United States Patent Office 2,892,791 Patented June 30, 1959

2,892,791

LUBRICANT COMPOSITION

Warren Lowe, Berkeley, William T. Stewart, El Cerrito, and Frank A. Stuart, Orinda, Calif., assignors to California Research Corporation, San Francisco, Calif., a corporation of Delaware

No Drawing. Original application February 3, 1956, Serial No. 563,207. Divided and this application March 14, 1957, Serial No. 645,893

4 Claims. (Cl. 252—56)

This invention relates to a novel lubricant composition, and it is particularly directed to the provision of a lubricant composition which is adapted to be employed in internal combustion engines.

With the refinements now being made in automotive and other internal combustion engines, a great deal of attention is being directed to the provision of a lubricant which will permit the engine to be operated at a high level of efficiency over long periods of time. The primary function of the lubricant is, of course, to reduce friction and thereby not only decrease the wear on pistons, piston walls, bearings and other moving parts, but also increase the efficiency of the engine. Additionally, it is also a function of the lubricant to prevent the deposition of solid products on the piston walls and other surfaces of the engine coming in contact with the lubricant. Such deposits seriously interfere with efficient engine operation for they accelerate piston ring and cylinder wall wear and also increase oil losses by plugging the oil ring grooves. The troublesome deposits which form on the face of the piston and on the other walls of the combustion chamber, as well as on valves and spark plugs are also partially attributable in many cases to the lubricant, and especially to various of the metal-containing additives employed therein. It is of importance to eliminate or at least minimize the formation of all such deposits, and it is the basic object of this invention to achieve such a result.

To a minor degree, certain of the deposits formed on engine surfaces have their origin in the oil itself, that is to say, in the decomposition products of the oil. A more important, though still minor, source of engine deposits lies in the additives with which oils are conventionally supplied. This is particularly the case with metal-containing additives as, for example, the organic, metal-containing salts which are incorporated in the oil to increase the detergency thereof, and the various metal-containing compounds which are added to increase the lubricity of the oil and reduce piston ring and cylinder wall wear. Whenever oil is burned in the engine (as occurs with the oil film present in the cylinder wall during the combustion stroke) any metal-containing additives present in the oil may form an ash which is partially deposited out on the various surfaces of the combustion chamber and on those of the spark plugs and valves. Accordingly, it is a particular object of this invention to provide a lubricant composition which is compounded with metal- or mineral-free detergents and wear-reducing additives.

While certain of the additives heretofore employed in oils (and to a lesser degree the oil itself) are partially responsible for deposits which form on engine surfaces, it is now recognized that the major source of such deposits or their precursors lies in the various aldehydes, acids, oxy-acids and other similarly reactive, partially-

oxidized combustion products of the fuel. These products are formed both under pre-ignition conditions as well as during the combustion step proper, particularly during the period before the engine has reached operating temperature. Accordingly, under city driving conditions where the engine is repeatedly started in the cold condition and is seldom driven for a distance sufficient to reach the most efficient operating temperatures, the formation of partial oxidation products is particularly severe. Many of these partial oxidation products are carried down into the crankcase of the engine along with other blow-by gases, and since most are insoluble or only sparingly soluble in lubricating oils, they tend to separate from the oil and adhere to engine surfaces or form large droplets. In either case, under the elevated temperature conditions prevailing in the engine, these reactive monomers quickly polymerize to form solid masses which readily deposit out on the engine wall surfaces.

It is the practice in the art to prevent the formation of such deposits by adding to the lubricant a material normally referred to as a detergent. Insofar as is known, all the detergent additives which have heretofore been successfully employed on a commercial scale are organic, metal-containing compounds such as calcium petroleum sulfonate, calcium cetyl phosphate, calcium octyl salicylate, calcium phenyl stearate, the barium salt of wax-substituted benzene sulfonate, or the potassium salt of the reaction product of phosphorus pentasulfide and polybutene. Various of these detergents act by reacting chemically with deposit precursors to form harmless compounds. Others act to prevent flocculation or coagulation of solid particles in the oil and maintain the same in a state of suspension as finely divided particles. Still others not only perform this dispersant function but also effect the solubilization or emulsification of the sparingly soluble monomers in the oil and thereby greatly reduce the rate of polymerization. In the latter case, such polymer materials as do then form within the body of the oil are smaller in size and can be peptized or dispersed in the oil much more readily than is the case with the large polymeric particles which are formed on exposed engine surfaces or in droplets lying without the oil.

Detergents capable of acting in the latter fashion are preferably employed wherever possible, particularly in automotive engines to be operated under city driving conditions. However, even among the metal-containing additives, few are available which are capable of solubiliziing any appreciable amount of all the many types of polymer precursors which are carried into the oil from the fuel. Accordingly, it is a more particular object of this invention to provide a lubricant composition incorporating a metal-free detergent which is capable of solubilizing or emulsifying in the lubricant large amounts of all the various partial oxidation products of the fuel which are carried into the oil, and which is also capable of maintaining in suspension in the oil the various solid polymeric materials which are present therein.

