetic lubricating oils. These oils are essentially hydrocarbons which possess lubricating properties regardless of their actual viscosity and include crude or refined petroleums, hydrogenated petroleum oils, or hydrogenated cracked petroleum oils, oily high molecular

weight hydrocarbons, such as are obtained by the polymerization of olefins or by the condensation of olefins with aromatic hydrocarbons, etc.

One or more of the above objects are accomplished according to the present invention by copolymerizing at least one alkyl acrylate, or alkyl methacrylate with N-vinyl-3-morpholinone (hereinafter designated VM). While a wide latitude is permissible in choosing the arcylic ester and the proportions thereof in the copolymer, it is essential (1) that the copolymer be oil-soluble, (2) that it contain at least one acrylic ester containing an alkyl radical of at least about 12 carbon atoms, and (3) that it contain sufficient VM to improve its sludge-dispersant properties. To meet the first requirement, it is preferred that the acrylic ester (i.e., the alkyl acrylate or mathacrylate) component consist predominantly of ester or esters wherein the alkyl radical or radicals contain at least 4, and preferably at least 6 carbon atoms. To meet the second requirement, at least about 20 percent, and preferably about 50–80 percent, of the acrylic ester component should contain an alkyl radical of at least 12 carbon atoms. Obviously, the first requirement will often inherently be met in fulfilling the second. The third requirement may be met by the inclusion in the copolymer of only a very small proportion of VM. As little as 3 percent usually produces a very evident improvement in the product, though it is generally necessary to use at least 5 percent or even 10 percent, to achieve optimum results. On the other hand, amounts in excess of about 20 percent are usually uneconomical and over about 30 percent produces little, if any, added improvement. Thus, the preferred copolymers contain about 3–30 percent of VM, the optimum usually being about 10–20 percent.

In view of the above considerations, the acrylic ester component of the copolymer of the invention ordinarily consists of one or more esters having the formula

$$CH_2=C(-(CH_2)_nH)-COOR$$

wherein n is an integer from 0 to 1 and R is an alkyl radical containing about 4 to 20 carbon atoms. Best results are obtained when R is a straight-chain primary alkyl radical. In a preferred embodiment, the acrylic ester component of the copolymer comprises at least one ester wherein R contains 4 to 8 carbon atoms and at least one ester wherein R contains 12–20 carbon atoms.

The copolymers of the invention are preferably prepared by dissolving one or more of the acrylates or methacrylates and VM in a diluent oil and copolymerizing at elevated temperatures under an oxygen-free atmosphere in the presence of a free-radical-producing compound which acts as a catalyst or initiator. Polymerization may also be induced by irradiation under the influence of high energy fields. The latter catalyzation may include the various actinic radiations, including such diverse forms of catalysis as ultraviolet, X-ray and gamma radiations, as well as radiation from radioactive materials and high energy electrons generated from linear accelerators, resonant transformers and the like.

Elevated temperatures are preferred during the course of the reaction in order to decrease the reaction time. Preferably, the temperature range is about 40° to about 90° C., but temperatures either higher or lower may be employed depending upon the catalyst.

The diluent oil is preferably a conventional low sulfur-content oil, such as the paraffinic hydrocarbon or ester type, which is suitable for addition to lubricating oils.

The monomers are suitably employed in such proportions that the diluent wherein they are copolymerized will contain, after polymerization, from about 15 percent to about 60 percent, and preferably about 25 percent to 40 percent of copolymer. All percentages specified

herein are by weight. And while copolymerization directly in a diluent oil of the type stated is the preferred method, other methods may be employed, as for example, polymerizing the monomers in the lubricating oil in which the copolymer is to be used or in an inert volatile hydrocarbon diluent such as hexane or toluene. However, alternate methods such as these are generally less desirable. For example, when a volatile solvent is employed in place of a diluent oil, it must be removed, e.g., by distillation, after the polymerization, and replaced with oil.

When the polymerization is brought about in a diluent oil, the oil containing the copolymer may be considered as a "concentrate" containing the copolymer in the aforesaid amount. The concentrate suitably is incorporated into a lubricating oil to the extent that the copolymer will be in an amount in the range of from about 0.1 percent to about 20 percent and preferably from 3 percent to 8 percent of the lubricating oil.

The following examples illustrate the practice of the present invention.

EXAMPLE 1

Into a reaction vessel equipped with a means for stirring, purging, and temperature control were placed 200 ml. of white mineral oil (180 SUS, Saybolt Universal seconds), 50 ml. of hexyl methacrylate, 60 ml. of lauryl methacrylate, 60 ml. of stearyl methacrylate, 30 ml. of VM and 1 gram of lauryl peroxide. The mixture was maintained at a temperature in the range of from 60° to 80° C. for 18 hours while under a nitrogen atmosphere. At the end of 18 hours, a concentrate of 50 percent copolymer in white mineral oil was obtained.

EXAMPLE 2

Into a reaction vessel equipped with a means for stirring, purging, and temperature control were placed 20.8 pounds of 180 SUS white mineral oil, 2.12 pounds of VM, 3.54 pounds of hexyl methacrylate, 5.1 pounds of lauryl methacrylate, 3.4 pounds of stearyl methacrylate, and 95 g. of lauryl peroxide. The mixture was maintained at a temperature of 63° C. for 15 hours while under a nitrogen atmosphere. At the end of 15 hours a concentrate of 40 percent copolymer in white mineral oil was obtained.

