United States Patent Office 2,737,496 Patented Mar. 6, 1956

2,737,496

LUBRICATING OIL COMPOSITIONS CONTAINING POLYMERIC ADDITIVES

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No Drawing. Application February 16, 1952, Serial No. 271,977

8 Claims. (Cl. 252—51.5)

This invention relates to lubricants and, more particularly, to new lubricating oil compositions of improved properties. The present application is a continuation-in-part of applicant's copending application Serial No. 214,853, filed March 9, 1951, now abandoned.

The principal market for lubricating oils is in internal combustion engines the efficiency of which depends to a large degree on the quality of the crankcase oils employed. A major problem in the operation of both spark ignition and diesel engines 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 that deposit on moving engine parts and separate as sludge that markedly impairs the lubricating properties of the oil. A major contribution to the sludge may also arise from decomposition of the fuel. Deposition of sludge on piston surfaces and around piston rings is particularly damaging. It is known that sludge formation and gum deposition are especially 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. However, no detergent or sludge dispersant additive for oils has heretofore been proposed that provides more than a partial answer to the problem of preventing sludge formation and varnish deposition in engines. Moreover, known oil detergents in many cases increase the rate of accumulation of inorganic deposits within the combustion chambers of internal combustion engines.

An object of the present invention is to provide improved lubricating oil compositions. A further object is to provide dispersive lubricating oil compositions having superior resistance to sludge formation and varnish deposition in internal combustion engines. A still further object is to provide such lubricating oil compositions having a low rate of change of viscosity with temperature. Other objects will be apparent from the description of the invention given hereinafter.

The above objects are accomplished according to the present invention by incorporating in a lubricating oil at least 0.1% by weight of the lubricating oil, of an oil-soluble, basic amino nitrogen-containing addition-type polymer of a plurality of polymerizable ethylenically unsaturated compounds, at least one of which is amino-free and contains from 8 to about 18 carbon atoms in an aliphatic hydrocarbon chain, which in the polymer is not part of the main polymer chain, preferably predominantly straight chain in nature, and one of which as it exists in the polymer contains a basic amino nitrogen in the side chain, said polymer containing 0.1% to 3.5%, by weight thereof, of basic amino nitrogen.

The optimum proportion of polymer in the lubricating oil will be determined by its inherent viscosity, which can be within the range of 0.1 to 3.0 as determined at 0.1% weight/volume concentration in benzene at 25° C., and

will range between 0.1% and 20% by weight of the lubricating oil. From a practical point of view, 0.25% to 10% of the polymer additive having an inherent viscosity between about 0.2 and 1.0 normally will be found to give optimum results.

Although the mechanism by which the lubricant compositions of this invention operate is not known, experimental work both in laboratory and engine tests has established certain basic requirements for the addition-type polymers as regards compositions, structure, and physical properties. For example, it is essential that at least one of the monomeric components employed in making the polymer should introduce an oil-solubilizing or oleophilic structure to insure that the polymer is soluble to the extent of at least 0.1% by weight in naphthenic, paraffinic, or ester type lubricating oils. In addition, the presence of basic amino groups, either primary, secondary, or tertiary, is necessary to impart the unique sludge dispersing properties which characterize these polymers. The proportion of basic amino nitrogen is best expressed in weight percent based on the total copolymer, and should be within the range of 0.1% to 3.5%. Introduction of the basic amino nitrogen structure can be accomplished by the use of at least one monomeric component containing the amino group or by use of a monomer containing a group which is reactive, when present in the polymer, toward ammonia, or primary or secondary nonaromatic amines. These monomers can also contain oleophilic structures that will assist in contributing to the requisite oil solubility. In addition, some of the polymers coming within the scope of this invention can, without sacrificing either oil solubility or dispersing properties, include certain proportions of monomers that do not themselves yield oil soluble polymers.

Copolymers useful in the practice of the invention can be prepared by conventional bulk, solution, or dispersion polymerization methods involving known initiators, including oxygen-yielding compounds, such as benzoyl peroxide, and azo compounds, such as alpha, alpha'-azodiisobutyronitrile. The polymerization processes usually are carried out in an inert atmosphere, e. g., nitrogen or carbon dioxide, at temperatures ranging from 30° C. to 150° C., depending on the catalyst used, and generally at temperatures between 50° C. and 70° C. when alpha,alpha'-azodiisobutyronitrile is used as the catalyst. It is important to carry the copolymerization substantially to completeness so that no unpolymerized monomers remain and the proportions of each component in the final product are essentially those of the original monomer mixture.

The following examples wherein all parts are by weight unless otherwise stated, illustrate typical polymers adapted for use in the present invention.

EXAMPLE I

47.5 parts of n-octyl methacrylate, 2.5 parts of beta-diethylaminoethyl methacrylate, and 0.25 part of alpha, alpha'-azodiisobutyronitrile were heated together in a polymerization reactor under an atmosphere of oxygen-free nitrogen at 58±3° C. for 18 hours, stirring being effected by bubbling a stream of nitrogen through the polymerization mixture. There was thus obtained an oil soluble, tacky, resinous copolymer of the two polymerizable components in essentially the proportions charged, i. e., 95/5.

EXAMPLE II

1020 parts of technical lauryl methacrylate, 100 parts of methacrylanilide, 60 parts of beta-diethylaminoethyl methyacrylate, 300 parts of mineral oil and 3.6 parts of alpha,alpha'-azodiisobutyronitrile were agitated together at 60±2° C. under nitrogen. After two hours some thickening of the charge was observed and during

the next 16 hours, 900 parts more of mineral oil was added gradually as the polymerization proceeded. There was thus obtained a barely stirrable oil solution of a copolymer of the three polymerizable components in essentially the proportions charged, i. e., 86.4/8.5/5.1.

The technical lauryl methacrylate used in the preparation above is the methacrylic acid ester of technical lauryl alcohol which is obtained by reduction of the fatty acids of coconut oil and is a mixture of saturated straight chain alcohols ranging from about 10 to 18 carbon atoms. A typical example will contain approximately 3% C_{10}, 61% C_{12}, 23% C_{14}, 11% C_{16} and 2% C_{18} alcohols.

EXAMPLE III

170 parts of technical lauryl methacrylate, 20 parts of methacrylanilide (N-phenylmethacrylamide), 10 parts of glycidyl methacrylate and 1.2 parts of alpha,alpha'-azodiisobutyronitrile were heated together in a polymerization reactor for 8 hours at 65° C., as in Example I. The 85/10/5 lauryl methacrylate/methacrylanilide/glycidyl methacrylate copolymer thus obtained was removed from the polymerization reactor and thoroughly mixed with twenty-two parts of technical diamylamine (2 molar proportions based on the copolymer) by careful milling on a two-roll rubber mill. The resultant mixture was placed in a closed container and warmed for 24 hours at about 60° C. to complete the reaction of the amine with the epoxide structures in the polymer. This reaction involves scission of the oxirane rings in the glycidyl methacrylate units by the diamylamine to give units containing gamma-diamylamino-beta-hydroxypropyl radicals as more fully disclosed in application Serial No. 176,918, filed July 31, 1950, now abandoned, in the name of M. E. Cupery, assigned to the assignee of this application. The final product is thus a lauryl methacrylate/methacrylanilide/gamma-diamylamino - beta - hydroxypropyl methacrylate copolymer.

