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OXIDATION RESISTANT LUBRICANT COMPOSITIONS

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This invention relates to lubricant compositions, and it is particularly directed to the provision of compositions of this character which are highly resistant to oxidative attack even when employed as a crankcase or other lubricant in internal combustion engines.

The lubricating art has now developed to the point where a large number of oils, both natural and synthetic, are available for many purposes. While these oils vary widely in make-up and in their physical and chemical properties, all, with minor exceptions, have a tendency to become oxidized in the presence of air, especially under the elevated conditions of temperature and pressure encountered in internal combustion engines. This oxidative attack is responsible in part for the formation of the various types of sludges which build up in oils with use, and, in the case of oils employed in engines, it is also responsible for the formation of the solid products which deposit out on the piston and cylinder wall surfaces of the engine.

It has also been noted that when oils are oxidized there are formed various acidic and/or peroxidic decomposition products which apparently either engender or promote corrosion of metal surfaces coming into contact with the oil. This corrosive attack becomes particularly severe in the case of metals such as the various copper-lead, cadmium-silver and cadmium-nickel alloys which are employed in the fabrication of bearings. Further, as these decomposition products are formed, they lead to a progressively more rapid oxidation of the remaining portions of the oil, evidently by a species of chain reaction.

Some success in inhibiting oxidation of oils has been obtained by using one or more of a considerable number of different compounds and classes of compounds which have been shown to possess anti-oxidant properties, and particularly good results have been obtained by using in the lubricant composition a minor percentage of an aromatic amine. However, while use of such compounds increases the resistance of lubricating oils against oxidative attack, appreciable oxidation of the oil still occurs, particularly under the severe conditions of use which are encountered in internal combustion engines. Accordingly, it would be desirable if means were available whereby oils could be made much more resistant to oxidative attack than has heretofore been possible.

It is our discovery that an exceptionally high degree of resistance against oxidative attack can be imparted to lubricating oils by incorporating therein an aromatic amine oxidation inhibitor together with a copolymer of a higher alkyl ester of an α,β -olefinically unsaturated carboxylic acid of from 3 to 8 carbon atoms and an amino lower alkyl ester of such an acid. Surprisingly enough, it has been found that the use in lubricant oils of both these additives imparts to the resulting lubricant composition a resistance to oxidative attack which is far superior to that imparted by the aromatic amine alone. This result is one which is entirely unexpected and could not be predicted since the copolymers, when used alone, have

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substantially no anti-oxidant effect on the lubricant composition.

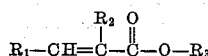
More specifically, the aromatic amines which are employed in the practice of this invention can be described as compounds of the type having the structural formula:



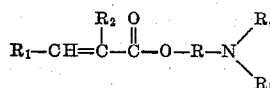
where the R_1 is an aryl group selected from the class consisting of phenyl, naphthyl, anthryl or phenanthryl radicals which may be either unsubstituted or substituted on their ring portions by groups such as amino, hydroxyl, mercapto, alkoxy, aryloxy, thioalkyl, aryl, alkaryl and aralkyl radicals, and the R_2 is a member of the group consisting of hydrogen and aryl groups of the same class as R_1 . Representative amino compounds which can be successfully employed in a practice of the present invention include α -naphthylamine, phenyl- α -naphthylamine, p-hydroxydiphenylamine, p,p'-dihydroxy-di-phenylamine, diphenyl-p-phenylenediamine, diphenylamine, phenothiazine, di- β -naphthylamine, p-isopropoxydiphenylamine, di(p-isopropylphenyl)-p-phenylenediamine, di- β -naphthyl-p-phenylenediamine, p,p'-diisooctyldiphenylamine, phenyl- α -anthrylamine and phenyl- α -phenanthrylamine, etc. Other aromatic amine oxidation inhibitors of this general variety are also well known in the art.

Preferred aromatic amine oxidation inhibitors in the compositions according to this invention are those containing from 10 to 16 carbon atoms in aryl groups attached to the nitrogen atom. Examples of these aromatic amine oxidation inhibitors containing from 10 to 16 aryl carbon atoms include phenyl- α -naphthylamine, p-hydroxydiphenylamine, phenothiazine, p,p'-dioctyldiphenyldiphenylamine, and α -naphthylamine. They are particularly effective in controlling the oxidation of lubricating oils in combination with the copolymer of the lubricating oil compositions in accordance with this invention. For present purposes, however, the most satisfactory of the foregoing amines are the secondary diarylamine oxidation inhibitors of from 10 to 16 aryl carbon atoms.