The problem of piston ring and cylinder wall wear, especially the control thereof, is also one which is closely related to the composition of the crankcase lubricant. Aside from abrasive wear, which is caused by dust and dirt and can be remedied by suitable filtering and air-cleaning means, a large part of the wear experienced by piston rings and cylinder wall is attributable to chemical attack by moisture and acidic products originating as by-products of fuel combustion. In engines operated at optimum temperature levels, these combustion products are largely discharged through the exhaust and breather pipe. However, under the relatively "cold" conditions

experienced in city driving, and especially at cylinder wall temperatures below about 150° F., the moisture and acid products are condensed on the engine surfaces where they promote corrosive attack and are in a position to work past the piston and accumulate within the engine and in the crankcase oil. This difficulty is one which the art has heretofore met most successfully by supplying the lubricating oil with additives such as the various metal salts of petroleum sulfonic acids and other metal-organic compounds, especially those having a basic reaction. However, this practice has a disadvantage of adding still another metal-containing ingredient to the oil and therefore of increasing the deposit-forming characteristics of the lubricant composition. Accordingly it forms still another object of this invention to provide a lubricant composition containing a metal- or mineral-free additive which effectively decreases the wear experienced by piston rings and cylinder walls, particularly during periods before the engine has become thoroughly warmed to operating temperatures.

The present invention is based on the discovery that certain copolymers, which contain no metal component and therefore are substantially free of any ash-forming tendency, have the ability to impart excellent detergent and antiwear qualities to lubricating oils employed in internal combustion engines. In particular, these copolymers have the ability to solubilize in the oil large amounts of all the various partially oxidized combustion products of the fuels employed in internal combustion engines, while also having the ability of maintaining in a state of suspension any solid polymeric products present in the oil. Additionally, the copolymeric additives of the present invention effectively reduce the wear experienced by piston rings and cylinder wall surfaces even under the most unfavorable operating conditions such as are experienced during the starting and warming up of the engine. These additives have the advantage that they do not combine chemically with the various polymer precursors which are solubilized or dispersed in the oil, nor apparently do they act by a neutralization reaction in counteracting the effect of the various acidic fuel combustion by-products. Accordingly, they are capable of giving excellent protection against engine deposits and wear over extended operating periods. It should also be noted that the copolymeric additives of this invention are noncorrosive to the various bearing metals employed in engines.

Since the additives of the present invention differ in kind from any heretofore proposed for either detergent or antiwear purposes, it would have been surprising to discover that they were effective for either of these purposes. However, that they possessed not one but both of said qualities was altogether unexpected and could not have been predicted.

The polymeric additives of the present invention are copolymers of (A) one or more oil-solubilizing compounds having a polymerizable ethylenic linkage (=C=C=) and a hydrocarbyl group of from 4 to 30 aliphatic carbon atoms and (B) one or more α,β-unsaturated monocarboxylic acids of from 3 to 8 carbon atoms each.

Representative copolymers coming within the scope of the present invention are for example those of dodecyl methacrylate with methacrylic acid; diisobutylene with acrylic acid; 2-ethylhexyl vinyl ether with methacrylic acid; dodecyl methacrylate with crotonic acid; diisobutylene with acrylic acid; hexadecylstyrene with methacrylic acid; and allyl stearate with angelic acid. The present invention also contemplates the use of copolymers formed from a plurality of one or more of each of the oil-solubilizing and acid monomer components of the polymer. Representative copolymers of this type are, for example, those of diisobutylene and dodecyl methacrylate (both oil-solubilizing monomers) with methacrylic acid; 1-octadecene and 2-ethylhexyl vinyl ether with acrylic acid; dodecyl methacrylate with acrylic and methacrylic acids; and dodecyl methacrylate and 2-ethylhexyl vinyl ether with methacrylic and angelic acids.

The oil-solubilizing monomer portion of the polymeric additives of this invention can be any compound having at least one ethylenic linkage (>C=C<), together with at least one substituent group which contains an oil-solubilizing hydrocarbyl group of from 4 to 30 aliphatic carbon atoms, and which is characterized by the ability to copolymerize through said ethylenic linkage with the polar monomer referred to above in the presence of a suitable catalyst. Alternatively, the oil-solubilizing aliphatic radical can be introduced into the copolymer, as will hereinafter be more fully described. This aliphatic radical, whether present in the original monomer or introduced into the copolymer, imparts oil solubility to the polymer and is preferably a branched or staight-chain alkyl radical or a cycloalkyl radical such as butyl, isobutyl, n-pentyl, n-hexyl, 2-ethylhexyl, decyl, dodecyl, tetradecyl, cyclohexyl, 4-ethylcyclohexyl, or the like, or an alkenyl radical such as oleyl, ricinoleyl, or the like, wherein the ethylenic double bond has substantially no copolymerizing tendency. Oil solubilizing monomers of this general character are well known in the art and are frequently employed as the oil-solubilizing portion of copolymers which are added to lubricating oils to improve the viscosity index and pour point characteristics thereof. They include such materials as olefins and ethylenically unsaturated ethers, esters, ketones, aldehydes, and the like.