EXAMPLE IV

90 parts of technical lauryl methacrylate and 10 parts of glycidyl methacrylate were copolymerized as in Example II by heating at 60° C. for 24 hours in solution in 100 parts of highly refined petroleum white oil in the presence of 0.6 part of alpha,alpha'-azodiisobutyronitrile. To the oil solution of the copolymer thus obtained there was then added 9.4 parts of technical diamylamine (0.85 molar proportion based on the copolymer) and the mixture was heated to 80° C. for about 1 hour to effect reaction of the diamylamine with the oxirane rings in the glycidyl methacrylate units in the copolymer in the manner explained in Example III, to obtain a white oil solution of a lauryl methacrylate/glycidyl methacrylate/gamma-diamylamino-beta-hydroxypropyl methacrylate copolymer.

EXAMPLE V

A mixture of 19 parts of vinyl laurate, 1 part of allyl glycidyl ether and 0.12 part of alpha,alpha'-azodiisobutyronitrile was heated for 6 hours at 65° C. as in Example III. To the resulting 95/5 vinyl laurate/allyl glycidyl ether copolymer was added 1.1 parts of technical diamylamine and the reaction mixture allowed to stand for several days at room temperature. There was thus obtained an oil-soluble vinyl laurate/allyl glycidyl ether/allyl gamma - diamylamino - beta - hydroxypropyl ether copolymer.

EXAMPLE VI

A pressure-resistant reaction vessel was charged with 20 parts of beta-diethylaminoethyl methacrylate, 50 parts of 2-ethylhexyl acrylate and 0.5 part of alpha,alpha'-azodiisobutyronitrile. The vessel was closed, flushed with nitrogen and evacuated, pressured with isobutylene under 3000 atmospheres pressure, and heated with agitation for 4 hours at about 65° C. The reactor was then cooled, vented to the atmosphere and the resinous product removed. There was thus obtained a 69/16.4/14.6 2-ethylhexyl acrylate/beta-diethylaminoethyl methacrylate/isobutylene copolymer as an oil-soluble, viscous, tacky resin.

Another copolymerization reaction was carried out as above, with 40 parts of lauryl methacrylate, 10 parts of beta-dimethylaminoethyl methacrylate, 50 parts of benzene, 0.5 part of alpha,alpha'-azodiisobutyronitrile and ethylene under 1000 atmospheres pressure. There was thus obtained a 64/18/18 lauryl methacrylate/beta-dimethyl-aminoethyl methacrylate/ethylene copolymer as an oil-soluble, viscous, tacky resin.

EXAMPLE VII

80 parts of sec.-capryl methacrylate (B. P. 70–72° C./0.5–0.7 mm. of mercury), prepared by ester interchange of sec.-capryl alcohol with methyl methacrylate in the presence of tetraisopropyl titanate as catalyst (as was fully disclosed in application Serial No. 256,373, filed November 14, 1951, in the name of J. H. Haslam and assigned to the assignee of the present application), 20 parts of beta-diethylaminoethyl methacrylate and 0.5 part of alpha,alpha'-azodiisobutyronitrile were heated together for 5 hours at 65° C. in the manner of Example III above. There was thus obtained an 80/20 sec.-capryl methacrylate/beta-diethylaminoethyl methacrylate copolymer as an oil-soluble, soft, sticky, rubbery resin.

EXAMPLE VIII

100 parts of tridecyl methacrylate from a commercially available, branched-chain primary tridecyl alcohol, 40 parts of beta-diethylaminoethyl methacrylate, 60 parts of styrene and 1 part of alpha,alpha'-azodiisobutyronitrile were heated for 20 hours at 65° C. in the manner of Example III. There was thus obtained a 50/20/30 tridecyl methacrylate/beta-diethylaminoethyl methacrylate/styrene copolymer as an oil-soluble, rather stiff, rubbery resin.

EXAMPLE IX

A mixture of 180 parts of lauryl methacrylate, 14.5 parts of N-(beta-vinyloxyethylformamide) (B. P. 87° C./0.9 mm. mercury, prepared by the aminolysis of methyl formate with beta-vinyloxyethyl amine as disclosed in application Serial No. 269,339, filed January 31, 1952, now abandoned, in the name of John C. Sauer and assigned to the assignee of the present application), and 1 part of alpha,alpha'-azodiisobutyronitrile were heated for 4 hours at 65° C. in the manner of Example III. There was thus obtained a lauryl methacrylate/N-(beta-vinyloxyethyl)formamide copolymer as an oil-soluble, clear, tacky, rubber-like resin.

EXAMPLE IX-A

To a solution of 90 parts of the above lauryl methacrylate/N-(beta-vinyloxyethyl)formamide copolymer in about 400 parts of benzene was added 110 parts of 18% aqueous hydrochloric acid and the resulting mixture heated at a gentle reflux for one hour with stirring. The resulting creamy emulsion was treated with an excess of 20% aqueous sodium hydroxide solution and the organic layer thereby obtained removed, washed well with water and any retained benzene-water removed by evaporation at steam bath temperatures under atmospheric pressure and finally under reduced pressure. There was thus obtained an oil-soluble, highly viscous, tacky copolymer which upon analysis was found to contain 0.25% primary amino nitrogen, indicating the presence of 1.4% combined beta-vinyloxyethyl amine groups.

EXAMPLE X

A branched chain ar-dodecylstyrene was prepared by acetylation of a commercial mixture of detergent intermediate type, branched chain dodecylbenzenes with acetyl chloride in the presence of aluminum chloride, selective catalytic hydrogenation of the resulting ketone with nickel catalyst, and dehydration of the carbinol by refluxing with xylene containing iodine. 9 parts of the ar-dodecyl-

styrene fraction (B. P. 135–140° C./4 mm. of mercury), 1 part of beta-diethylaminoethyl methacrylate and 0.07 part of alpha,alpha'-azodiisobutyronitrile were heated for 5 hours at 65° C. There was obtained a 90/10 ardodecylstyrene/beta-diethylaminoethyl methacrylate copolymer as an oil-soluble, highly viscous product, tacky at room temperature.

The polymer additives used in preparing the dispersive lubricating compositions of this invention can be incorporated in the lubricating oils by simply blending with stirring at ordinary temperature or, if desired, a mixture of the oil and the additive polymer or polymers can be heated to elevated temperatures, e. g., 100–130° C. with agitation. In many instances it is convenient to carry out the preparation of the additive polymer directly in solution in a lubricating oil since the addition of such solutions to lubricating oils to obtain the desired concentration offers a ready method of incorporating the additive polymer in the lubricating oil.

