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DETERGENT COPOLYMERS

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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 the 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 compound 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 solubilizing 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 the 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) oil-solubilizing compounds having a polymerizable ethylenic linkage (>C=C<) and containing a hydrocarbyl group of from 4 to 30 carbon atoms, (B) nitrogenous monomers selected from the group consisting of amides of α,β-unsaturated monocarboxylic acids of from 3 to 6 carbon atoms and α,β-unsaturated, α,β-dicarboxylic acids of from 4 to 12 carbon atoms and hydrocarbon-substituted amides and amine salts of said acids wherein the nitrogen atom constituting the amide or amine salt linkage is attached to a hydrocarbon group and (C) acidic compounds selected from the group consisting of α,β-unsaturated monocarboxylic acids of from 3 to 6 carbon atoms, α,β-unsaturated, α,β-dicarboxylic acids of from 4 to 12 carbons atoms, anhydrides thereof and half-amides and monoamine salts thereof as defined in (B).

Representative copolymers coming within the scope of the present invention are, for example, those of dodecyl acrylate, 2-ethylhexyl methacrylamide and acrylic acid; allyl stearate, didodecyl maleate, N,N'-didodecyl maleamide and N-dodecyl maleamic acid; vinyl 2-ethylhexyl ether, N-dodecyl methacrylate (salt) and methacrylic acid; octadecene-1, methacrylamide and methacrylic acid; didodecyl maleate, dodecyl maleamate and maleic anhydride; and octadecyl methacrylate, octyl acrylate, N-dodecyl methacrylamide and methacrylic acid.

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 straight-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.

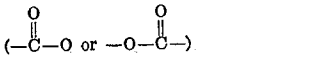
The oil-solubilizing monomers of component A may also be illustrated by the following general formula:

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

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-eidosenyl 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
Dimethylcyclohexyl 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 scale 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.

The Lacquer Deposition Test is 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 mono-oleate 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		

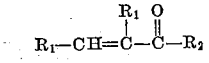
*In 140 Neutral Mineral Lubricating Oil from solvent-refined waxy California crude.
[a] Polyethylene glycol of 704 M.W.
[b] Polyethylene glycol of 220 M.W.
[c] Polyethylene glycol of 880 M.W.
[d] Polyethylene glycol of 440 M.W.

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.

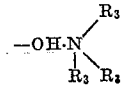
Since the functionality of the individual polar groups differs and is largely empirical in nature, no conclusion is intended to be drawn concerning equivalency of the various copolymeric lubricating oil additives employed as detergents in this illustration. The polar groups of the particular class of 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.

Suitable monomeric nitrogenous components of the polymeric additives of the present invention as previously mentioned are the amides of α,β-unsaturated monocarboxylic acids of from 3 to 6 carbon atoms (e.g., methacrylic, acrylic, crotonic, tiglic and like acids). Also suitable are the amides and amine salts of these acids wherein the nitrogen atom of the amide or amine salt is linked to at least one hydrocarbon radical.

A preferred group of such nitrogenous monomers is one of the type having the general formula



wherein the R_1's are hydrogen atoms or methyl groups, and R_2 is a radical having the structure



(in the case of amine salts), or



(in the case of amides),

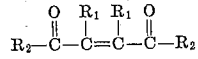
where the R_3's, which may be the same or different from one another, represent hydrogen atoms and/or monovalent hydrocarbon radicals. Preferably, the amide or amine salt is one of acrylic or methacrylic acid wherein the R_3's are hydrogen atoms or hydrocarbon radicals of from 1 to 18 carbon atoms. The most preferred hydrocarbon radicals are alkyl radicals containing from 1 to 18 carbon atoms each.

Representative nitrogenous monomer components of the above type employed in the copolymers of this invention include:

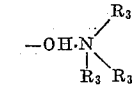
Ethylamine salt of methacrylic acid
Diethylamine salt of methacrylic acid
Trimethylamine salt of methacrylic acid
Pyridine salt of acrylic acid
Methacrylamide
N-ethylmethacrylamide
N-dodecylmethacrylamide
N,N-didodecylmethacrylamide
N-(2-ethylhexyl)-methacrylamide
N,N-dimethylmethacrylamide
N-phenylmethacrylamide
N,N-ditolylmethacrylamide
Acrylamide
N-methylacrylamide
N,N-diphenylacrylamide
N-methyl-N-dodecylacrylamide
N-tolylacrylamide
N,N-di(2-ethylhexyl)-acrylamide
Crotonamide
N,N-diethylcrotonamide
Tiglamide

