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BORON-CONTAINING COPOLYMERS AND LUBRICATING OILS CONTAINING THEM

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This invention relates to novel, oil-soluble boron-containing copolymers, and more particularly to oil-soluble copolymers of unsaturated esters of boronic acids, and to improved lubricants containing these copolymers.

Lubricants for many present-day internal combustion engines are required not only to lubricate and to cool engine parts, but also to maintain the engine parts contacted by the lubricant in clean condition. Uncompounded lubricating oils are frequently found to be less than fully satisfactory with respect to the last-mentioned function, especially under severe operating conditions, in that they permit buildup of carbonaceous deposits that result in part from deterioration of the oil itself, but that result principally from fuel combustion products. These deposits interfere with proper engine functioning. In order to improve the ability of oils to maintain an engine in clean condition, a wide variety of metal-organic compounds (principally alkaline earth metal salts), such as salts of substituted phenols and petroleum sulfonic acids, salicylates, thiophosphoric acids, and carboxylic acids have been proposed. Unfortunately, metal-organic detergents themselves tend to form still other deposits, that is, combustion ash deposits, in the combustion chambers of internal combustion engines upon combustion of oils containing such metal-organic addition agents. Also, the increased corrosion of copper-lead and cadmium-silver bearings that frequently accompanies the use of detergents has been attributed to the cleansing acition of detergents, which prevents deposition on bearings of acid-resistant, protective lacquer deposits.

It has also been proposed to overcome viscosity deficiencies that often appear in uncompounded lubricating oils at high temperatures by incorporating therein small proportions of viscosity index improvers comprising oil-soluble, non-metallic organic polymeric materials. By means of these materials the viscosity of lubricating oils can be maintained relatively constant notwithstanding increases in temperature. However, typical, commercial viscosity index improvement agents exhibit little or no cleansing ability in lubricating oils.

The present invention relates to new copolymers for improving the detergency and viscosity characteristics of hydrocarbon oil lubricants, whereby such lubricants are rendered more suitable for their intended use. It has been found that improved lubricants of the character indicated can be obtained by incorporating therein a small amount of an oil-soluble boron-containing copolymer of monomeric components that each contain a copolymerizable ethylenic linkage, and at least one of which is a boron-free material and contains an oleophilic, saturated aliphatic hydrocarbon substituent containing 8 to 18 and preferably 12 to 18 carbon atoms. Especially good results are obtainable with higher fatty esters of lower, alpha-beta unsaturated monocarboxylic acids, such as acrylic acid or a lower alpha-alkacrylic acid. An example of a preferred boron-free monomer is lauryl methacrylate, but other materials can be used. Another of the monomeric components from which the oil-soluble boron-containing copolymer is derived is a diester of a boronic acid whose boronyl substituent is a saturated aliphatic hydrocarbon radical containing 2 to 18 carbon atoms or an aryl radical, including aralkyl and alkaryl, containing 6 to 18 carbon atoms. Examples of preferred boronyl substituents are the nonyl and phenyl radicals, but the invention is not limited to these particular substituents. For example, the boronyl substituent can be butyl or cyclohexyl or other hydrocarbon radicals as indicated. At least one of the ester substituents of the boronic acid diester is an unsaturated aliphatic hydrocarbon radical containing 2 to 12, and preferably 2 to 4, carbon atoms and an ethylenic linkage that is copolymerizable with the ethylenic linkage of the boron-free monomeric component. A preferred ester substituent is the allyl group, but other substituents of the indicated class are also suitable. The other ester substituent of the boronic acid diester is either a radical of the same class, as is preferred, or another hydrocarbon radical containing 1 to 18 carbon atoms. Exceptionally good results are obtained when the boron-containing copolymers also contain as one of the monomeric components a nitrogenous monomer having an ethylenic linkage that is copolymerizable with the ethylenic linkages of the above-described boron-containing and boron-free monomeric components and having an organic, nitrogenous substituent that has as at least one of its N-substituents a hydrocarbon radical containing 1 to 18 carbon atoms. Especially good results are obtainable with nitrogenous esters of alpha-beta unsaturated monocarboxylic acids and alkylolamines whose alkylol substituents contain not more than 7 carbon atoms. Thus, esters of alkylolamines whose alkylol substituents contain 2 to 4 carbon atoms are effective. An example of a preferred material is di(Oxo-octyl)aminoethyl methacrylate. However, other nitrogenous copolymerizable monomers of the class indicated can be used. The monomeric boron-containing component is present in the copolymers of this invention in weight ratios of about 0.03 to 1:1, with respect to the boron-free monomeric component or components. In the case of the two-component copolymers, the boron-containing and the boron-free monomeric components are preferably employed in weight ratios of about 0.05:1 to 0.75:1. When a nitrogenous monomeric component is additionally included, it is also preferably employed in similar weight ratios as the boron-containing component. Examples of especially advantageous copolymers are the 0.33:1 weight ratio copolymer of diallyl nonylboronate and lauryl methacrylate and the 0.12:0.12:1 weight ratio terpolymer of diallyl nonylboronate, di(Oxo-octyl)aminoethyl methacrylate and lauryl methacrylate, but other copolymers prepared with other monomer weight ratios within the range indicated can be used. Oil-soluble, boron-containing copolymers of the class disclosed herein containing at least 0.03 percent by weight of the herein-disclosed boron-containing monomers will normally be characterized by a boron content of about 0.05 percent to 4 percent by weight. Copolymers containing at least 0.08 percent and preferably about 0.17 percent to 1.75 percent by weight boron have been found to produce excellent results for the purposes of this invention and are therefore preferred. We prefer to employ the herein-disclosed copolymers in hydrocarbon lubricants in proportions of about 0.5 to 5 percent by weight, but other proportions can be used. For example, the copolymers can be employed in amounts of 0.1 to 10 percent or more by weight.