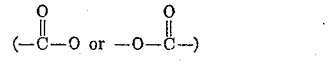
The oil solubilizing monomers of component (A) may also be illustrated by the following general formula:

$$R_1(G')_{n'}CH{=}CH(G)_nR_2$$

in which R_1 and R_2 are members of the group consisting of hydrogen and hydrocarbon radicals of from 4 to 30 carbon atoms, at least one of which contains an aliphatic hydrocarbon group of from 4 to 30 carbon atoms as described above, G and G' are members of the class consisting of oxy (—O—), carbonyl



and carbonyloxy



groups and combinations thereof with not more than two alkylene groups of from 1 to 7 carbon atoms each, and n and n' are 0 or 1. When R_1 and R_2 are hydrocarbon radicals, they may be alkyl, cycloalkyl, alkenyl, cycloalkenyl, aryl, alkaryl or aralkyl in structure, as illustrated by radicals such as 2-ethylhexyl, cyclohexyl, hexenyl, cyclohexenyl, phenyl, naphthyl, tertiary butylphenyl benzyl, etc., with the preferred radicals being as previously mentioned.

Representative oil-solubilizing monomer compounds which can be employed to form the copolymeric additives of the present invention include the following:

OLEFINS

Hexene-1
2-ethylhexene-1
Di- and triisobutylene
Tripropylene
Dodecene-1
Hexadecene-1
Cyclohexene
Octadecene-1
4-octylcyclohexene-1
3-phenylhexadecene-1
p-Octylstyrene
Vinylcyclohexane
2-hexadecylbutadiene-1,3
p-Tertiarybutylstyrene

ETHERS

Vinyl n-butyl ether
Vinyl 2-ethylhexyl ether
Allyl n-butyl ether
Allyl isobutyl ether
Allyl cyclohexyl ether
Allyl 4,4,8,8-tetramethyl-docosyl ether
Methallyl n-hexyl ether
Methallyl n-decyl ether
Methallyl 2-ethylhexyl ether
Methallyl octadecyl ether
Propenyl 2-ethylhexyl ether
Crotyl n-octyl ether
Isopropenyl dodecyl ether
1-decenyl butyl ether
1-eicosenyl decyl ether
Vinyl p-octylphenyl ether
Methallyl p-tert. butylphenyl ether
1-decenyl p-cetylphenyl ether
1-decenyl 2-phenylbutyl ether

ESTERS

Vinyl caproate
Vinyl palmitate
Vinyl oleate
Allyl caprylate
Allyl laurate
Allyl oleate
Allyl palmitate
Allyl stearate
Allyl 2-ethylhexanoate
Allyl ricinoleate
Allyl esters of babassu acids
Allyl esters of lard acids
Allyl naphthenate
Methallyl caproate
Methallyl naphthenate
Methallyl ricinoleate
Methallyl p-octylbenzoate
Methallyl oleate
Methallyl cyclohexane carboxylate
Methallyl palmitate
Crotyl oleate
Crotyl naphthenate
α-Methylcrotyl palmitate
1-propenyl naphthenate
1-propenyl elaidate
Dodecyl acrylate
Hexadecyl methacrylate
Isobutyl α-decylacrylate
Vinyl p-n-octyl benzoate
Allyl 3,5-diisobutyl benzoate
Cyclohexyl methacrylate
Cyclohexyl 2-dodecenoate
Decyl vinylacetate
Isooctyl α-chloroacrylate
p-Isoamylphenyl 2-hexadecenoate
4-p-tolylbutyl 2-octadecenoate
Undecyl cinnamate
Methylcyclohexyl 2-ethyl-2-hexenoate
5-ethyldocosyl crotonate
Octadecyl isocrotonate
n-Butyl-2-eicosenoate
p-Tert. amylphenyl octadecyl maleate
p-Hexadecylphenyl 2-ethylhexyl maleate
o-Tolyl 2-octadecylcyclohexyl maleate
o-Nonylphenyl-hexadecyl maleate
Dihexadecyl maleate
Di-methylcyclohexyl maleate
Mono-2-ethylhexyl maleate
Di-2-ethylhexyl maleate
Di-dodecyl maleate
Di-dodecyl mesaconate
Di-dodecyl citraconate
o-Tolyl octadecyl itaconate
Mono-hexadecyl itaconate
Isopropenyl palmitoleate
1-decenyl laurate
1-hexadecenyl myristate