The concentration of the additive polymer used in the lubricating oil will not normally be less than 0.1%, nor exceed 20% by weight of the oil. However, master batches containing 50% or higher of the additive polymers by weight of the oil may be made for convenience in handling prior to preparation of large batches of the lubricant compositions. Thus, a 50% solution of one or more of the additive polymers in a lubricating oil will serve by direct addition to further quantities of the base oil to produce approximately a 50-fold larger batch of the final lubricating composition. The lubricating oils may contain in addition to the herein considered polymers conventional modifiers (in solution or suspension) which impart other desirable characteristics to the oil, e. g., antioxidants, corrosion inhibitors, and the like.

Although the preferred compositions of this invention comprise the lubricating compositions made up from oils boiling at about 345° C. or above at 1 atm. pressure, the same additive polymers can be added to power converting fluids such as used in automatic transmissions, particularly those of SAE–20 to 30 grade oil, torque converters, and the like, as well as to hydraulic oils, turbine oils and other such oils, and similarly impart to these other oils the same desirable dispersive, sludge suspending characteristics.

Probably the most important problem currently remaining in the lubricating field is the question of sludge formation and deposition on important working areas in internal combustion engines, particularly under the operating conditions in ordinary stop and go driving. This type of operation, which is typical for urban passenger cars, and in door to door and other similar light driving services, accounts for perhaps as much as three-quarters of all internal combustion engine operations today. This type of operation entails a considerable proportion of starting, idling, constant shifting with resultant changes in load and torque ratios and short term operating at relatively higher engine speeds, and, in almost all instances, involves operation with the crankcase lubricant at relatively low temperatures. This type of engine operation will be referred to as low-duty operation. Varnish and sludge which form under such low-duty operating conditions have characteristic peculiarities which distinguish them from the varnish and sludge formed under heavy-duty conditions such as exist for internal combustion engines in heavily loaded trucks, tractors, and the like. Consequently, commercial lubricating oil additives, which have been designed for, and operate with moderate success in solving these problems for heavy-duty engine operation, are relatively ineffective in low-duty operation, even when used at higher concentrations which are obviously less desirable from the cost standpoint. Actually, insofar as known, no successful solution to these problems for low-duty operation has yet been taught.

To evaluate in the laboratory under control conditions the suitability of lubricating compositions for this important low-duty operation, a special test has been developed to simulate those conditions. This test is similar to a variety of tests employed in the oil industry for the same purposes, and is itself employed by oil companies to a considerable extent because of its superior correlation with results obtained on the road in actual long-term service tests. As will be seen from the data presented in the table below which are discussed in detail there, this test clearly demonstrates the need of a lubricating composition which at reasonable concentrations will promote engine cleanliness under low-duty operation, the ineffectiveness of the presently available materials under these conditions, and, finally, the outstanding behavior of lubricating compositions of this invention containing the oleophilic, basic amino nitrogen-containing addition-type polymers.

This test is carried out using a standard Chevrolet passenger car engine which has been modified so that piston ring land corners are beveled and three of the six oil rings have slots which are only half the normal width to promote oil ring clogging. The various oils are tested as lubricants in clean Chevrolet engines modified as above by operating the engine for two-hour periods under conditions designed to simulate each of the normally encountered driving conditions, i. e., idling, high load-low temperature (as in the period following start-up or in cold weather), and high load-high temperature (as in continued operation). These periods are repeated successively for a total of 96 hours. Specific conditions for the three types of operation are as follows:

	Idling	High Load-Low Temperature	High Load-High Temperature
Speed, R. P. M.	500	2,500	2,500
Load, Brake-Horsepower	0	45	45
Air-Fuel Ratio	9:1	14.5:1	14.5:1
Coolant Out Temp., °F.	125	100	200
Oil Sump Temp., °F.	100–125	165	245

At the end of the test, the engine is disassembled and inspected for varnish and sludge deposits on specified engine areas. Deposits are rated on a scale ranging from 0 for extremely heavy deposits to 10 for total absence of deposit.

This test was carried out using a standard premium fuel and the following lubricating compositions; with the results given in Table I below:

Oil A—Mid-Continent solvent extracted oil, SAE 20 grade, without additives

Oil B—A commercial oil prepared from oil A, SAE 20 grade, with conventional additives [1] to pass performance specification MIL–0–2104

Oil C—Oil like B except that it is SAE 30 grade

Oil D—Oil A with 1.5% of a 90/10 lauryl methacrylate/beta-diethylaminoethyl methacrylate copolymer. Blend is SAE 30 grade

Oil E—Oil D with 0.5% of a commercial antioxidant

Oil F—Oil A with 0.5% of the same antioxidant

Oil G—A commercial oil of Mid-Continent origin with conventional additives [1] to pass performance specification MIL–0–2104–B, Supplement 1

Oil H—A conventionally refined Gulf Coast oil without additives

Oil I—Oil H with 1.5% of a 90/10 lauryl methacrylate/beta-diethylaminoethyl methacrylate copolymer and 0.5% of the above antioxidant

Oil J—A solvent extracted Pennsylvania oil without additives

Oil K—Oil J with 1.5% of a 90/10 lauryl methacrylate/beta-diethylaminoethyl methacrylate copolymer and 0.5% of the above antioxidant.

[1] These additives are, in general, mineral salts of petroleum sulfonates which, in contrast to the additives of this invention, deposit inorganic ash.

Table I

Oil	Average Piston Varnish Score	Oil Ring Plugging	Average Sludge Rating	Average Varnish Rating
A	4.3	Medium	4.5	3.9
B	4.9	Nil-Trace	6.5	5.2
C	5.0	Light	5.6	5.0
D	8.3	Nil	7.9	6.3
E	9.0	Nil	7.8	7.6
	9.3	Nil	8.2	6.5
F	4.0	Nil-Trace	6.3	5.2
G	5.8	Trace	6.7	5.4
	5.3	Nil-Trace	6.4	5.3
H	*3.0	Heavy*	*3.5	*4.8
I	8.5	Nil	8.1	6.9
J	4.0	Light	5.6	5.6
K	9.2	Nil-Trace	7.8	7.5

*Test was discontinued after 82 hours because of piston seizure.

Oils A through D are related as to source and process of refining. Comparison of the data obtained using oil E with the data obtained for oils B and C demonstrates the superiority of the oleophilic, basic amino nitrogen-containing copolymer additives over the conventional detergent-antioxidant type. Oil G has been particularly recommended for superior low-duty performance. Comparison of the data obtained with this oil and those for oil E demonstrates the outstanding superiority of lubricant compositions containing oleophilic, basic amino nitrogen-containing copolymers.

Since it is recognized that the source of the crude and the refining methods used in preparing the lubricating oil have a great effect on the performance of lubricant additives, data on oils H and I, J and K have been included in the above table to show the effectiveness of the preferred additive copolymers in both Gulf Coast and Pennsylvania oils.