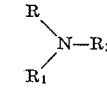
Although it should be emphasized that the invention is not limited to any particular theory of operation, it is considered that the detergency function is at least in part attributable to some sort of selective association between the boronic ester functional structure of the copolymers with sludge particles or perhaps with sludge precursors. To this end the relative proximity of the boron atom to the copolymer chain is advantageous in that the aforesaid aggregates of copolymer and sludge or sludge precur-

sors are rendered relatively more stable to attack by dissociating influences by reason of the shielding or hindrance effect of the polymer chain.

The boron-containing copolymers disclosed herein can be conveniently prepared by causing to react the boron-containing monomer and the boron-free monomer or monomers in the weight ratios indicated herein, in the presence of a diluent, preferably a solvent, such as toluene, benzene, ethyl acetate, or other solvents having similar chain-transfer activity, at a temperature in the range of −75° C. to 150° C., preferably 25° C. to 150° C., in the presence of a few hundredth percent to 2 percent, preferably 0.2 to 1.0 percent, of a free radical catalyst such as benzoyl peroxide, lauroyl peroxide, or alpha,alpha'-azodiisobutyronitrile, preferably in the substantial absence of oxygen, until the rate of formation of larger polymer molecules has declined substantially, usually after about 30 minutes to 35 hours. The time at which the reaction may be terminated is determinable by periodic sampling of the reaction mixture and observing for a decline in the rate of increase in viscosity (or molecular weight) of the mixture. Alternatively, instead of the procedure described above, conventional bulk or dispersion polymerization methods can be used, as can other conventional polymerization catalysts.

The boron-free monomers from which the boron-containing copolymers described herein are derived can be any unsaturated compound containing a copolymerizable, carbon-to-carbon double bond and having an oleophilic extralinear (with respect to the copolymer) substituent containing 8 to 18 carbon atoms, especially 12 to 18 carbon atoms, preferably where at least six of the carbon atoms are in a straight chain. The extralinear substituent can be linked to the polymerizable portion of the monomer molecule through other than a carbon-to-carbon linkage. For example, such substituents can be linked to the polymerizable portion of the monomer molecule through linkages involving nitrogen, oxygen, sulfur, and/or phosphorus, as for example in the case of esters, ethers, or the like. Excellent copolymers are obtainable from higher fatty esters of acrylic or lower alpha-alkacrylic acids, of which lauryl methacrylate is a preferred example. The expression "higher fatty esters" is used in its usual sense to indicate an aliphatic hydrocarbon substituent containing 8 or more carbon atoms. Specific examples of other boron-free monomers useful in the preparation of the herein-described copolymers include other long-chain saturated and unsaturated esters of acrylic or lower alpha-alkacrylic or other copolymerizable, lower, alpha-beta unsaturated monocarboxylic acids, particularly the 3 to 5 carbon atom acids, such as octyl acrylate, oleyl methacrylate, or the lauryl esters of crotonic, tiglic, angelic and senecioic acids, or corresponding esters of alpha-beta unsaturated dicarboxylic acids, such as methyl lauryl fumarate and dioctyl maleate.

Effective copolymers also are obtainable from nitrogenous monomers containing an ethylenic linkage that is copolymerizable with the ethylenic linkage of the boron-containing monomeric components and containing an organic nitrogen-containing substituent group. The organic nitrogen-containing substituent groups of these nitrogenous monomers are characterized by the presence of at least one hydrocarbon N-substituent containing 1 to 18, preferably 8 to 18 carbon atoms. The organic nitrogen-containing substituent group can be associated with the copolymerizable portion of the nitrogenous monomer molecule in various ways. For example, the substituents can be linked to the monomer chain through an ester linkage or in other ways as by salt linkages, including both quaternary ammonium salt and addition salt linkages, as well as those involving dehydrated addition salt, that is, amido, linkages. The preferred nitrogenous monomers are the mono- and di-alkyl aminoalkylol esters of methacrylic acid wherein the alkyl radicals contain 1 to 18 carbon atoms and the alkylol radicals contain 2 to 4 carbon atoms, said alkylaminoalkylol having the general formula



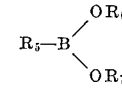
wherein R is selected from the group consisting of hydrogen and alkyl radicals containing 1 to 18 carbon atoms, R_1 is an alkyl radical containing 1 to 18 carbon atoms and R_2 is an alkylol radical containing 2 to 4 carbon atoms. In the above formula, R is preferably hydrogen or an alkyl radical containing 2 to 8 carbon atoms; when R is an alkyl radical containing 2 to 8 carbon atoms, R_1 is preferably an alkyl radical which is the same as R. Specific examples of preferred nitrogenous monomers are isooctylaminoethyl methacrylate and diisooctylaminoethyl methacrylate.

Still other boron-free ethylenically unsaturated monomers that are useful in the preparation of the herein-described copolymers include esters of ethylenically unsaturated alcohols and long-chain fatty acids such as vinyl stearate, vinylphenyl oleate, unsaturated ethers such as vinyl octyl ether and vinyl lauryl ether, unsaturated thioethers such as vinyl lauryl sulfide, and olefins such as 1-octene, 1-nonene and 1-dodecene.