Although any of the oil solubilizing compounds described above will give effective copolymer compositions for lubricant compositions in accordance with the present invention, higher alkyl esters of α,β-unsaturated monocarboxylic acids of from 3 to 6 carbon atoms having alkyl groups of from 8 to 30 carbon atoms are most preferred, both for availability and effectiveness of copolymers prepared from them. Representative acids of this type are the acrylic, methacrylic, crotonic, tiglic, angelic, α-ethylacrylic, α-methylcrotonic, α-ethylcrotonic, β-ethylcrotonic, β-propylcrotonic, and hydrosorbic acids and the like. Even more desirable are the alkyl esters of acrylic and methacrylic acids containing from 10 to 20 carbon atoms in the alkyl groups, since they are found to provide highly superior polymers for the lubricant compositions of the invention and are obtainable in commercial quantities.

Various copolymers employing representative oil-solubilizing monomers of the foregoing types were prepared to illustrate the oil solubilizing effect of the monomers on the resultant copolymers. The solubility of the copolymers in oil and their suitability as lubricating oil additives were demonstrated by incorporating the copolymers into lubricating oils. The lubricant compositions thus obtained were tested to determine their detergency and deposition properties. The results of these tests are given in Table I below.

In the tests the base oil, unless otherwise indicated, is a solvent-refined, wax-free, SAE-30 grade mineral lubricating oil having a viscosity index of 85 which is derived from California waxy crude. Various amounts of the copolymers are incorporated into the oil as indicated in terms of percent by weight.

The piston varnish ratings of the lubricant compositions were obtained by the standard FL-2 test procedure as set out in the June 21, 1948, report of the Coordinating Research Council. In this test the lubricating oil compositions were tested as crankcase lubricants in a 6-cylinder Chevrolet engine, using a low-grade gasoline especially prone to cause engine deposits. At the end of each test the engine was dismantled and the detergency or deposition properties of the lubricant compositions were determined by examining the engine deposits on the piston and visually rating them as to the amount of piston varnish present. The piston varnish ratings of the compositions are given in numerical terms on a smale of 0–10 with "10" representing the complete absence of deposits.

The deposition characteristics of the lubricant compositions containing the copolymeric additives were also determined in the lacquer deposition test. In this test typical engine fuel combustion products were passed into the lubricant compositions and the ability of the lubricant compositions to solubilize and retain the lacquer-forming materials was observed by weighing the amount of lacquer deposits formed on a fresh iron catalytic surface for a standard period of time. The lacquer deposit of the lubricant composition is taken as the number of milligrams deposit on the metal surface, and may be correlated directly to the piston varnish rating obtained in the standard FL-2 test procedure outlined in the above paragraph.

Both the FL-2 test procedure and the lacquer deposition test are more fully described in the disclosure which follows with regard to the particular lubricant composition of the present invention.

Table I

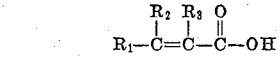
Lubricant composition	Ratio of (1) monomer to (2) monomer to (3) monomer	Piston varnish rating	Lacquer deposit (milligrams)	Piston varnish rating (estimated from lacquer deposit)
Base oil alone		3.0	850	
2.8% (1) dodecyl methacrylate, (2) N,N'-di-2-hydroxy-ethyl maleamide	20/1		450	5.0
2.8% (1) dodecyl methacrylate, (2) allyl stearate, (3) maleic anhydride	20/1/1		405	5.2
1.5% (1) dodecyl methacrylate, (2) N-(2-hydroxyethyl) methacrylamide	7/1	6.3		
3.0%* (1) tridecyl methacrylate, (2) octadecyl methacrylate, (3) monododecyl ether of hexadecaethylene glycol [a] methacrylate	10/6/1	8.4		
2.5% (1) allyl stearate, (2) didodecyl maleate, (3) di-(hydroxyethyl) ethylenediamine salt of monododecyl maleate	5/5/2	5.5		
2.8% (1) vinyl ethylhexoate, (2) itaconic acid	15/1		500	4.5
2.8% (1) vinyl stearate, (2) maleic anhydride, (3) monododecyl ether of pentaethylene glycol [b] methacrylate, (4) methacrylamide	30/1/2/1		325	6.0
2.5% (1) allyl stearate, (2) ethylene glycol monooleate monomaleate, (3) mono-N,N'-di(2-hydroxy-ethyl) ethylenediamine maleate (salt)	5/4/1	4.0		
2.8% (1) octadecene, (2) monododecyl maleate, (3) monopentaerythritol maleate	2/1/1		500	4.5
2.8% (1) hexene-1, (2) dodecyl methacrylate, (3) methacrylic acid, (4) monododecyl ether of eicosaethylene glycol [c] methacrylate	25/25/1/4		400	5.5
2.8% (1) di-2-ethylhexyl fumarate, (2) octadecene-1, (3) crotonic acid, (4) monotridecyl ether of decaethylene glycol [d] methacrylate	25/25/8/2		570	4.0
2.8% (1) allylethyl ether, (2) vinyl stearate, (3) itaconic acid, (4) monododecyl ether of decaethylene glycol [d] crotonate	14/50/7/3			
3.0% (1) vinyl 2-ethylhexyl ether, (2) tetradecylphenyl maleate, (3) dodecyl maleate, (4) maleic acid	6/3/1/2	4.6		
1.5% (1) dodecyl acrylate, (2) monododecyl ether of decaethylene glycol [d] acrylate, (3) acrylic acid	780/9/1	5.6		
1.5% (1) hexadecyl styrene, (2) methacrylic acid	5.8/1	5.9		