Another laboratory test used to evaluate lubricating compositions is the L–4 test carried out in a standard Chevrolet passenger car engine according to the procedure CRC L–4–949 in Appendix F of the "Laboratory Engine Tests of Sulfur in Motor Gasoline Field Test Fuels," January 1950, by the Coordinating Research Council, Inc. This test is a well-known research procedure used to evaluate the ease of oxidation of an oil, its corrosiveness to bearings, and its effect on general engine cleanliness. Although it does not directly evaluate the most outstanding property of the lubricant compositions of this invention, i. e., detergency, particularly under low-duty operation, it does give results which correlate with the performance of oils under heavy-duty conditions in the field.

Results of this test are reported as (1) a corrosion value which is the weight loss per whole copper-lead alloy connecting rod bearing and (2) an engine score which is the summation of varnish and/or sludge ratings on a 0 to 10 scale for certain engine parts which give a perfect total score of 100. The results shown in Table II below were obtained in this test using the specific lubricating compositions discussed in Table I.

Table II

Oil	Engine Score	Corrosion [1] Gms. Loss/ Bearing
A	77.2	0.65
C	87.4	0.15
D	94.7	1.11
E	95.3	0.21
F	77.0	0.09
G	97.0	0.15

[1] This value should be 0.25 or less for good performance in the field.

The data in Table II indicate (comparison of oils A and D) that the oleophilic, basic amino nitrogen-containing addition-type polymers contribute a high degree of engine cleanliness but at the same time enhance corrosiveness. This latter effect is usual for dispersant-detergent additives

in unstabilized motor oils and is conventionally controlled by the addition of antioxidants as may be seen by comparison of the data obtained with oils D and E. Note that these added antioxidants have no effect on detergency as may be seen by the data obtained with oil F. The over-all cleanliness and corrosiveness of the lubricant compositions of this invention with conventional added antioxidants demonstrate clearly that these compositions are essentially equivalent to heavy-duty commercial lubricant compositions under heavy-duty operating conditions which constitute a relatively minor proportion of lubricant uses and for which the compositions of the present invention were not particularly designed (comparison of data for oil E with oils C or G). On the other hand, as indicated in the previously discussed low-duty test, these commercially available, heavy-duty oils fail to combat successfully the problems encountered under the far more important low-duty driving conditions.

Rather than test all new lubricating compositions in the above rather complete engine tests, several much less time-consuming sorting tests (which correlate with the more thorough engine tests and with actual service behavior) are conventionally used in this field to determine the over-all properties and suitability of new lubricating compositions. Data are presented in Tables III to VIII demonstrating the outstanding properties exhibited by the dispersive lubricating compositions of this invention in certain of these tests described below:

A. VISCOSITY INDEX AND SLOPE

Lubricating oil compositions having a low rate of change of viscosity with temperature are highly desirable. Judgment of the suitability of a lubricating oil composition for use over a wide range of operating temperatures is afforded by the "viscosity index" of the oil which is calculated from the measured viscosities (expressed in Centistokes) of the lubricating composition at 100° F. and 210° F. by the standard A. S. T. M. method, D–567–41. In this test lubricating compositions exhibiting the highest viscosity index show the least change in viscosity with change in temperature. An increase of 5 viscosity index units is a significant improvement. In data below, the polymer is added at 1.5% concentration.

Another measurement of value for judging the suitability of lubricating oil compositions is the calculated slope of the line joining the points of intersection of the viscosities of the oil composition at 100° F. plotted as ordinants with the viscosities at 210° F. plotted as abscissas for different concentrations of additives. This slope value is conveniently calculated from the following equation:

$$\text{Slope} = \frac{\text{Viscosity of lubricating composition at 100° F. minus viscosity of lubricating oil alone at 100° F.}}{\text{Viscosity of lubricating composition at 210° F. minus viscosity of lubricating oil alone at 210° F.}}$$

In this calculation, oils having the lowest values for slope exhibit the least change in viscosity with changes in temperature.

B. PREFORMED SLUDGE TESTS

The procedure for this test is as follows: To 0.05 g. of the pentane insoluble portion of sludge from oil oxidized in an Underwood apparatus dissolved in 20 ml. of benzene and contained in a 50 ml. beaker, is added 10 ml. of a kerosene solution of the additive being evaluated at the desired concentration. The sludge remains in solution at this time. The benzene is then evaporated by heating at 100–105° C. for a period of 45 minutes, while the liquid is stirred, using carefully controlled conditions of heating and rate of stirring so as to achieve maximum reproducibility.

The evaporation of benzene leaves the sludge suspended in kerosene since it is insoluble in that liquid. Rapid settling of the sludge occurs unless agents are present that tend to suspend or solubilize the material. The settling tendencies of the resultant sysem are observed in 5 cc. graduated cylinders.

In the following tables, action of additives is classified as follows:

Very good—sludge suspension is clear or very slightly hazy after two days in the presence of 0.4% additive.

Good—sludge is suspended but hazy after two days in the presence of 0.4% additive.

Moderate—sludge is not suspended at 0.4% concentration of additive, but is suspended for two days or more by 0.8%.

Poor—sludge is not suspended by 0.8% additive concentration but settles or coagulates slowly in over half a day.

Negligible—sludge settles or coagulates in less than half a day in the presence of 0.8% additive.

C. LAUSON ENGINE TEST

A vitally important property which should be exhibited in the highest degree in good lubricating compositions is the ability of the lubricant to maintain in suspension the sludge normally formed during engine operation, i. e., the ability to prevent sludge deposition on important operating portions of the engine such as the piston rings, the pistons themselves, and the like, under the actual operating conditions encountered in an internal combustion engine. The so-called Lauson engine test (see The Oil and Gas Journal, January 8, 1948, p. 59) has been designed to evaluate this property of a lubricant and it is used as a standard in the lubricating field.

The Lauson data reported in the tables below for the various lubricants are obtained in 40-hour runs in a Lauson engine operating at 1840±20 R. P. M. under a load of 1.86 horsepower using a fan brake with the engine operating at a jacket coolant temperature of 350° F. and an oil temperature of 200° F., no crankcase ventilation, an air:fuel ratio of 12.5±0.5:1, and a spark advance of 25° BTDC. The compositions are scored on the basis of their performance in these engine tests according to the following system: a ring sticking effect is rated at 20 times the percentage of the rings free at the end of the test, thereby making the maximum score for this item 20; piston skirt lacquer formation is rated on the following decreasing scale: no lacquer formation, 10 points; tan lacquer, 8 points; light brown lacquer, 6 points; brown lacquer, 4 points; darker brown lacquer, 2 points; black lacquer, 0 points, thus leaving the maximum score possible in this property, 10 points; oil-ring blocking is evaluated by multiplying 10 by the percentage of the ring open, thus making the maximum score possible on this effect, 10 points; finally, under piston deposition is rated according to the following decreasing scale: no deposition, 10 points; trace deposition, 8 points; light deposition, 6 points; medium deposition, 4 points; heavy deposition, 2 points; very heavy deposition, 0 points; thereby allotting 10 points to the maximum score on this effect. Thus, the total maximum score for all four effects is 50 on this scoring method. Normally, the totals arrived at are multiplied by 2 on which basis a perfect score is, of course, 100.