From the hereinabove paragraphs relating to the boron-free monomers, a general formula illustrating the boron-free monomers which can be used in making the polymers of this invention is R_3COOR_4 wherein R_3 is an aliphatic hydrocarbon radical containing 2 to 17 carbon atoms and R_4 is an aliphatic hydrocarbon radical containing 2 to 18 carbon atoms, at least one of said aliphatic hydrocarbon radicals represented in the foregoing formula as R_3 and R_4 containing an ethylenic linkage that is copolymerizable with the corresponding linkage of the boron-containing monomer. In the above formula, R_3 is preferably an alkenyl radical containing 2 to 4 carbon atoms and R_4 is a saturated aliphatic hydrocarbon radical containing 8 to 18, especially 12 carbon atoms.

The boron-containing monomers from which the copolymers disclosed herein can be prepared can be any unsaturated diester of a boronic acid whose boronyl substituent is a saturated aliphatic hydrocarbon radical containing 2 to 18 carbon atoms or an aryl radical containing 6 to 18 carbon atoms and having as at least one ester substituent an aliphatic hydrocarbon radical, including cycloaliphatic radicals, that contain 2 to 12 carbon atoms and that contain an ethylenic linkage that is copolymerizable with that of the boron-free monomeric component, and that has as its other ester substituent either a radical of the same kind or another hydrocarbon radical containing 1 to 18 carbon atoms.

The boron-containing monomers used in making the polymers of this invention are represented by the following general formula



wherein R_5 is selected from the group consisting of saturated aliphatic hydrocarbon radicals containing 2 to 18 carbon atoms and aryl radicals containing 6 to 18 carbon atoms, R_6 is an unsaturated aliphatic hydrocarbon radical containing 2 to 12 carbon atoms and an ethylenic linkage that is copolymerizable with the corresponding linkage of the boron-free monomer, and R_7 is a hydrocarbon radical containing 1 to 18 carbon atoms. In the above formula R_6 and R_7 are preferably like alkenyl radicals containing 2 to 4 carbon atoms.

The aliphatic hydrocarbon ester substituents represented by R_6 and R_7 in the foregoing formula can be unsubstituted or substituted with nonhydrocarbon substituents, such as oxygen, nitrogen, sulfur, halogen or the like, provided that such substituents do not interfere with the co-

polymerization reaction or with the thermal stabilizing properties of the copolymers. Examples of substituents of this kind are the furfuryl radical and alkylaminoalkyl radicals such as the diethylaminoethyl group. Boronic acid esters whose boronyl substituents represented by R_5 in the foregoing formula are saturated aliphatic hydrocarbon radicals, including cycloaliphatic configurations, or aromatic hydrocarbon radicals are preferred, as the presence of these non-copolymerizable radicals tend to minimize excessive cross-linking. Thus, good results are obtainable with boronic acid esters whose boronyl substituents are alkyl radicals such as ethyl or butyl, but we prefer those esters whose boronyl substituents contain 6 to 18 carbon atoms, such as octyl, nonyl, octadecyl, cyclohexyl, methylcyclohexyl, or aryl groups containing the same number of carbon atoms, including alkaryl and aralkyl radicals, such as phenyl, naphthyl, tolyl, dodecylphenyl, benzyl, methylbenzyl, decylbenzyl, or the like. Boronic acid esters can be used having as one ester substituent an unsaturated, copolymerizable radical, particularly alkenyl groups containing 2 to 4 carbon atoms, such as vinyl, allyl, crotyl, or, alternatively a higher alkenyl group such as 1-dodecenyl, or an unsaturated heterocyclic radical such as furfuryl or the like, and having as the other ester substituent either an ethylenically unsaturated hydrocarbon radical of the same kind or some other hydrocarbon radical containing 1 to 18 carbon atoms, such as methyl or butyl, or a radical of the same kind as the boronyl substituent. Preferably, the second ester substituent is a radical like the first-mentioned ester substituent, such as allyl, but this is not necessary. Excellent results are obtainable when the boronyl substituent is nonyl or phenyl, and when the ester substituents are allyl groups, specific examples of such materials being diallyl nonylboronate and diallyl phenylboronate. Examples of other boronic acid diesters are diallyl cyclohexylboronate, divinyl butylboronate, diallyl butylboronate, butyl allyl butylboronate, and dicrotyl nonylboronate.

The herein-described copolymers can be derived not only from the boron-containing and the boron-free unsaturated monomeric compounds described above, but also they can be derived from one or more additional monomeric compounds copolymerizable therewith that may or may not contribute to the oil-solubility or thermal stability-promoting properties of the copolymers, provided that the proportions of these additional monomeric compounds are such as not to diminish significantly the desired thermal stabilizing and minimum oil-solubility properties of the copolymers. Examples of such compounds include ethylenically unsaturated copolymerizable monomers such as vinyl, allyl, and crotyl acetates, butyrates, and the like, ethylene, propylene, 1-butene, styrene, acrylic acid, acrylonitrile, or the like. The preferred copolymers disclosed herein are those in which the boron-containing monomer and the nitrogen-containing monomer, when present, are each present in the ultimate copolymer in weight ratios in the range of about 0.05 to 0.75:1 part by weight of the other boron-free monomeric compound, but copolymers derived from these monomers in other weight ratios can be used, for example, copolymers can be used involving weight ratios in the range of about 0.03 to 1 part by weight of boron-containing to 1 part by weight of boron-free monomer or monomers.