*In 140 Neutral Mineral Lubricating Oil from solvent-refined waxy California crude.
[a] Polyethylene glycol of 704 M.W.
[b] Polyethylene glycol of 220 M.W.
[c] Polyethylene glycol of 880 M.W.
[d] Polyethylene glycol of 440 M.W.

From the above test data it will be seen that all of the various oil-solubilizing monomers representative of the aforementioned types were effective in the production of useful, copolymeric lubricating oil additives which are capable of preventing deposits from lubricant compositions under typical engine operating conditions. These monomers, as previously described, constitute a definite, recognized class of compounds which have been used heretofore in the art in the production of polymeric lubricating oil additives of the nonpolar type, such as VI improvers and pour point depressants. Although the results demonstrate beyond any reasonable doubt the suitability of the different oil-solubilizing monomers within the terms of the description in the production of oil soluble copolymers, it should be understood that the efficacy of each individual class of copolymers as detergents is primarily dependent upon the particular polar or functional group in the so-called polar monomer and its relationship to the rest of the copolymer.

Since the functionality of the individual polar groups differs and is largely empirical in nature, no conclusion is intended to be drawn concerning equivalency of the various copolymeric lubricating oil additives employed as detergents in this illustration. The polar groups of the particular class of copolymers of the compositions of this invention and their balance or relationship to the remainder of the copolymers are more fully discussed in the disclosure which follows, along with additional examples of the invention.

The α,β-unsaturated monocarboxylic acid monomers of the copolymeric additives employed in this invention have the general formula



where the R_1's, R_2's and R_3's, which can be the same as or different from one another, are selected from the group consisting of hydrogen atoms and alkyl groups of from 1 to 4 carbon atoms. Representative acids of this type, any one or more of which can be employed in forming the copolymers hereof, are acrylic, methacrylic, crotonic, tiglic, angelic, α-ethylacrylic, α-methylcrotonic, α-ethylcrotonic, β-ethylcrotonic, α-butylcrotonic, hydrosorbic and α-ethylhydrosorbic acids, and the like. A preferred group of acids is made up of acrylic and methacrylic acids.

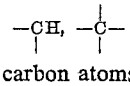
In preparing the copolymers of this invention, it is necessary that conditions be chosen which will insure copolymerization and the formation of copolymers having the requisite oil solubility. The oil-solubilizing monomers vary somewhat in their solubilizing characteristics. Thus, in some cases, oil-solubilizing/acid (A) and (B) monomer ratios as low as 1:1 can be employed, while in others, ratios as high as about 20:1 can be used in order to obtain a copolymer product having optimum solubility characteristics. However, copolymers having excellent detergent and antiwear characteristics, together with the requisite oil solubility (which is at least 2%, and is preferably greater than 10% by weight of the lubricant composition) can be prepared by employing oil-solubilizing (A) monomer to acid (B) monomer ratios of from about 15:1 to 3:1, and such a range is therefore preferably employed wherever possible.

The copolymers employed in a practice of this invention can be prepared by one or more of a variety of different methods known in the art. Thus, one may simply polymerize a given oil-solubilizing monomer with a given acid to form the desired copolymer. Alternatively, suitable precursor compounds can be employed in the copolymerization reaction, with the desired monomer components of the copolymer then being formed by the appropriate treatment of the polymerized reaction product. For example, a copolymer of dodecyl methacrylate and methacrylic acid can be prepared by (1) directly copolymerizing the two monomers; or (2) starting with a homopolymer of dodecyl methacrylate, subjecting the polymer to partial hydrolysis in order to free the desired proportion of carboxyl groups. Other possible variations in the nature of the reactants and in the selection of a suitable reaction path would also suggest themselves to those skilled in the art.