Table IV.—SAE–20 furfural extracted Mid-Continent oil

No.	Polymer Added	Preformed Sludge Test	Lauson Score [1]
1	None, base oil control	Negligible	75–78
2	None, base oil plus 0.5% commercial sulphurized terpene corrosion inhibitor.	do	71
3	beta-Methacrylyloxyethyldiethylammonium stearate.	do	54
4	beta-Methacrylyloxyethyldicyclohexylammonium stearate.	do	50
5	90/10 Lauryl methacrylate/beta-diethylaminoethyl methacrylate.	Very good	80
6	90/10 Lauryl methacrylate/beta-diethylaminoethyl methacrylate plus 0.5% antioxidant.	do	90 [2] (71)
7	70/30 Lauryl methacrylate/beta-diethylaminoethyl methacrylate.	do	78
8	60/40 Lauryl methacrylate/beta-diethylaminoethyl methacrylate.	Good	70
9	50/50 Lauryl methacrylate/beta-diethylaminoethyl methacrylate.	Moderate	46
10	85/5/10 Lauryl methacrylate/4-dimethylaminocyclohexyl methacrylate/methacrylanilide.	Good	88
11	85/15 Lauryl methacrylate/4-vinylpyridine.	do	85
12	90/10 Lauryl methacrylate/4-dimethylaminocyclohexyl methacrylamide.	Very good	85 [2] (65)
13	60/40 Lauryl methacrylate/beta-dicyclohexylaminoethyl methacrylate.	do	73
14	85/5/10 Lauryl methacrylate/beta-dicyclohexylaminoethyl methacrylate/methacrylanilide.	Good	88 [2] (60)
15	60/10/30 Lauryl methacrylate/beta-diethylaminoethyl methacrylate/styrene.	Moderate	85
16	30/10/60 Lauryl methacrylate/beta-diethylaminoethyl methacrylate/N-tert. octyl acrylamide.	do	88

[1] Polymer additive used at 1.5% concentration in the oil.
[2] Scores in ( ) are the control scores, which are obtained in each case, for the particular oil and fuel combination used when these scores differ from the main base score of 75–78.

Table V.—SAE–20, "Duosol" extracted Mid-Continent oil

Polymer	Lauson Engine Score [1]
1. none-base oil control	58
2. none-control, base oil plus 0.5% antioxidant	63
3. 92.5/5/2.5 lauryl methacrylate/beta-diethylaminoethyl methacrylate/methacrylanilide	91
4. 89/1/10 lauryl methacrylate/beta-diethylaminoethyl methacrylate/methacrylanilide	81
5. 85/5/10 lauryl methacrylate/beta-diethylaminoethyl methacrylate/methacrylanilide	90
6. 85/5/10 lauryl methacrylate/beta-dibutylaminoethyl methacrylate/methacrylanilide	85
7. 85/5/10 tridecyl methacrylate/beta-diethylaminoethyl methacrylate/methacrylanilide	90
8. 85/5/10 octadecyl methacrylate/betadiethylaminoethyl methacrylate/methacrylanilide	82
9. 65/10/25 lauryl methacrylate/beta-diethylaminoethyl methacrylate/N-tert.-octylacrylamide	90
10. 85/10/5 lauryl methacrylate/methacrylanilide/glycidyl methacrylate reacted with secondary cocoamine (see Ex. III)	82
11. 85/5/10 lauryl methacrylate/diallyl amine/methacrylanilide	80
12. 90/10 lauryl methacrylate/N-(4-dimethylaminocyclohexyl) methacrylamide	[2] 85

[1] Polymer added at 1.5% concentration.
[2] No added antioxidant.

Table III.—SAE–20, "Duosol" extracted Mid-Continent oil

No.	Polymer Added	Viscosity Index	Slope	Preformed Sludge Test	Lauson Score [1]
1	None, base oil control	97.		15 min	52–58, av. 55.
2	95/5 n-Decylacrylate/p-dimethylaminomethylstyrene	116.0	5.7	Good	79 (1%).
3	95/5 Lauryl methacrylate/p-dimethylaminomethylstyrene	118.0	6.1	Very good	82 (1%).
4	85/5/10 Lauryl methacrylate/p-dimethylaminomethylstyrene/methacrylanilide.	131.0	4.48	Good	82.
5	62.4/20.4/17.2 Lauryl ethyl maleate/beta-diethylaminoethyl methacrylate/ethylene.	110.0	3.1	Very good	
6	93/7 Lauryl fumarate/beta-diethylaminoethyl methacrylate	115.0	6.9	do	
7	85/15 Lauryl methacrylate/beta (alpha-methylbenzyl) ethyl methacrylate.	110.0		do	
8	85/10/5 Lauryl methacrylate/methyacrylanilide/glycidyl methacrylate reacted with diamylamine (see Ex. III).	145.0	4.04		84.
9	75/25 Lauryl methacrylate/beta-dimethylaminoethyl methacrylate				80 (1%).
10	85/5/10 Lauryl methacrylate/2-methyl-5-vinyl pyridine/methacrylanilide.				70 (1%).

[1] Unless otherwise noted in parentheses, Lauson scores are obtained on lubricant compositions containing 1.5%, by weight of base oil, of the added polymer.

Table VI.—SAE–20, "Duosol" extracted Mid-Continent oil

Polymer	Preformed Sludge Test
1. None, base oil control	15 minutes.
2. beta-di(2-ethylhexyl)aminoethyl methacrylate	Negligible.
3. beta-methacrylyloxyethyldi(2-ethylhexyl) ammonium stearate.	Do.
4. 97.5/2.5 lauryl methacrylate/beta-diethylaminoethyl methacrylate.	Good.
5. 80/20 Sec. capryl methacrylate/beta-diethylaminoethyl methacrylate.	Do.
6. 90/10 decyl methacrylate/beta-diethylaminoethyl methacrylate.	Very good.
7. 80/20 tridecyl methacrylate/beta-diethylaminoethyl methacrylate.	Do.
8. 80/20 hexadecyl methacrylate/beta-diethylaminoethyl methacrylate.	Do.
9. 80/20 octadecyl methacrylate/beta-diethylaminoethyl methacrylate.	Do.
10. 80/20 octadecenyl methacrylate/beta-diethylaminoethyl methacrylate.	Do.
11. 90/10 lauryl methacrylate/2,2-dimethyl-3-dimethylaminopropyl methacrylate.	Do.
12. 80/20 lauryl methacrylate/tert. octylaminoethyl methacrylate.	Do.
13. 85/15 lauryl methacrylate/beta(alpha-methylbenzyl)-aminoethyl methacrylate.	Good.
14. 93/7 lauryl fumarate/beta diethylaminoethyl methacrylate.	Very good.
15. 90/10 vinyl laurate/vinyl beta-dimethylaminoethyl ether.	Do.
16. 80/20 vinyl lauryl ether/vinyl beta-diethylaminoethyl ether.	Good.
17. 67/33 cyclohexylstyrene/beta(tert. octylamino)ethyl methacrylate.	Moderate.
18. 90/10 dodecylstyrene/beta-diethyl-aminoethyl methacrylate.	Do.
19. 97/3 lauryl methacrylate/vinyl beta-aminoethyl ether.	Good.