As stated above, the copolymers employed in the practice of the present invention are ones of higher alkyl esters of α,β -olefinically unsaturated carboxylic acids and amino lower alkyl esters of such acids. Expressed structurally, said copolymers are those of an ester having the structural formula:



with an amino alkyl ester having the structural formula:



In said formulae, R is a lower alkylene group (from 1 to 7 carbon atoms); R_1 and R_2 represent hydrogen atoms or methyl groups; R_3 represents a higher alkyl group (8 carbon atoms or more) such as octyl, 2-ethylhexyl, nonyl, decyl, 1-ethyloctyl, 1,1-dimethylhexyl, dodecyl, pentadecyl, hexadecyl, heptadecyl, octadecyl, cyclopentyl, 4-ethylcyclohexyl, or the various radicals obtained in the polymerization of propene, butene and other alkenes; R_4 and R_5 represent hydrogen atoms of the same or different lower alkyl groups. Representative lower alkyl radicals which R_4 and R_5 may represent are methyl, ethyl, propyl, isopropyl, butyl, tertbutyl, isobutyl, amyl, hexyl, cyclopentyl, cyclohexyl and the like.

More specifically, representative copolymers which can be employed in the practice of the present invention are those which can be formed by reacting one or more of the higher alkyl ester compounds given in Table I below

with one or more of the amino lower alkyl ester compounds given in said table.

TABLE I

Higher alkyl esters:

2-ethylhexyl acrylate
Dodecyl acrylate
Pentadecyl acrylate
2-ethylhexyl methacrylate
Decyl methacrylate
3,6-dimethyldecyl methacrylate
Dodecyl methacrylate
Pentadecyl methacrylate
1,1-dimethyloctyl methacrylate
Octyl crotonate
Dodecyl crotonate
2-ethylhexyl tiglate
Dodecyl tiglate
Octadecyl tiglate
Octyl angelate
Pentadecyl angelate
Octadecyl angelate
Dodecyl hydrosorbate
Pentadecyl hydrosorbate

Amino lower alkyl esters:

Dimethylaminoethyl acrylate
Diethylaminobutyl acrylate
Aminoethyl acrylate
Diethylaminoethyl methacrylate
Dimethylaminoethyl methacrylate
Aminoheptyl methacrylate
Dimethylbutyl crotonate
Aminoethyl crotonate
Dimethylaminoethyl tiglate
Dimethylaminobutyl tiglate
Propylhexylaminoethyl tiglate
Aminoheptyl tiglate
Diethylaminoethyl angelate
Dimethylaminohexyl angelate
Methylhexylaminoethyl angelate
Aminoethyl angelate
Diethylaminoethyl hydrosorbate
Ethylhexylaminobutyl hydrosorbate
Aminopropyl hydrosorbate

Particularly good results have been obtained with copolymers formed by using high (C_8 and above) alkyl esters of methacrylic acid with dialkylaminoalkyl methacrylates in which the alkyl groups are lower alkyl groups; accordingly, such copolymers form a more preferred group for use in the practice of this invention.

The copolymers of this invention can be prepared by conventional bulk, solution, or emulsion methods, the copolymerization reaction going forward on the application of heat or various light rays, and/or in the presence of a polymerization catalyst. Exemplary catalysts which can be employed for this purpose are the organic peroxides (e.g., benzoyl peroxide, acetyl peroxide, ditertiaryamyl peroxide, lauroyl peroxide, etc.), hydrogen peroxide, alkali metal perborates and persulfates, boron trifluoride, 1,1-azodicyclohexane carbonitrile, alpha, alpha'-azodiisobutyronitrile, and the like, the preferred catalysts being those of the free radical-liberating type such as the various peroxy compounds. The polymerization normally is conducted at elevated temperatures, the exact temperature selected depending more particularly on the reaction initiator employed. As a general rule, temperatures of from about 50 to 150° C. or higher are suitable.

Suitable copolymers for use in the present invention can be obtained by using from about 2 to 35% of the amino lower alkyl ester compound and about 98 to 65% of the higher alkyl ester. If desired, mixed copolymers can

be employed by reacting two or more of the higher alkyl ester compounds with one or more of the amino lower alkyl esters, or vice versa.

The aromatic amine oxidation inhibitor and copolymer is present in a minor proportion, sufficient to inhibit oxidation. In general, good results are obtained when the amount of the aromatic amine oxidation inhibitor employed in the lubricating oil composition ranges from about 0.01 to 5% by weight, although a preferred range is from about 0.05 to 2% by weight. The copolymer ingredient of the composition may comprise from about 0.5 to 10% by weight thereof, and a preferred range is from about 1 to 5% by weight.