Other suitable nitrogenous monomer components of the copolymeric additives of this invention, as mentioned above, are the derivatives of aliphatic, α,β-unsaturated dicarboxylic acids of from 4 to 12 carbon atoms (e.g., maleic, fumaric, citraconic, mesaconic, α-hydromuconic, and like acids) wherein at least one of the carbonyl carbon atoms of the acid is linked (either as an amide or as an amine salt) to a nitrogen atom which in turn is attached to hydrogen atoms and/or hydrocarbon radicals. The remaining carboxyl groups, if any, in the monomer which are not amide or amine salt derivatives of the type described above can be left as free carboxyl groups or converted to one or more of various cyano, ester or amido linkages to hydrocarbon groups.

A preferred group of such nitrogenous monomers is made up of those of the type defined in the foregoing paragraph, but where the dicarboxylic acid is one of the α,β-unsaturated, α,β-dicarboxylic variety (e.g., maleic acid, fumaric acid, citraconic acid, or the like). A still more preferred group is made up of nitrogenous monomers of the type having the structural formula



where the R_1's, which can be the same as or different from one another, are hydrogen atoms or alkyl groups of not more than 8 carbon atoms and wherein at least one of the R_2's is a radical having the structure



(in the case of amine salts), or



(in the case of amides),

the R_3's in said formulae, which may be the same or different from one another, being hydrogen atoms and/or hydrocarbon radicals. Any remaining R_2 in the structural formula may be an —OH, or —OR group, R being a monovalent hydrocarbon radical and preferably an alkyl radical of from 1 to 18 carbon atoms. When R_3 is a hydrocarbon radical, it is preferred that it contain from 1 to 18 carbon atoms. Still more preferred are the alkyl radicals of from 1 to 18 carbon atoms.

Representative nitrogenous monomer components of the above type, any one or more of which can be used in the copolymeric oil additives of this invention are:

N,N'-diethyl maleamide
N-propyl maleamic acid
Mono-N-ethylamine salt of maleic acid
Dodecyl N-ethyl maleamate
Dodecyl N-phenyl maleamate
N-ethyl-N'-phenyl maleamide
N-ethyl fumaramic acid
N,N'-diethyl fumaramide
Dodecyl N'-ethyl fumaramate
N,N'-dihexyl citraconamide
Dodecyl N-ethyl citraconamate
Dipyridine salt of glutaconic acid

For present purposes the most preferred nitrogenous monomers of the types illustrated above are the amides and hydrocarbon-substituted amides of the α,β-unsaturated monocarboxylic acids of from 3 to 6 carbon atoms and, more particularly, the amides and N-alkyl amides of acrylic and methacrylic acids in which the alkyl groups contain from 1 to 18 carbon atoms each. Representative copolymers of such monomers in lubricant compositions as hereinafter described have been found to provide excellent detergent and antiwear properties.

The acidic compounds or component C of the co-copolymer may be any of the mono- and dicarboxylic acids of the type described above, including anhydrides, half-amides, and monoamine salts of the latter, wherein the amides and amine salts are as defined in connection with the B monomers of the foregoing description.

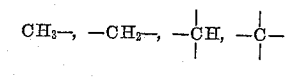
In preparing the copolymers of this invention, it is only necessary that conditions be chosen which will insure copolymerization and the formation of copolymers having the requisite oil-solubility. The oil-solubilizing A monomers vary somewhat in their solubilizing characteristics. Thus, in some cases it is possible to obtain copolymers which are soluble in oil by employing oil-solubilizing nitrogenous A and B monomer ratios as low as 1:1; while in others it is advantageous to raise this ratio to much higher values, e.g., about 20:1, in order to obtain a copolymer product having optimum oil-solubility characteristics. As a general rule, however, copolymers having excellent detergent and antiwear characteristics, together with the requisite oil-solubility (which should be 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 polar B monomer ratios of from about 3:1 to 15:1, and such a range is preferably employed wherever possible.