The average molecular weight of the copolymers disclosed herein will normally be greater than about 2,000, and preferably greater than about 7,500, as determined by conventional methods. Usually, the average molecular weight of the copolymers will not exceed about 500,000, but the molecular weights can be greater, provided that they are not so great as to render the copolymers insoluble in the liquid hydrocarbon fuel distillates disclosed herein. Copolymers within the preferred molecular weight range are characterized by intrinsic viscosities in the range of about 0.15 to about 0.75 deciliter per gram.

The copolymers described herein can be incorporated in a wide variety of hydrocarbon lubricating oils. For example, the copolymers can be added to lubricating oils that have been derived from paraffinic, naphthenic, or mixed base crude petroleum oils, and that have been subjected to solvent or sulfuric-acid treatment, aluminum chloride treatment, hydrogenation and/or other refining treatments.

The herein-described copolymers can be incorporated in the hydrocarbon oils in any convenient way. Thus, the copolymers as such can be added directly to the oils in the form of concentrated solutions in solvents such as kerosene or light lubricating oil in order to facilitate blending. If desired, such concentrated solutions also can contain other compatible addition agents designed to improve one or more properties of the oil. In the case of blending lubricating oils, the herein-disclosed copolymers can be added to one of the component oils prior to blending. Some stirring, possibly with mild heating, may be desirable to facilitate more rapid formation of a homogeneous mixture, but this is not absolutely essential.

The herein-disclosed copolymers can be added to the hydrocarbon lubricants in any amount sufficient to improve the detergency characteristics of the oils. The minimum and optimum effective proportions can vary somewhat according to the nature of the particular copolymer, which are not necessarily equivalent in effectiveness. An appreciable improvement will usually be obtained by the use in lubricants of as little as 0.1 percent of the copolymers described herein. A major improvement will normally be obtained by the use of 0.5 to 5 percent of the copolymers, and such proportions are normally preferred. However, in the case of oils requiring relatively greater detergent characteristics, as much as 10 percent or more of the copolymers can be used. The use of the herein-described copolymers in proportions sufficient to improve the detergency of the oils is ordinarily accompanied by an increase in the viscosity index of the oil and may be accompanied by an increase in the bearing corrosion inhibiting characteristics of the oil.

The copolymers of this invention and their preparation are further illustrated by the following specific examples.

EXAMPLE I

A 1:9 weight ratio copolymer of diallyl nonylboronate and lauryl methacrylate was prepared by heating with stirring a mixture of 10 parts by weight of diallyl nonylboronate, 90 parts of lauryl methacrylate, 1 part by weight of alpha,alpha'-azodiisobutyronitrile and 50 parts by volume of toluene for one hour at 70° C. The toluene was then removed by evaporation under reduced pressure. A copolymer prepared as described above had an average molecular weight of 54,000±10 percent and had a boron content of 0.28 percent. The theoretical boron content for the copolymer was 0.43.

EXAMPLE II

A 2.5:7.5 weight ratio copolymer of diallyl nonylboronate and lauryl methacrylate was prepared by heating with stirring a mixture of 57 parts by weight of diallyl nonylboronate, 171 parts by weight of lauryl methacrylate, 2.5 parts by weight of alpha,alpha'-azodiisobutyronitrile, and 114 parts by volume of toluene for one hour at 75° C. The solvent was then removed by vacuum in an evaporator.

Examples of other copolymers prepared similarly as described in the preceding examples are as follows:

EXAMPLE III

Diallyl butylboronate:lauryl methacrylate, 1:9 weight ratio.

EXAMPLE IV

Diallyl butylboronate:lauryl methacrylate, 2:8 weight ratio.

EXAMPLE V

Bis(2-methylbutenyl)butylboronate:lauryl methacrylate, 1:9 weight ratio.

EXAMPLE VI

Bis(2-methylbutenyl)butylboronate:lauryl methacrylate, 2:8 weight ratio.

EXAMPLE VII

Difurfuryl butylboronate:lauryl methacrylate, 1:9 weight ratio.

EXAMPLE VIII

Diallyl nonylboronate:lauryl methacrylate, 1:19 weight ratio.

EXAMPLE IX

Diallyl nonylboronate:lauryl methacrylate, 2:8 weight ratio.

EXAMPLE X

Diallyl nonylboronate:lauryl methacrylate, 3:7 weight ratio.

EXAMPLE XI

Diallyl cyclohexylboronate:lauryl methacrylate, 2:8 weight ratio.

EXAMPLE XII

Diallyl phenylboronate:lauryl methacrylate, 1:9 weight ratio.

EXAMPLE XIII

Diallyl phenylboronate:lauryl methacrylate, 2:8 weight ratio.

EXAMPLE XIV

2-methylbutenyl diethylaminoethyl nonylboronate:-lauryl methacrylate, 1:9 weight ratio.

EXAMPLE XV

Diallyl nonylboronate:vinyl stearate, 2:8 weight ratio.

EXAMPLE XVI

Diallyl nonylboronate:diisooctylaminoethyl methacrylate, 1:1 weight ratio.

EXAMPLE XVII

A 1:1:8 weight ratio terpolymer of diallyl nonylboronate, diisooctylaminoethyl methacrylate and lauryl methacrylate was prepared from a mixture of 25 parts by weight of diallyl nonylboronate, 25 parts by weight of diisooctylaminoethyl methacrylate, 200 parts by weight of lauryl methacrylate, 2.5 parts by weight of alpha,alpha'-azodiisobutyronitrile and 100 parts by volume of toluene. This mixture was heated together for five hours at 76–78° C. To initiate the reaction, the mixture was first heated for 20 minutes at 85–90° C. and the temperature was then decreased to 76° C. At the conclusion of the five-hour period the solvent was removed by flash evaporation.