The compounding agents of this invention can be used with good effect in the case of any oil of lubricating viscosity which is subject to oxidative attack. This oil can be a refined Pennsylvania or other paraffin base oil, a refined naphthenic base oil, or a synthetic hydrocarbon or nonhydrocarbon oil of lubricating viscosity. As synthetic oils there can be mentioned alkylated waxes and similar alkylated hydrocarbons of relatively high molecular weight, hydrogenated polymers of hydrocarbons, and the condensation products of chlorinated alkyl hydrocarbons with aryl compounds. Other suitable oils are those which are obtained by polymerization of lower molecular weight alkylene oxides such as propylene and/or ethylene oxide. Still other synthetic oils are obtained by etherification and/or esterification of the hydroxy groups in alkylene oxide polymers such as, for example, the acetate of the 2-ethylhexanol-initiated polymer of propylene oxide. Another important class of synthetic oils comprises the high molecular weight esters as, for example, di(ethylhexyl) sebacate. The silicate esters such as the tetraalkylorthosilicates and polyalkoxypolysiloxanes, for example, tetra(2-ethylhexyl)orthosilicate and hexa(2-ethylhexyl)disiloxane, and blends thereof constitute still another important class of synthetic oils of lubricating viscosity. If desired, the oil can be a mixture of mineral and synthetic oils.

The compounded oils of this invention may be utilized as turbine oils, cable oils, electric switch oils, transformer oils, hydraulic oils and the like, as well as crankcase and other lubricants for automotive, aircraft, Diesel and other internal combustion engines. These oils, in addition to the anti-oxidants described above, can also contain additional ingredients such as metal salt detergents (e.g., polyvalent metal phenates, sulfonates, thiophosphates, etc.), pour point depressants, oiliness agents, extreme pressure addition agents, other anti-oxidants, blooming agents, compounds for enhancing the viscosity index of the oil, thickening agents and/or metal soaps in grease-forming proportions or in amounts insufficient to form grease, as in the case of mineral castor machine oils or other compounded liquid lubricants.

A convenient method of measuring the resistance of oxidation possessed by lubricant compositions is by the use of the apparatus and procedure described in Industrial and Engineering Chemistry, vol. 28, p. 26 (1936), wherein the rate of oxygen absorption at constant pressure by a definite weight of oil is regarded as a measure of the oxidative stability of the oil. According to this procedure, the oil sample is placed in an absorption cell provided at its bottom with a fine-fritted glass filter to disperse the oxygen stream which is circulated through the system at a constant rate. The particular apparatus employed in obtaining the data presented in Table II below was made up of an oxidation or absorption cell constructed of a large glass tube provided with a head portion having a connection for introducing oxygen, a fitting for the insertion of a stirrer, and an annular space surrounding the tube and communicatory with the interior thereof for the reception of potassium hydroxide pellets which serve to remove water, carbon dioxide, volatile aldehydes and the like. The oil sample is contained in the lower portion of the tube which, during the test,

is immersed in an oil bath maintained at 340° F. The oil is stirred vigorously during the test and is kept under a pressure of about 1 atmosphere of pure oxygen. The time in hours required for 100 grams of the oil to absorb 1200 cc. of oxygen is called the "induction period."

The data presented in Table II below illustrate the anti-oxidant effect exerted on the base oil (a highly refined, mineral base white oil, which itself has an induction period of substantially 0 hours) by the addition of the recited additives.

TABLE II

Anti-oxidant effect of amine + copolymer on white oil

Amine	Copolymer	Induction period (hrs.)
0.1% by wt. phenyl- α -naphthylamine.	None	2.1
0.2% by wt. p-hydroxy-di-phenylamine.	do.	1.5
0.2% by wt. phenothiazine.	do.	1.4
0.2% by wt. α -naphthylamine.	do.	0.0
None	5% dodecyl, methacrylate/diethylaminoethyl methacrylate (PL-164) ¹	
0.1% by wt. phenyl- α -naphthylamine.	do.	15.4
0.2% by wt. p-hydroxy-di-phenylamine.	do.	2.8
0.2% by wt. phenothiazine.	do.	28.6
0.2% by wt. α -naphthylamine.	do.	2.8

¹ PL-164 is a product manufactured and sold by E. I. du Pont de Nemours & Company of Wilmington, Delaware.

Analysis of the product discloses it to be a solution in oil of a copolymer of dodecyl methacrylate and diethylaminoethyl methacrylate in a weight ratio of about 6.5:1. The percentages employed in the table for the PL-164 are, however, on an oil-free basis.