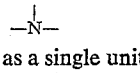
Having selected the desired monomeric reactants, the copolymer of this invention can be prepared by conventional bulk, solution or emulsion methods of addition polymerization in the presence of an addition polymerization initiator. Preferably, however, the copolymerization is effected in an inert organic solvent such as benzene, toluene, xylene or petroleum naphtha in the presence of a free radical-liberating type of initiator such as a peroxy compound, for example, benzoyl peroxide, acetyl peroxide, tert.-butyl hydroperoxide, di-tert. butyl peroxide, di-benzoyl peroxide, or di-tert. amyl peroxide, or an azo initiator such as 1,1'-azodicyclohexane-carbonitrile or α,α'-azodiisobuteronitrile. The catalyst, or polymerization initiator, can be employed in an amount of from about 0.1 to 10%, with a preferred range being from about 0.25 to 2%. If desired, the catalyst can be added in increments as the reaction proceeds. Likewise, additional portions of the solvent can also be added from time to time in order to maintain the solution in a homogenous condition. The temperature of copolymerization varies from about 75 to 150° C., with the optimum temperature depending on the solvent selected, the concentration of monomers present therein, the catalyst selected, and the time of the reaction. Much the same conditions prevail when the copolymerization is effected in bulk rather than in the presence of an inert solvent.

The copolymer additives of the invention have apparent molecular weights as determined by standard light scattering methods of at least 2,000 and preferably at least 8,000. For practical purposes, molecular weights of from 100,000 to 1,000,000 are most suitable from the standpoint of viscosity and other physical characteristics of the polymeric additives.

In a preferred application of the copolymeric lubricating oil detergent additives of the present invention in mineral lubricating oil, it has been noted that a certain optimum relationship between the total number of aliphatic carbon atoms to polar groups within the molecule appears to exist. Evidence has been obtained that for a given concentration the copolymer compositions containing a ratio of aliphatic carbon atoms to polar groups within the range of from 50 to 225, preferably 75 to 125, appear to embrace the optimum composition for deposit reduction effectiveness. In determining this apparent balance between the polar and nonpolar constituents, the aliphatic carbon atoms to be considered are the following: CH_3—, —CH_2—,



and excluding aromatic ring carbon atoms or the carbon atom of the carbonyl groups. As polar groups, the following representative radicals are included: —OH (either acid, alcohol or phenol), —NH_2,



and an acid anhydride group as a single unit.

Although this concept of copolymer compositions appears to correlate generally with their performance in all of the oils of lubricating viscosity, there may be additional composition factors which alter the effect of these improving agents in various types of lubricating oil systems and service. However, on the basis of these assumptions, it becomes evident that variations in the aliphatic carbon to polar ratio and hence performance efficacy may be accomplished by the choice of the acid derivative radical and degree of neutralization in the modification of polar component (B).

Typical methods for preparing the copolymers which

can be exployed with success as detergents and antiwear oxidants in lubricant compositions are given in the following examples.

EXAMPLE I

In this operation a homopolymer of dodecyl methacrylate having an apparent molecular weight of about 20,000 was employed as a starting material from which was prepared a copolymer of dodecyl methacrylate and methacrylic acid. The preparation was as follows: A solution of 14 grams of potassium hydroxide in 300 cc. of 2-ethylhexanol was prepared, and to this solution was added 800 cc. of a 40% solution in mineral oil of the methacrylic homopolymer, this amount of KOH constituting a slight excess over that theoretically required to effect the desired saponification of approximately 15% of the ester groups present in the polymer. The resulting solution was heated to 320° F. and maintained at this temperature, with stirring, for 10 hours. To this solution was then added 50 cc. of benzene along with a 50% excess of 6N HCl over the amount theoretically required to liberate the free carboxyl groups from the corresponding salt. The acidified solution was then refluxed for 2 hours, after which it was cooled, diluted with ethyl ether, and water washed (along with a small amount of ethyl alcohol to break the emulsion) until neutral to litmus. The solution was then placed in a steam bath to remove the ether and thereafter distilled in vacuo until a pot temperature of 350° F. at 3 mm. Hg was reached in order to remove the 2-ethylhexanol and the dodecyl alcohol present, leaving as the oil-soluble residue, the desired copolymer of dodecyl methacrylate and methacrylic acid in approximately 7:1 molar ratio.

EXAMPLE II

The preparation of the copolymer of dodecyl methacrylate with methacrylic acid as described in the foregoing example was repeated adjusting the proportions of dodecyl methacrylate and methacrylic acid to give the copolymer of dodecyl methacrylate and methacrylic acid in approximately 14:1 molar ratio.

EXAMPLE III

Dodecyl methacrylate and acrylic acid were copolymerized in accordance with the procedure outlined in the above examples to produce the copolymer of dodecyl methacrylate and acrylic acid in approximately 7:1 molar ratio.