Examples of other similarly prepared terpolymers are as follows:

EXAMPLE XVIII

Diallyl butylboronate:dissooctylaminoethyl methacrylate:lauryl methacrylate, 1:1:8 weight ratio.

EXAMPLE XIX

Bis(2-methylbutenyl)butylboronate:diisooctylaminoethyl methacrylate:lauryl methacrylate, 1:1:8 weight ratio.

EXAMPLE XX

Diallyl nonylboronate:diethylaminoethyl methacrylate:lauryl methacrylate, 1:1:8 weight ratio.

EXAMPLE XXI

Diallyl nonylboronate:diisooctylaminoethyl methacrylate:lauryl methacrylate, 1:2:7 weight ratio.

EXAMPLE XXII

Diallyl nonylboronate:diisooctylaminoethyl methacrylate:lauryl methacrylate, 2:1:7 weight ratio.

EXAMPLE XXIII

Diallyl cyclohexylboronate:diisooctylaminoethyl methacrylate:lauryl methacrylate, 1:1:8 weight ratio.

EXAMPLE XXIV

Diallyl phenylboronate:diisooctylaminoethyl methacrylate:lauryl methacrylate, 1:1:8 weight ratio.

The foregoing examples are illustrative only, and similar products of the class disclosed can be obtained by the substitution in the foregoing examples of other boron-containing and boron-free monomers disclosed herein in the same or other proportions disclosed herein.

The detergency characteristics, as well as viscosity index improving properties of the copolymers of this invention have been demonstrated by preparing and testing of various compounded lubricating oil compositions containing representative members of the class of copolymers disclosed. Thus, there were prepared and tested separate samples of an SAE 10W lubricating oil containing various proportions of the copolymers of Examples I, II, XVII, and XXII, and the viscosity index and pour point for each of the test samples were measured. Each of the test samples was also subjected to an accelerated test adapted to evaluate the detergency characteristics of the test sample at relatively higher temperatures. In accordance with this test, the oil sample to be tested, preheated to a temperature of about 150° to 165° F. in a reservoir provided with a heating means and an oil splashing means comprising a number of stainless steel wires attached to a rotatable steel shaft, is splashed on the surface of a prepolished and tared aluminum test panel heated to a temperature of 500° F. Air is introduced into the oil reservoir at the rate of 10 liters per hour for the eight-hour test period. At the conclusion of the test, the panel is removed and allowed to drain and cool. After cooling, the test panel is washed free from oil, dried and reweighed. The increase in weight of the panel in milligrams is recorded.

The low temperature detergency characteristics of the herein-disclosed copolymers were also demonstrated by subjecting compounded crankcase lubricating oils containing the above-indicated copolymers to the standard Chevrolet FL–2 engine cleanliness test procedure. The base oil in this test also contained 1.0 percent by weight zinc diicooctyl dithiophosphate and 0.5 percent of a commercial polymethacrylate viscosity index improvent agent (Acryloid 618), neither of which has any appreciable low-temperature detergency characteristics. Briefly, in accordance with the FL–2 test procedure, a standard, six-cylinder Chevrolet automotive engine is operated with the test oil as the crankcase lubricant for 40 hours subsequent to a one-hour warm-up period at a constant speed of 2500±25 r.p.m., under a load of 45±1 B.H.P., with a cooling jacket outlet temperature of 95° F.±5°, an inlet temperature of 85° F.±2°, and a crankcase oil temperature of 165° F.±5°. Performance of the test oil is judged by examination of the engine pistons for deposits. In testing lubricating oils by this procedure a fuel that tends to promote engine deposits is used. At the conclusion of the test period, the engine is disassembled and the pistons are rated on the basis of deposits. The internal engine parts are also given a total varnish rating and a total sludge rating. Each of the above-indicated ratings is then combined in a weighted average to form a total engine cleanliness rating, a rating of 100 being considered perfect.

The make-up of the test samples and the results of the

above-described tests were as indicated in the following table:

Table

Test sample make-up, percent by wt.	Reference Oil A	Reference Oil B	Reference Oil C	Reference Oil D	Ex. I copolymer	Ex. II copolymer	Ex. XVII terpolymer	Ex. XXII terpolymer
SAE 10W Oil Base A	100				97.0			
SAE 10W Oil Base B		100				97.0		
SAE 10W Oil Base C			100				97.0	
SAE 10W Oil Base D				100				97.0
Additives, percent by wt.:								
Example I copolymer					3.0			
Example II copolymer						3.0		
Example XVII terpolymer							3.0	
Example XXII terpolymer								3.0
Inspections—								
Detergency test:								
Temperature, ° F	475	475	475	475	475	475	475	475
Deposit wt., mg	35	85	27	33	2.7	3.1	2.3	0.3
Pour point	0	0	0	15	−15	0	−10	−10
Viscosity index	112	112	112	112	132	137	145	128
Chevrolet FL-2 test:								
Average piston varnish (10 perfect)					3.5	5.5	6.5	6.0
Total varnish (50 perfect)					33.5	36.0	39.0	38.0
Total sludge (50 perfect)					37.0	38.0	37.0	36.0
Total engine rating (100 perfect)					70.5	74.0	76.0	74.0
Nos. improvement					1	6	7	5