Table VII.—SAE–20, "Duosol" extracted Mid-Continent oil

No.	Polymers	Viscosity in Centistokes		Viscosity Index	Slope
		100° F.	210° F.		
1	None, base oil control			97.0	
2	92.5/7.5 Lauryl methacrylate/beta-formamidoethylvinyl ether.	75.62	11.85	137.0	5.4
3	95/5 Vinyl laurate/betadiethylaminoethyl methacrylate.	49.76	7.15	111.0	4.84
4	95/5 Vinyl laurate/allyl glycidyl ether reacted with diamylamine[a] (See Ex. V).	50.66	7.21	110.0	5.65
5	90/10 Lauryl methacrylate/glycidyl methacrylate reacted with diamylamine (See Ex. IV).	55.59	8.59	129.0	4.28
6	85/5/10 Lauryl methacrylate/diallyl amine/methacrylanilide.	50.66	7.41	114.0	4.44
7	64/18/18 Lauryl methacrylate/beta-dimethylaminoethyl methacrylate/ethylene (See Ex. VI).	59.89	8.55	121.0	6.5
8	69/16.4/14.6 2-Ethylhexylacrylate/beta-diethylaminoethyl methacrylate/isobutylene (See Ex. VI).	51.53	7.31	111.0	6.1
9	90/10 Vinyl laurate/betadimethylaminoethyl vinyl ether.	48.81	6.95	108.0	4.88
10	92.5/1.4/6.1 Lauryl methacrylate/beta-aminoethyl vinyl ether/beta-formamidoethyl vinyl ether.	72.27	10.86	133.0	5.9
11	90/10 sec.-Capryl[b] methacrylate/beta-diethylaminoethyl methacrylate (See Ex. VII).	66.0	10.07	132.0	5.42
12	50/20/30 Tridecyl methacrylate/beta-diethylaminoethyl methacrylate/styrene[c] (See Ex. VIII).	53.38	7.81	119.0	5.1
13	90/10 Dodecylstyrene/betadiethylaminoethyl methacrylate (See Ex. IX).	57.02	8.78	130.0	4.51

Table VII.—SAE–20 "Duosol" extracted Mid-Continent oil.—Continued

ESTER LUBRICANT (DI-2-ETHYLHEXYL SEBACATE)

No.	Polymers	Viscosity in Centistokes		Viscosity Index	Slope
		100° F.	210° F.		
1	Di-2-ethylhexyl sebacate (control).	12.75	3.36	156.0	
2	50/50 n-Decyl acrylate/beta-diethylaminoethyl methacrylate[d].	16.52	4.22	183.0	4.38
3	50/48/2 n-Decyl acrylate/beta-diethylaminoethyl methacrylate/methacrylanilide.[d]	16.66	4.26	184.0	4.35
4	85/5/10 Lauryl methacrylate/beta-diethylamino-ethyl methacrylate/methacrylanilide.	22.22	5.81	182.0	3.87

[a]Polymer added at 3% concentration based on the oil rather than at 1.5% concentration.
[b]Methyl-n-hexylcarbinol.
[c]This illustrates the use of 30% of unmodified styrene in a polymer additive without undue loss in solubility and other desirable properties. Alkylation of styrene, however, improves the oil-solubility of its copolymers and oil-soluble products can be obtained by the copolymerization with suitable amino-containing monomers. Particularly desirable products are obtained by the copolymerization of an amine-containing monomer with an alkyl styrene having an alkyl group of seven to twelve carbon atoms attached to the benzene nucleus as in No. 13.
[d]Polymer added at 3% concentration based on the lubricant rather than at 1.5% concentration.

The effectiveness of the lubricant compositions of this invention may be further shown by the carbon suspension test used in the lubricating oil field as a standard bench test to determine detergent activity. In this test 30 grams of a carbon black is pebble-milled for 24 hours with sufficient refined white mineral oil to make a thin paste (usually 300–400 grams required). A 10-gram portion of the resulting paste is placed in a 4-ounce petroleum sample bottle, 0.2 gram of the particular polymer being tested (dissolved in kerosene) added, the bottle filled to the shoulder with kerosene, the resulting suspension shaken well, and the rate of settling observed.

In Table VIII below results of this carbon suspension test are given which show the effectiveness of polymers used in the instant invention, even where one or more of the components of the polymer are present only in relatively small proportion. The figures represent the percent of the total volume of the test suspension in which settling is not visible after the period indicated.

Table VIII

Polymer	1 hour	3 hours	24 hours	48 hours	72 hours	7 days
1. 90/10 dodecylstyrene/betadiethylaminoethyl methacrylate (see Example IX)	100	100	96			
2. 97/1/2 lauryl methacrylate/beta-diethylaminoethyl methacrylate/methacrylanilide	100	100	90	79	67	37
3. 90/0.5/9.5 lauryl methacrylate/beta-diethylaminoethyl methacrylate/methacrylanilide	100	100	90	80	67	33
4. Lauryl methacrylate (control)	100	98	14	13	12	10
5. None-blank	27	19	14			

It will be observed that polymers containing as little as 0.5% of the basic amino nitrogen-containing component, show appreciably improved detergent activity in comparison with both the blank and the unmodified lauryl methacrylate control, being about 85% better than the blank after 24 hours and, even after 7 days, still more than 300% better than unmodified lauryl methacrylate polymer.

It will be understood that while the foregoing examples and tables have disclosed a considerable number of specific polymers adapted for use in the composition of the present invention, these are merely illustrative and that the present invention broadly comprises a lubricating oil con-

taining at least 0.1% by weight thereof of an oil-soluble, basic amino nitrogen-containing addition-type polymer of a plurality of polymerizable ethylenically unsaturated compounds at least one of which is amine-free and contains from 8 to about 18 carbon atoms in an aliphatic hydrocarbon chain, which in the polymer is not part of the main polymer chain, the polymer containing 0.1% to 3.5%, by weight thereof, of basic amino nitrogen.

The polymers used in the present invention are actually copolymers derived from at least two different polymerizable compounds one of which must be amine-free, at least one of which must contain at least 8 carbon atoms in an aliphatic chain which in the polymer does not form part of the main chain, thereby providing an oleophilic structure, and at least one of which must contain a basic amino nitrogen structure, and the copolymers must contain at least 0.1% but not more than 3.5%, by weight thereof, of basic amino nitrogen, preferably between 0.2% and 3.0%. The polymer can be derived from not only two different polymerizable compounds as above but also from one or more additional polymerizable compounds that do not by themselves form oil-soluble polymers, providing the proportions are restricted to insure that the polymers have the requisite oil solubility and that no substantial change in the valuable properties of these polymers as sludge dispersants and viscosity index improvers. A basic requirement is that the copolymer formed must have at least a limited solubility in the oil, i. e., at least 0.1% by weight. The term "oil-soluble" is used herein to denote a solubility of at least 0.1%, by weight, of the polymer in the oil.