EXAMPLE IV

349 g. of mineral oil concentrate containing 40% by weight of hexadecylstyrene and 350 ml. of toluene were introduced to a reaction vessel. The mixture was stirred at about 245° F. and 20 ml. portions of a 5% solution of benzoyl peroxide in toluene were added at approximately hourly intervals over a period of about 24 hours. During this period 68 g. of glacial methacrylic acid dissolved in 370 ml. of toluene was added in approximately the same portions and intervals. The polymeric product was precipitated with acetone and methanol. The product was a copolymer of hexadecylstyrene and methacrylic acid in approximately 6:1 molar ratio.

In general, excellent detergent and antiwear properties can be imparted to lubricating oils by dissolving therein a quantity of from about 0.1 to 10% by weight of the copolymers of the type described above, although a preferred range is from about 0.5 to 5% by weight. The copolymeric additives of this invention can be used with good effect in the case of any one of a wide variety of oils of lubricating viscosity, or of blends of such oils. Thus, the base oil can be a refined Pennsylvania or other paraffin base oil, a refined naphthenic base oil, or a synthetic hydrocarbon or non-hydrocarbon 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 aromatic 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 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. Other important classes of synthetic oils include the various esters as, for example, di-(2-ethylhexyl) sebacate, tricresyl phosphate and silicate esters. If desired, the oil can be a mixture of mineral and synthetic oils.

While satisfactory lubricant compositions can be obtained by adding to the base oil employed only one or more of the copolymeric additives of the type described above, it also falls within the purview of this invention to provide lubricant compositions which contain not only such copolymers, but also other additives such as pour point depressants, oiliness and extreme pressure agents, antioxidants, corrosion inhibiting agents, blooming agents, thickening agents, and/or compounds for enhancing the temperature-viscosity characteristics of the oil. The present invention also contemplates the addition to the lubricant composition (particularly when the amount of copolymer employed is relatively small) of auxiliary detergents and/or antiwear agents.

The efficacy of copolymeric additives of the type described above as detergents and antiwear agents in lubricating oils is illustrated by data from a number of tests. In the tests from which the data is obtained the base oil, unless otherwise specified, is a solvent-refined, wax-free SAE–30 grade mineral lubricating oil having a viscosity index of 85 which is derived from California waxy crude. Various amounts of the copolymeric additives are incorporated into the oil as noted in terms of percent by weight.

In the lacquer deposition test the low temperature detergency of the oils tested is measured by determining the ability of the oil to solubilize and retain typical engine fuel deposits and precursors thereof which are formed due to incomplete combustion of the fuel. Retention of these deposits in a given oil depends upon their dispersal and upon minimizing their polymerization to lacquer.

Briefly described, the lacquer deposition test involves condensing fresh cool flame oxidation products from a standard test fuel, simulating the fuel combustion products of an internal combustion engine in a steel vessel containing a certain amount of the lubricating oil being tested. The steel surface of the vessel acts as an iron catalyst for polymerization of the fuel oxidation products to lacquer in the same manner as the steel surfaces in an internal combustion engine. After the oxidation products have been condensed, the steel vessel containing the lubricating oil is heated for 24 hours at a temperature selected to correspond with actual engine conditions. The test oil is then decanted while hot from the lacquer deposits formed in the steel vessel due to polymerization and the lacquer deposits are de-oiled and weighed.

In the actual test a low grade gasoline is employed of the type described in connection with the standard FL–2 test procedure given below. The gasoline at a rate of 13.3 cc. per hour is vaporized and mixed with air, the air rate being 1.75 liters per minute. The vapor mixture of gasoline and air is then fed into an elongated cool flame combustion chamber of standard design having a diameter of 1½ inches. The cool flame combustion chamber is maintained at 695° F. The test is continued for 1 hour during which the oxidation products issuing from the cool flame combustion chamber are condensed into the weighed steel catalyst vessel which contains 30 g. of the oil being tested at about room temperature. The steel vessel containing test oil and condensed oxidation products is then heated for 24 hours at 110° F. The

oil is decanted from the lacquer deposits in the vessel, following which the deposits are de-oiled by washing with petroleum solvent. The increase in weight of the steel vessel due to the lacquer deposits is then determined and recorded in milligrams as "LD" or "lacquer deposit."

The lacquer deposit for any given lubricant composition obtained in accordance with the procedure described above is directly correlated to the "piston varnish rating" or "PVR" obtained for the same lubricant composition in the standard FL–2 test procedure previously referred to and hereinafter more particularly described. Table II which follows gives the correlated values for both the lacquer deposits and piston varnish ratings.