Comparison of the results obtained with the reference oils and with the compounded test oils indicates that the copolymers of this invention produced an appreciable improvement in the detergency characteristics of hydrocarbon lubricating oils and that such copolymers also exert a marked pour point depressant and viscosity index improvement effect upon the base oils. Comparison of the improvements obtained by the various copolymers indicates that especially good detergency characteristics are obtained when the boron-containing monomer is present in the copolymer in a weight ratio with respect to the boron-free monomer of at least 0.25:1 and also when the copolymer contains a nitrogenous boron-free monomer. Not only did the copolymers of the invention produce an improvement in the viscosity index of the base oil, as shown by the data presented in the preceding table, but also these copolymers exhibited good resistance to shear when oils containing the same were subjected to sonic and ultrasonic shear stability tests.

The specific embodiments set forth above are illustrative only and similar improvements in detergency, viscosity index and/or pour point can be obtained by the use in the base oils of the preceding embodiments or other base oils disclosed herein of the same or equivalent proportions of other copolymers of the class disclosed herein.

While the boron-containing copolymers of this invention have been described with particular reference to their ability to improve detergency, viscosity index, and pour point characteristics in hydrocarbon lubricants, it may also be noted that the copolymers have also been found to improve the thermal stability of hydrocarbon fuels boiling in the combustion gas turbine fuel range, particularly aviation turbine fuels.

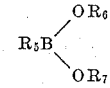
It will be understood that there can also be added to the compounded lubricants of this invention other improvement agents that are capable of improving the oils in one or more respects. Thus, there can be added to the lubricant compositions of this invention antioxidants, bloom control agents, dyes, antifoam agents, rust and corrosion inhibitors, antiwear agents, other detergents, viscosity index improvement agents and pour point reducing agents, and soaps or other thickening agents.

The expression "isooctyl" is used herein to denote the mixed branched-chain isomeric C_8 radicals, mostly dimethylhexyl, derived from Oxo-octyl alcohol, a mixture of isomeric branched-chain octyl alcohols prepared by the Oxo-synthesis process.

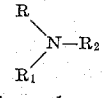
Numerous modifications and variations of the invention as herein set forth can be resorted to without departing from the spirit or scope of the invention. Accordingly, only such limitations should be imposed as are indicated in the claims appended hereto.

I claim:

1. An oil-soluble boron-containing copolymer having an average molecular weight greater than about 2,000 consisting of monomeric components each containing a copolymerizable ethylenic linkage and at least one of which monomeric components is a boron-free monomer having the formula R_3COOR_4 wherein R_3 is an aliphatic hydrocarbon radical containing 2 to 17 carbon atoms and R_4 is an aliphatic hydrocarbon radical containing 2 to 18 carbon atoms, at least one of said aliphatic hydrocarbon radicals identified as R_3 and R_4 containing an ethylenic linkage that is copolymerizable with the corresponding linkage of the boron-containing monomer; where another of said monomeric components is a boron-containing monomer having the formula



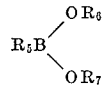
wherein R_5 is selected from the group consisting of saturated aliphatic hydrocarbon radicals containing 2 to 18 carbon atoms and aryl radicals containing 6 to 18 carbon atoms, R_6 is an unsaturated aliphatic hydrocarbon radical containing 2 to 12 carbon atoms and an ethylenic linkage that is copolymerizable with the corresponding linkage of said boron-free monomer and R_7 is a hydrocarbon radical containing 1 to 18 carbon atoms; and where another of said monomeric components is a nitrogenous monomer selected from the group consisting of mono- and di-alkyl aminoalkylol esters of methacrylic acid, said alkylaminoalkylol having the formula



wherein R is selected from the group consisting of hydrogen and alkyl radicals containing 1 to 18 carbon atoms, R_1 is an alkyl radical containing 1 to 18 carbon atoms and R_2 is an alkylol radical containing 2 to 4 carbon atoms; said boron-containing monomer and said nitrogenous monomer each being present in the copolymer in a weight ratio of about 0.03 to 1:1 with respect to said boron-free monomer.

2. An oil-soluble boron-copolymer having an average molecular weight greater than about 2,000 consisting of monomeric components each containing a copolymerizable ethylenic linkage and at least one of which monomeric components is a boron-free monomer having the formula R_3COOR_4 wherein R_3 is an alkenyl radical containing 2 to 4 carbon atoms and R_4 is a saturated aliphatic

hydrocarbon radical containing 8 to 18 carbon atoms; where another of said monomeric components is a boron-containing monomer having the formula



wherein R_5 is selected from the group consisting of saturated aliphatic hydrocarbon radicals containing 2 to 18 carbon atoms and aryl radicals containing 6 to 18 carbon atoms, R_6 and R_7 are like alkenyl radicals containing 2 to 4 carbon atoms; and where another of said monomeric components is a nitrogenous monomer consisting of a dialkylaminoalkylol ester of methacrylic acid, said dialkylaminoalkylol having the formula



wherein R and R_1 are like alkyl radicals containing 2 to 8 carbon atoms and R_2 is an alkylol radical containing 2 to 4 carbon atoms; said boron-containing monomer and said nitrogenous monomer each being present in the copolymer in a weight ratio of about 0.05:1 to 1:1 with respect to said boron-free monomer.