As the oleophilic components of copolymers useful in the preparation of the improved lubricating compositions of this invention there can be employed polymerizable esters, amides, ethers, and hydrocarbons characterized by the presence of at least eight carbon atoms, preferably with six or more in a straight chain, and at least one carbon-carbon double bond capable of participation in free radical initiated addition copolymerization reactions. Examples of oleophilic components that come within the purview of this invention are: saturated and unsaturated long-chain esters of unsaturated carboxylic acids such as decyl acrylate, 3,5,5-trimethylhexyl methacrylate, 9-octadecenyl methacrylate; unsaturated esters of long-chain carboxylic acids such as vinyl stearate; long-chain esters of vinylene dicarboxylic acids such as methyl lauryl fumarate; N-long-chain hydrocarbon substituted amides of unsaturated acids such as N-octadecyl acrylamide; long-chain monoolefins such as the alkyl or acyl substituted styrenes, e. g., dodecylstyrene, and the like. Obviously, these components can be employed alone or in various combinations and, in general, make up the majority of the polymeric additive in order to insure proper oleophilic character. The technical lauryl methacrylate obtained from the commercial mixture of long-chain alcohols in the C_{10} to C_{18} range derived from coconut oil is an especially useful oleophilic component of the copolymer but the group of acrylic and alkacrylic esters of aliphatic alcohols of at least eight carbons are, in general, well suited as the oleophilic component of the copolymer.

The basic amino nitrogen-containing component that imparts sludge dispersant properties to the polymers useful in this invention, can be introduced through the use of appropriate copolymerizable monomers containing primary secondary or tertiary amino nitrogen that is attached ultimately to the chain of the polymer as part of an extralinear substituent group in which the nitrogen is joined extranuclearly only to non-benzenoid carbon atoms. There can be employed in the copolymerization monomers such as glycidyl acrylate or vinyl chloroacetate which introduce groups reactive toward ammonia or amines and thus provide a means of attaching the necessary basic amino groups to the polymer chain. Attachment of the amino groups to the main copolymer carbon chain can be through strictly hydrocarbon structures or through ether, ester, or amide linkages.

Particular examples of the basic amino-containing monomers include the basic amino substituted olefins such as p-(beta-diethylaminoethyl)styrene; basic nitrogen-containing heterocycles carrying a polymerizable ethylenically unsaturated substituent, e. g., the vinyl pyridines and the vinyl alkyl pyridines such as 2-vinyl-5-ethyl pyridine; esters of basic amino alcohols with unsaturated carboxylic acids such as the alkyl and cycloalkyl substituted aminoalkyl and cycloalkyl esters of the acrylic and alkacrylic acids, e. g., beta-methylaminoethyl acrylate, 4-diethylaminocyclohexyl methacrylate, beta, beta-didodecylaminoethyl acrylate, and the like; unsaturated ethers of basic amino alcohols such as the vinyl ethers of such alcohols, e. g., beta-aminoethyl vinyl ether, beta-diethylaminoethyl vinyl ether, and the like; amides of unsaturated carboxylic acids wherein a basic amino substituent is carried on the amide nitrogen such as N-(beta-dimethylaminoethyl)acrylamide; polymerizable unsaturated basic amines, e. g., diallylamine, and the like.

In this specification and claims the term "basic amino nitrogen" is used in the generic sense to cover the primary, secondary and tertiary amines including, as stated above, the basic nitrogen-containing heterocycles.

Because of their relatively greater basicity and more effective sludge suspending properties, the polymerizable ethylenically unsaturated compounds containing a basic tertiary amino group are preferred and those having only primary basic amino groups are least desirable. Particularly outstanding and readily available basic amino nitrogen-containing components are the alkyl and cycloalkyl substituted tertiary aminoalkyl and cycloalkyl esters of acrylic and alkacrylic acids.

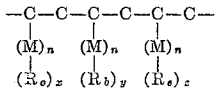
The basic amino nitrogen-containing component of the copolymer must be present in a minor proportion by weight corresponding to no more than 3.5% and no less than 0.1% of basic amino nitrogen by weight of the polymer. Above the higher level, which, for example, corresponds to about 50% by weight of amino monomer in a lauryl methacrylate/beta-diethylaminoethyl methacrylate copolymer, and at less than the lower level, the performance of the polymer as an oil detergent falls off rapidly. It is preferred that the basic amino nitrogen content be within the range of 0.2% to 3.0% by weight of the polymer.

The oil detergent polymers used in this invention can contain limited amounts of copolymerizable components that do not necessarily contribute either to improve solubility or detergent action but merely serve as fillers or extenders for the active components. Typical examples of these filler components include the well-known shorter-chain ethylenically unsaturated addition polymerizable monomers such as the vinyl and allyl formates, acetates, propionates, butyrates, and the like; polymerizable unsaturated short-chain hydrocarbons, e. g., the monoolefins such as ethylene, propylene, isobutylene, styrene, vinyltoluene, and the like, and the short-chain dienes such as 1,3-butadiene, isoprene, and the like; unsaturated short-chain carboxylic acids and their derivatives such as the alpha-methylenecarboxylic acids and their derivatives, e. g., acrylic acid, methyl methacrylate, acrylonitrile, methacrylamide, and the like; the short-chain unsaturated ethers, particularly the vinyl and allyl ethers, e. g., ethyl vinyl ether, butyl vinyl ether, and the like. These and other familiar monomers that are available at moderate cost can be employed for this purpose in proportions ranging up to as much as 79%, by weight, in representative polymers although it is preferred they should not exceed 65% by weight of the polymer.

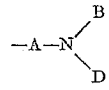
In addition, inclusion of minor proportions of N-hydrocarbon-substituted amides of unsaturated carboxylic acids will be found beneficial, particularly if exceptional improvement of the lubricating oil with respect to viscos-

ity index is desired. Especially suitable as polymerizable components of the polymer are the N-hydrocarbon-substituted acrylamides including N-tertiary-butylacrylamide, N-tertiary-octylacrylamide, and, particularly, the N-aryl-acrylamides such as methacrylanilide and acrylanilide.

The polymers employed in the improved lubricating compositions of this invention can be represented by the following schematic formula:



wherein M is the structural unit joining the various substituent groups to the main chain of the polymer, R_o is the required oleophilic structure, R_b is the basic amino containing structure that imparts sludge dispersency, and R_e is the optional extender structure; and x, y and z represent the proportions of these various structures in the polymer. M can be an ether, ester or amide group and n is a cardinal number no greater than 1, i. e., 0 or 1; R_o is a straight or branched chain hydrocarbon radical of from 8 to about 18 carbon atoms, R_e is a monovalent organic radical free of reactive hydrogen and is preferably a solely hydrocarbon radical of less than 8 carbon atoms and when n is 0, R_e can be hydrogen; and R_b is a primary, secondary, or tertiary amino radical of the structure



in which the nitrogen is bonded extra-nuclearly only to hydrogen or aliphatic carbon and in which A is a hydrocarbon radical of 1–18, preferably 2 to 6 carbon atoms, B and D are hydrogen or hydrocarbon radicals of no more than about 18 and, preferably, no more than 6, carbon atoms, and B or D can be joined with A to form a heterocycle. The proportions of the various structures in the polymer, as represented by x, y and z in the schematic formula, normally will be in the range: x from 20% to 99%; y from 0.5% but, preferably, from 1% to 50%; and z from 0% up to 79% but, preferably, only up to 65%, all percentages being by total weight of the polymer. Within these ranges, optimum proportions will be determined both by the properties contributed to the polymer by the individual polymerizable components going into its composition and the particular properties of the polymer which it is desired to emphasize.