Table II

LD	PVR	LD	PVR
140	9.5	335	6.0
170	9.0	370	5.5
190	8.5	420	5.0
220	8.0	480	4.5
245	7.5	570	4.0
275	7.0	700	3.5
305	6.5	850	3.0

The correlated values in the above table provide an accurate means for estimating from the lacquer deposits determined for a given oil the piston varnish rating to be obtained in the standard FL–2 Chevrolet engine test.

In the test where the piston varnish ratings are obtained, a given lubricating oil composition is tested as the crankcase lubricant in a 6-cylinder Chevrolet engine using a low grade gasoline especially prone to cause engine deposits, the condition being those defined in the standard FL–2 test procedure as described in the June 21, 1948, report of the Coordinating Research Council. This procedure requires the maintenance of a jacket temperature of 95° F. and a crankcase oil temperature of 155° F. at 2500 r.p.m. and 45 brake horsepower of 40 hours, and therefore closely simulates the relatively "cold" engine conditions which are normally experienced in city driving. At the end of each test, the engine is dismantled and the amount of engine deposits on the piston determined and expressed as the piston varnish rating. This value is obtained by visually rating (on a scale of 0 to 10, with 10 representing the absence of any deposit) the amount of deposit on each piston skirt and averaging the individual ratings so obtained for the various pistons. Under the conditions of this test, a piston varnish rating of 4.5 is indicative of satisfactory performance, though preferably this rating should be 5 or above. The wear experienced by the piston rings during the test is also measured in certain cases and expressed in mgs. of metal lost per hour. 5 mgs. per hour is regarded as satisfactory, though preferably the loss should be 3 mgs. or less per hour. In the case of the base oil alone without the addition of any additives it is found that the piston varnish rating is approximately 3.0 and the piston ring weight loss is 5.5 mgs./hr. On the other hand, as indicated by the data presented in Table III below, when the base oil is compounded with the indicated amounts of a copolymer, greatly superior results are obtained.

Table III

Lubricant composition	Ratio of (1) monomer to (2) monomer to (3) monomer	Piston varnish rating	Lacquer deposit (milligrams)	Piston varnish rating (estimated from lacquer deposit)	Piston ring wear rate, mg./hr.
Base oil alone		3.0	850		5.0
1.5% (1) dodecyl methacrylate and (2) methacrylic acid in base oil	7/1	6.1			2.4
1.5% (1) dodecyl methacrylate and (2) methacrylic acid in base oil	14/1	4.8			3.6
1.5% (1) dodecyl methacrylate and (2) acrylic acid in base oil	7/1	5.5			3.0
1.5% (1) hexadecylstyrene and (2) methacrylic acid in base oil	6/1	5.9			

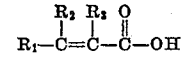
From the test results of the foregoing table it will be seen that each of the illustrative compositions containing the copolymeric lubricating oil additives according to the invention possess greatly improved lubricating properties compared to the base oil alone.

In the foregoing description of the invention, the term "hydrocarbyl" is used with reference to the class of organic groups commonly known as "hydrocarbon groups." As employed herein, this term is considered to be a more convenient and concise generic expression for describing said hydrocarbon groups.

This application is a division of Lowe, Stewart, and Stuart patent application Serial No. 563,207, filed February 3, 1956, which in turn is a continuation-in-part of Lowe, Stewart and Stuart patent application Serial No. 328,151, filed December 26, 1952, and now abandoned.

We claim:

1. A lubricant composition comprising a major portion of an oil of lubricating viscosity, together with from about 0.1 to 10% by weight of a copolymer of monomers consisting of (A) a higher alkyl ester of an α,β-unsaturated carboxylic acid of from 3 to 6 carbon atoms in which the alkyl group contains from 8 to 30 carbon atoms and (B) an acid having the general structural formula



where R_1, R_2 and R_3 are radicals selected from the group consisting of hydrogen atoms and alkyl groups of from 1 to 4 carbon atoms, said components being present in the copolymer in the ratio of from about 3 to 15 monomer units of the ester (A) for each monomer unit of the acid (B) and said copolymer having a molecular weight of at least 2,000.

2. The composition of claim 1, wherein the acid component (B) of the copolymer is acrylic acid.

3. The composition of claim 1, wherein the acid component (B) of the copolymer is methacrylic acid.

4. A lubricant composition comprising a major portion of an oil of lubricating viscosity, together with about 0.1 to 10% by weight of a copolymer of monomers consisting of (A) dodecyl methacrylate and (B) methacrylic acid, said components being present in the copolymer in the ratio of about 3 to 15 monomer units of the ester component (A) for each monomer unit of the acid component (B) and said copolymer having a molecular weight of at least 2,000.

References Cited in the file of this patent

UNITED STATES PATENTS

2,653,133	Catlin	Sept. 22, 1953
2,737,496	Catlin	Mar. 6, 1956
2,800,450	Bondi et al.	July 23, 1957