3. The copolymer of claim 2 where said boron-free monomer is lauryl methacrylate, where said boron-containing monomer is diallyl nonylboronate and where the nitrogenous monomer is diisooctylaminoethyl methacrylate.

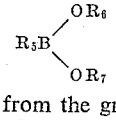
4. The copolymer of claim 2 where the boron-free monomer is lauryl methacrylate, where said boron-containing monomer is diallyl butylboronate and where the nitrogenous monomer is diisooctylaminoethyl methacrylate.

5. The copolymer of claim 2 where said boron-free monomer is lauryl methacrylate, where said boron-containing monomer is diallyl nonylboronate and where the nitrogenous monomer is diethylaminoethyl methacrylate.

6. The copolymer of claim 2 where said boron-free monomer is lauryl methacrylate, where said boron-containing monomer is diallyl cyclohexylboronate and where the nitrogenous monomer is diisooctylaminoethyl methacrylate.

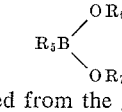
7. The copolymer of claim 2 where said boron-free monomer is lauryl methacrylate, where said boron-containing monomer is diallyl phenylboronate and where the nitrogenous monomer is diisooctylaminoethyl methacrylate.

8. An oil-soluble boron-containing copolymer having an average molecular weight greater than about 2,000 consisting of monomeric components each containing a copolymerizable ethylenic linkage and at least one of which monomeric components is a boron-free monomer having the formula R_3COOR_4 wherein R_3 is an aliphatic hydrocarbon radical containing 2 to 17 carbon atoms and R_4 is an aliphatic hydrocarbon radical containing 2 to 18 carbon atoms, at least one of said aliphatic hydrocarbon radicals identified as R_3 and R_4 containing an ethylenic linkage that is copolymerizable with the corresponding linkage of the boron-containing monomer; and where another of said monomeric components is a boron-containing monomer having the formula



wherein R_5 is selected from the group consisting of saturated aliphatic hydrocarbon radicals containing 2 to 18 carbon atoms and aryl radicals containing 6 to 18 carbon atoms, R_6 is an unsaturated alipahtic hydrocarbon radical containing 2 to 12 carbon atoms and an ethylenic linkage that is copolymerizable with the corresponding linkage of said boron-free monomer, and R_7 is a hydrocarbon radical containing 1 to 18 carbon atoms; said boron-containing monomer being present in the copolymer in a weight ratio of about 0.03 to 1:1 with respect to said boron-free monomer.

9. An oil-soluble boron-containing copolymer having an average molecular weight greater than about 2,000 consisting of monomeric components each containing a copolymerizable ethylenic linkage and at least one of which monomeric components is a boron-free monomer having the formula R_3COOR_4 wherein R_3 is an alkenyl radical containing 2 to 4 carbon atoms and R_4 is a saturated aliphatic hydrocarbon radical containing 8 to 18 carbon atoms; and where another of said monomeric components is a boron-containing monomer having the formula



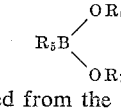
wherein R_5 is selected from the group consisting of saturated aliphatic hydrocarbon radicals containing 2 to 18 carbon atoms and aryl radicals containing 6 to 18 carbon atoms, R_6 and R_7 are like alkenyl radicals containing 2 to 4 carbon atoms; said boron-containing monomer being present in the copolymer in a weight ratio of about 0.05:1 to 0.75:1 with respect to said boron-free monomer.

10. The copolymer of claim 9 where said boron-free monomer is lauryl methacrylate and said boron-containing monomer is diallyl nonylboronate.

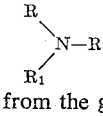
11. The copolymer of claim 9 where said boron-free monomer is lauryl methacrylate and said boron-containing monomer is diallyl butylboronate.

12. The copolymer of claim 9 where said boron-free monomer is lauryl methacrylate and said boron-containing monomer is diallyl phenylboronate.

13. A lubricant composition comprising a major amount of a hydrocarbon lubricating oil and a small amount, sufficient to improve the detergent characteristics of said oil, of an oil-soluble boron-containing copolymer having an average molecular weight greater than about 2,000 consisting of monomeric components each containing a copolymerizable ethylenic linkage and at least one of which monomeric components is a boron-free monomer having the formula R_3COOR_4 wherein R_3 is an aliphatic hydrocarbon radical containing 2 to 17 carbon atoms and R_4 is an aliphatic hydrocarbon radical containing 2 to 18 carbon atoms, at least one of said aliphatic hydrocarbon radicals identified as R_3 and R_4 containing an ethylenic linkage that is copolymerizable with the corresponding linkage of the boron-containing monomer; where another of said monomeric components is a boron-containing monomer having the formula



wherein R_5 is selected from the group consisting of saturated aliphatic hydrocarbon radicals containing 2 to 18 carbon atoms and aryl radicals containing 6 to 18 carbon atoms, R_6 is an unsaturated aliphatic hydrocarbon radical containing 2 to 12 carbon atoms and an ethylenic linkage that is copolymerizable with the corresponding linkage of said boron-free monomer, and R_7 is a hydrocarbon radical containing 1 to 18 carbon atoms; and where another of said monomeric components is a nitrogenous monomer selected from the group consisting of mono- and di-alkyl aminoalkylol esters of methacrylic acid, said alkylaminoalkylol having the formula

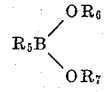


wherein R is selected from the group consisting of hydrogen and alkyl radicals containing 1 to 18 carbon atoms, R_1 is an alkyl radical containing 1 to18 carbon atoms and R_2 is an alkylol radical containing 2 to 4 carbon atoms; said boron-containing monomer and said nitrog-

enous monomer each being present in the copolymer in a weight ratio of about 0.03 to 1:1 with respect to said boron-free monomer.