An advantage of the present invention is that it provides an economical and practical means of greatly improving the efficiency of lubricating oils. An outstanding advantage of the invention is its improvement of lubricating oils for use in internal combustion engines, particularly under low-duty driving conditions. Under these severe operating conditions, which account for the majority of present day driving, an extremely high rate of sludge formation and subsequent deposition on moving engine parts is encountered. The deposits thus formed are quite deleterious to engine operation resulting in overall sluggish behavior and particularly in oil ring clogging leading to excessive oil consumption and in oil screen plugging resulting in circulatory failure with subsequent bearing destruction. The lubricating compositions thus far available have proven singularly ineffective in combating these low-duty operating problems. The lubricating oil compositions of this invention by preventing the undesirable sludge and varnish deposition offer the only known solution to this difficult problem.

The instant lubricating oil compositions have a further advantage in that the polymer additive does not deposit inorganic ash; whereas, many of the known oil detergents, which are of questionable utility under low-duty operating conditions, deposit inorganic ash and actually contribute to the accumulation of undesirable non-combustible material in the engine. Finally, the lubricating oil compositions of the present invention also exhibit markedly improved viscosity characteristics, a desirable feature often achieved by the use of special additives. In particular, the dispersive polymer additives improve the viscosity index of the lubricating oils while still maintaining a relatively low viscosity at atmospheric temperature. However, these latter advantages are subordinate to the detergent properties of these compositions and especially to their low-duty performance.

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

The invention claimed is:

1. A petroleum base lubricating oil containing at least 0.1% by weight of an oil soluble, basic amino nitrogen-containing addition type copolymer containing in combined form as its essential monomeric components copolymerizable ethylenically unsaturated compounds each containing only one polymerizable ethylenic linkage, at least one of which components is amine-free and contains from 8 to about 18 carbon atoms in an aliphatic hydro-carbon chain which in the copolymer is not part of the main chain, and one of the components as it exists in the copolymer containing a basic amino nitrogen in the side chain, said copolymer containing 0.1% to 3.0% by weight of basic amino nitrogen, said copolymer having an inherent viscosity of 0.1 to 3.0 as determined at 0.1% weight/volume concentration in benzene at 25° C., and said copolymer being one which does not contain as a component a N-hydrocarbon-substituted acrylamide.

2. A petroleum base lubricating oil as set forth in claim 1, wherein 0.25% to 10% of said copolymer is incorporated in said lubricating oil and said copolymer has an inherent viscosity of 0.2 to 1.0 as determined at 0.1% weight/volume concentration in benzene at 25° C.

3. A petroleum base lubricating oil in claim 1 in which the basic amino nitrogen in the side chain of the copolymer is in a teritary amino group.

4. A petroluem base lubricating oil containing at least 0.1% by weight of an oil soluble, basic amino nitrogen-containing addition type copolymer containing in combined form as its essential monomeric components copolymerizable ethylenically unsaturated compounds, one of which is from the group consisting of acrylic and alkacrylic esters of aliphatic alcohols of from 8 to about 18 carbon atoms and one of the components containing a basic teritary amino group in the side chain, said copolymer containing 0.1% to 3.0% by weight of basic amino nitrogen, said copolymer having an inherent viscosity of 0.1 to 3.0 as determined at 0.1% weight/volume concentration in benzene at 25° C., and said copolymer being one which does not contain as a component a N-hydrocarbon-substituted acrylamide.

5. A petroleum base lubricating oil containing at least 0.1% by weight of an oil soluble, basic amino nitrogen-containing addition type copolymer containing in combined form as its essential monomeric components copolymerizable ethylenically unsaturated compounds, one of which is from the group consisting of acrylic and alkacrylic esters of aliphatic alcohols of from 8 to about 18 carbon atoms and one of the components is from the group consisting of alkly and cycloalkyl substituted tertiary aminoalkyl and amino cycloalkyl esters of acrylic and alkacrylic acids, said copolymer containing 0.1% to 3.0% by weight of basic amino nitrogen, said copolymer having an inherent viscosity of 0.1 to 3.0 as determined at 0.1% weight/volume concentration in benzene at 25° C., and said copolymer being one which does not contain as a component a N-hydrocarbon-substituted acrylamide.

6. A petroleum base lubricating oil containing from 0.25% to 10% by weight of an oil soluble, basic amino

nitrogen-containing, additional type copolymer containing in combined form as its essential monomeric components copolymerizable ethylenically unsaturated compounds, one of which is from the group consisting of acrylic and alkacrylic esters of aliphatic alcohols of from 8 to about 18 carbon atoms and one of the components is beta-diethylaminoethyl methacrylate, said copolymer containing 0.1% to 3.0% by weight of basic amino nitrogen, said copolymer having an inherent viscosity of 0.1 to 3.0 as determined at 0.1% weight/volume concentration in benzene at 25° C., and said copolymer being one which does not contain as a component a N-hydrocarbon-substiuted acrylamide.

7. A petroleum base lubricating oil containing from 0.25% to 10% by weight of an oil soluble, basic amino nitrogen-containing addition type copolymer containing in combined form as its essential monomeric components copolymerizable ethylenically unsaturated compounds, one of which is lauryl methacrylate and one of which is beta-diethylaminoethyl methacrylate, said copolymer containing 0.1% to 3.0% by weight of basic amino nitrogen, said copolymer having an inherent viscosity of 0.1 to 3.0 as determined at 0.1% weight/volume concentration in benzene at 25° C., and said copolymer being one which does not contain as a component a N-hydrocarbon-substituted acrylamide.

8. A petroleum base lubricating oil as set forth in claim 1, containing from 0.1% to about 50% by weight of the oil soluble basic amino nitrogen-containing addition type copolymer.

References Cited in the file of this patent

UNITED STATES PATENTS

2,091,627	Bruson	Aug. 31, 1937
2,104,796	Dietrich	Jan. 11, 1938
2,291,214	Dietrich	July 28, 1942
2,311,548	Jacobson	Feb. 16, 1943
2,489,281	Foehr	Nov. 28, 1949
2,584,968	Catlin	Feb. 12, 1952
2,613,184	Catlin	Oct. 7, 1952
2,653,133	Catlin	Sept. 22, 1953
2,666,044	Catlin	Jan. 12, 1954