The above test data demonstrate the remarkable improvement in resistance to oxidation provided by mineral lubricating oil compositions containing the combination of aromatic amine oxidation inhibitor and copolymer of a higher alkyl ester of an alpha-beta olefinically unsaturated monocarboxylic acid of from 3 to 8 carbon atoms and an amino lower alkyl ester of such an acid in accordance with the invention. Although the aromatic amine oxidation inhibitors alone in the lubricating oil are shown to provide certain amounts of inhibition, usually about 1.5 hours, a surprising increase in the inhibition period up to as high as 28.6 hours is obtained when the aromatic amine oxidation inhibitor is employed in combination with a representative copolymer of the aforementioned type. Such a result is wholly unexpected since the copolymer by itself in mineral lubricating oil apparently has no oxidation inhibiting effect.

In further illustration of the anti-oxidant effect obtained in lubricating oil compositions in accordance with this invention, a commonly available synthetic base oil of lubricating viscosity and subject to oxidative attack was employed in the same test as described above. The synthetic oil in this case was hexa-(2-ethylhexoxy)disiloxane. The test results are presented in Table III which follows:

TABLE III

Anti-oxidant effect of amine and copolymer on synthetic oil

Amine	Copolymer	Induction period (hrs.)
0.1% by wt. phenyl- α -naphthylamine.	None	28.8
None	5% dodecyl methacrylate/diethylaminoethyl methacrylate (PL-164) ¹	0.0
0.1% by wt. phenyl- α -naphthylamine.	do.	41.6

¹ PL-164 is as described above in Table II.

The test data of the above tables show that the unusual improvement in resistance to oxidation obtained in accordance with this invention by the combination of aromatic amine oxidation inhibitor and copolymer also applies with recognized synthetic oils of lubricating viscosity. Although the phenyl- α -naphthylamine oxidation inhibitor is fairly effective alone in the hexa-(2-ethylhexoxy)disiloxane lubricating oil, a remarkable improvement is obtained when the same aromatic amine oxidation inhibitor is used together with the copolymer of a higher alkyl ester of an alpha-beta olefinically unsaturated monocarboxylic acid of 3 to 8 carbon atoms and an amino lower alkyl ester of such an acid. This is indeed remarkable when it is considered that the copolymer of itself provides no oxidation inhibition to the hexa-(2-ethylhexoxy)disiloxane synthetic lubricating oil.

In the described tests both the representative mineral lubricating oil and the synthetic lubricating oil when employed alone have no apparent resistance to oxidation, and give induction periods of 0.0 hr.

From the above detailed description, it will be apparent that the combination of ingredients herein disclosed give a new composition having new and highly useful properties. It is immaterial for the purpose of the present invention whether the components be separately new or old, since it is the discovery of the combination of ingredients and the unexpected properties obtained thereby which comprise the applicants' contribution to the art.

We claim:

1. A lubricating oil composition having improved resistance against oxidation, said composition consisting essentially of a major proportion of a mineral lubricating oil, from about 0.1 to about 5% by weight of a secondary diarylamine oxidation inhibitor selected from the group consisting of phenyl- α -naphthylamine and phenothiazine and from about 0.5 to about 10% by weight of a copolymer consisting essentially of dodecyl methacrylate and diethylaminoethyl methacrylate in a weight ratio of about 6.5:1.

2. A lubricating oil composition having improved resistance against oxidation, said composition consisting essentially of a major proportion of a mineral lubricating oil, from about 0.1 to about 5% by weight of phenyl- α -naphthylamine and from about 0.5 to about 10% by weight of a copolymer consisting essentially of dodecyl methacrylate and diethylaminoethyl methacrylate in a weight ratio of about 6.5:1.

3. A lubricating oil composition having improved resistance against oxidation, said composition consisting essentially of a major proportion of a mineral lubricating oil, from about 0.1 to about 5% by weight of phenothiazine and from about 0.5 to about 10% by weight of a copolymer consisting essentially of dodecyl methacrylate and diethylaminoethyl methacrylate in a weight ratio of about 6.5:1.

4. A lubricating oil composition having improved resistance against oxidation, said composition consisting essentially of a major proportion of a normally oxidizable oil of lubricating viscosity selected from the group consisting of mineral lubricating oil and hexa-(2-ethylhexoxy)disiloxane, from about 0.1 to about 5% by weight of a secondary diarylamine oxidation inhibitor selected from the group consisting of phenyl- α -naphthylamine and phenothiazine and from about 0.5 to about 10% by weight of a copolymer consisting essentially of dodecyl methacrylate and diethylaminoethyl methacrylate in a weight ratio of about 6.5:1.

5. A lubricating oil composition having improved resistance against oxidation, said composition consisting essentially of a major proportion of hexa-(2-ethylhexoxy)disiloxane, from about 0.1 to about 5% by weight of phenyl- α -naphthylamine and from about 0.5 to about 10% by weight of a copolymer consisting essentially of

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dodecyl methacrylate and diethylaminoethyl methacrylate in a weight ratio of about 6.5:1.

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