14. The lubricant composition of claim 13 where said small amount is 0.1 to 10 percent by weight of the composition.

15. A lubricant composition comprising a major amount of a hydrocarbon lubricating oil and a small amount, sufficient to improve the detergent characteristics of said oil, of an oil-soluble boron-containing copolymer having an average molecular weight greater than about 2,000 consisting of monomeric components each containing a copolymerizable ethylenic linkage at least one of which monomeric components is a boron-free monomer having the formula R_3COOR_4 wherein R_3 is an alkenyl radical containing 2 to 4 carbon atoms and R_4 is a saturated aliphatic hydrocarbon radical containing 8 to 18 carbon atoms; where another of said monomeric components is a boron-containing monomer having the formula



wherein R_5 is selected from the group consisting of saturated aliphatic hydrocarbon radicals containing 2 to 18 carbon atoms and aryl radicals containing 6 to 18 carbon atoms, R_6 and R_7 are like alkenyl radicals containing 2 to 4 carbon atoms; and where another of said monomeric components is a nitrogenous monomer consisting of a dialkylaminoalkylol ester methacrylic acid, said dialkylaminoalkylol having the formula



wherein R and R_1 are like alkyl radicals containing 2 to 8 carbon atoms and R_2 is an alkylol radical containing 2 to 4 carbon atoms; said boron-containing monomer and said nitrogenous monomer each being present in the copolymer in a weight ratio of about 0.05:1 to 1:1 with respect to said boron-free monomer.

16. The lubricant composition of claim 15 where said boron-free monomer is lauryl methacrylate, where said boron-containing monomer is diallyl nonylboronate, and where the nitrogenous monomer is diisooctylaminoethyl methacrylate.

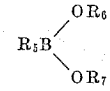
17. The lubricant composition of claim 15 where the boron-free monomer is lauryl methacrylate, where said boron-containing monomer is diallyl butylboronate and where the nitrogenous monomer is diisooctylaminoethyl methacrylate.

18. The lubricant composition of claim 15 where the boron-free monomer is lauryl methacrylate, where said boron-containing monomer is diallyl nonylboronate and where the nitrogenous monomer is diethylaminoethyl methacrylate.

19. The lubricant composition of claim 15 where the boron-free monomer is lauryl methacrylate, where said boron-containing monomer is diallyl phenylboronate and where the nitrogenous monomer is diisooctylaminoethyl methacrylate.

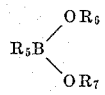
20. A lubricant composition comprising a major amount of a hydrocarbon lubricating oil and a small amount, sufficient to improve the detergent characteristics of said oil, of an oil-soluble boron-containing copolymer having an average molecular weight greater than about 2,000 consisting of monomeric components each containing a copolymerizable ethylenic linkage and at least one of which monomeric components is a boron-free monomer having the formula R_3COOR_4 wherein R_3 is an aliphatic hydrocarbon radical containing 2 to 17 carbon atoms and R_4 is an aliphatic hydrocarbon radical containing 2 to 18 carbon atoms, at least one of said aliphatic hydrocarbon radicals identified as R_3 and R_4 containing

an ethylenic linkage that is copolymerizable with the corresponding linkage of the boron-containing monomer; and where another of said monomeric components is a boron-containing monomer having the formula



wherein R_5 is selected from the group consisting of saturated aliphatic hydrocarbon radicals containing 2 to 18 carbon atoms and aryl radicals containing 6 to 18 carbon atoms, R_6 is an unsaturated aliphatic hydrocarbon radical containing 2 to 12 carbon atoms and an ethylenic linkage that is copolymerizable with the corresponding linkage of said boron-free monomer, and R_7 is a hydrocarbon radical containing 1 to 18 carbon atoms; said boron-containing monomer being present in the copolymer in a weight ratio of about 0.03 to 1:1 with respect to said boron-free monomer.

21. A lubricant composition comprising a major amount of a hydrocarbon lubricating oil and a small amount, sufficient to improve the detergent characteristic of said oil, of an oil-soluble boron-containing copolymer having an average molecular weight greater than about 2,000 consisting of monomeric components each containing a copolymerizable ethylenic linkage and at least one of which monomeric components is a boron-free monomer having the formula R_3COOR_4 wherein R_3 is an alkenyl radical containing 2 to 4 carbon atoms and R_4 is a saturated aliphatic hydrocarbon radical containing 8 to 18 carbon atoms; and where another of said monomeric components is a boron-containing monomer having the formula



wherein R_5 is selected from the group consisting of saturated aliphatic hydrocarbon radicals containing 2 to 18 carbon atoms and aryl radicals containing 6 to 18 carbon atoms, R_6 and R_7 are like alkenyl radicals containing 2 to 4 carbon atoms; said boron-containing monomer being present in the copolymer in a weight ratio of about 0.05:1 to 0.75:1 with respect to said boron-free monomer.

22. The lubricant composition of claim 21 where said boron-free monomer is lauryl methacrylate and said boron-containing monomer is diallyl nonylboronate.

23. The lubricant composition of claim 21 where said boron-free monomer is lauryl methacrylate and said boron-containing monomer is diallyl butylboronate.

24. The lubricant composition of claim 21 where said boron-free monomer is lauryl methacrylate and said boron-containing monomer is diallyl phenylboronate.

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