This composition was blended and tested in an engine according to the Co-ordinating Research Council (C.R.C.) FL–2 technique. The blend was made by mixing 1.5 pounds of the above concentrate with 30 pounds of 150 SUS solvent-refined neutral petroleum oil. This produced a petroleum oil containing 2 percent of copolymer. In addition, 0.8 percent of zinc dialkyl dithiophosphate was added as an oxidation inhibitor. The blend had the following properties and give the following results:

	Blend	Base Oil 150 SUS
210° F. viscosity	10.1	6.0
100° F. viscosity	60.4	39.0
Viscosity Index	140	108
Pour Point, °C	−30	−10
Sludge rating	68.4 out of possible 80.	
Varnish rating	15.0 out of possible 20.	

As shown by the above results, the lubricant containing 2 percent copolymer exhibited excellent improvement with regard to dispersant and detergent properties, VI, pour point, and prolonged resistance to sludge and varnish formation. The sludge dispersant characteristic is especially noticeable due to the total sludge rating of 68.4 out of a possible 80 and the varnish rating of 15.0 out of a possible 20. The combined sludge and varnish rating of 83.4 is very high.

EXAMPLE 3

Into a reaction vessel equipped with a means for stirring, purging and temperature control were placed 210 g. of white mineral oil, 9 g. of VM, 27 g. of hexyl methacrylate, 33 g. of lauryl methacrylate, 21 g. of stearyl methacrylate, and 1 g. of lauryl peroxide. The mixture was maintained at a temperature of 65° C. for 18 hours while under a nitrogen atmosphere. At the end of 18 hours a concentrate of 30 percent copolymer in white mineral oil was obtained.

This composition was blended and tested in an engine according to the C.R.C. FL–2 techinque. The blend was prepared by mixing a sufficient amount of the 30 percent copolymer into 150 SUS solvent refined neutral pteroleum oil to produce a 2 percent mixture and in addition, ½ percent of a 50 percent oil blend of zinc diamyl dithiocarbamate, ½ percent of an octylated and styrenated diphenylamine, ½ percent of a zinc dialkyl dithiophosphate, and 0.4 percent of a calcium-organic compound containing combined sulfur, were added as oxidation inhibitors. The blend had the following properties and give the following results:

	Blend	Base Oil 150 SUS
210° F. viscosity	10.3	6.0
100° F. viscosity	61.0	39.0
Viscosity Index	142	108
Pour Point, °C	−33	−10
Sludge rating	67.6 out of possible 80.	
Varnish rating	14.4 out of possible 20.	

EXAMPLE 4

A carbon dispersion test was performed to evaluate the copolymers with regard to their efficiency in improving lubricating oils. A paste was prepared by thoroughly blending 20 percent of carbon black into white mineral oil. For the test, 3 g. of this paste were blended with 70 ml. of kerosene containing 1.5 percent of the compound to be tested. The results are given in Table 1 and it is pointed out that the longer the dispersion stands without settling, the better is the additive. Also, in Table 1, there is a column labeled "wet." Since moisture accumulates in a crankcase and is destructive with regard to the efficieny of the additive, this column shows the result obtained when 0.3 ml. of water was added to the suspension.

Table 1

Product	Days required for Carbon to Settle	
	Dry	Wet
(1) 1.5 percent of copolymer from Example 1	14	14
(2) 1.5 percent of copolymer from Example 2	14	14
(3) 1.5 percent of a neutral barium sulfonate	6	3
(4) 1.5 percent of a calcium sulfonate	6	1
(5) 1.5 percent of a copolymer of 30 percent hexyl methacrylate, 10 percent butyl methacrylate, 40 percent lauryl methacrylate, 20 percent stearyl methacrylate	1	1

EXAMPLE 5

A hexane-insolubles suspension test was performed to further evaluate the polymer with regard to its efficiency in improving lubricating oils. For this test, hexane-insoluble material was obtained from oil oxidized in a Doornte type oxidation machine and these insolubles were washed with hexane, dried and dissolved in benzene in an amount sufficient to form a solution of 2.5 g. per liter. In order to test the ability of the additives to suspend sludge, it was necessary to precipitate the oxidized oil insolubles in the presence of the additives. This was accomplished by mixing 20 ml. of the benzene solution with 10 ml. of a kerosene solution containing

1.5 percent copolymer and heating with stirring. Removal of the benzene was effected in 30 to 40 minutes. Vials of this suspension were then observed and the results obtained are shown in Table 2.

Table 2

Product:	Observation
(1) 1.5 percent of copolymer of Example 1	Clear solution; no sediment.
(2) 1.5 percent of barium sulfonate	Cloudy solution; sediment.
(3) 1.5 percent of calicum sulfonate	Cloudy solution; sediment.
(4) 1.5 percent of a copoylmer like No. 5 of Table 1	Heavy sediment.

I claim:

1. A hydrocarbon lubricating oil having dissolved therein, in an amount to improve the viscosity index thereof, a copolymer of

(a) 3 to 30 percent of N-vinyl-3-morpholinone and

(b) at least one acrylic ester having the formula

$$CH_2=C(-(CH_2)_nH)-COOR$$

wherein n is an integer from 0 to 1 and R is an alkyl radical containing 4 to 20 carbon atoms, at least 20 percent of said copolymer consisting of an acrylic ester as defined above wherein R contains at least 12 carbon atoms, said copolymer being made by the copolymerization of the appropriate monomers under an oxygen-free atmosphere, in the presence of a free-radical-producing initiator, at a temperature of about 40–90° C. and for a time sufficient to effect substantially complete polymerization of said monomers.

2. A lubricating oil as defined in claim **1**, wherein the proportion of copolymer is 0.1 to 20 percent.

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DANIEL E. WYMAN, *Primary Examiner.*

JULIUS GREENWALD, *Examiner.*