The copolymers of this invention can be prepared by one or more of a variety of different methods known in the art. As regards the reactants per se, there can be employed a given oil-solubilizing monomer, or a mixture of such monomers, together with a nitrogen monomer and an acidic monomer or a combination of such monomers. However, it is also possible to employ monomer reactants other than those which finally compose the copolymer. Thus, in the case where ester monomers are to form a part of the copolymer, one may employ, instead of the ester, the corresponding unsaturated alcohol or unsaturated acid, with the balance of the ester monomer unit being supplied by subjecting the copolymer intermediate to an appropriate esterification treatment. Again, instead of employing the monomeric amide or amine salt to form the copolymer, one can employ the corresponding unsaturated acid or acid anhydride, or the acid chloride, or a half-ester of the acid, for example, with the desired amide or amine salt then being formed after the polymerization reaction is complete. Thus, a copolymer of dodecyl methacrylate, N,N'-diethyl maleamide and N-ethyl maleamic acid can be formed by first copolymerizing equimolar amounts of dodecyl methacrylate and maleic anhydride and then forming the desired amide linkages by treating the copolymer with 75% of the amount of ethylamine required for complete amidization of the maleic anhydride.

In another example, assuming that the copolymer is to be formed from related monomers, as from an alkyl methacrylate and methacrylamide or methacrylate amine salt with methacrylic acid, one may first homopolymerize the ester, then effect partial hydrolysis of the homopolymer, and finally convert the liberated carboxyl group to the desired substituted amide or amine salt form. In any event, however, the present invention contemplates the formation of only those copolymers which are soluble to the extent of at least 2% by weight in hydrocarbon mineral oils, and which contain at least one polar-substituted amide or amine salt monomer unit and at least one acidic monomer unit for each twenty oil-solubilizing monomer units present in the copolymer, and at most one such nitrogenous monomer unit and one each acidic monomer unit for each monomer unit of the oil-solubilizing compound.

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, dibenzoyl peroxide, or di-tert. amyl peroxide, or an azo initiator such as 1,1'-azodicyclohexanecarbonitrile, or α,α'-azodiisobutyronitrile. 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:



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, —NH, —N—, 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 components B and C.

Typical methods for preparing the copolymers which can be employed with success as detergents and antiwear

agents in lubricant compositions are given in the following examples:

EXAMPLE I

This example illustrates the preparation of a representative oil-soluble copolymer of dodecyl acrylate, N-2-ethylhexyl methacrylamide and acrylic acid. 95 g. dodecyl acrylate, 5.1 g. N-2-ethylhexyl methacrylamide and 1.9 g. of acrylic acid are dissolved in 200 g. of benzene. To the resulting solution is then added 0.25 g. of azodiisobutyronitrile. The solution is heated in an atmosphere of nitrogen for about 18 hours at 70° C. with stirring. Heating is then discontinued and the viscous copolymeric product is precipitated from the reaction mixture by the addition of a sixfold volume of methanol. The polymeric product analyzes about 0.4% nitrogen. It is the copolymer of dodecyl acrylate, N-2-ethylhexyl methacrylamide and acrylic acid in 15/1/1 molar ratio.

EXAMPLE II

In this operation an oil-soluble copolymer is prepared of dodecyl methacrylate, methacrylamide and methacrylic acid. 120 g. of dodecyl methacrylate, 2.7 g. of methacrylamide and 2.7 g. of methacrylic acid are dissolved in 245 g. of benzene. 0.18 g. of azodiisobutyronitrile catalyst is added to the solution. The solution is heated to about 70° C. under an atmosphere of nitrogen and maintained at these conditions with stirring for about 18 hours. Following this, heating is discontinued and a sixfold volume of methanol is added to the reaction mixture to precipitate the viscous polymeric product. Analysis of the product indicates 0.31% nitrogen. The product thus obtained is the copolymer of dodecyl methacrylate, methacrylamide and methacrylic acid in 15/1/1 molar ratio.

EXAMPLE III

In this example, an oil-soluble copolymer is prepared of octadecyl methacrylate, 2-ethylhexyl acrylate, N-dodecyl methacrylamide and methacrylic acid. 66 g. octadecyl methacrylate, 54 g. 2-ethylhexyl acrylate, 8 g. N-dodecyl methacrylamide and 2.7 g. methacrylic acid are dissolved in 256 g. of benzene. To this solution is added 0.19 g. azodiisobutyronitrile as catalyst. The solution is heated under an atmosphere of nitrogen with stirring for about 18 hours at 70° C. Heating is then stopped and the viscous polymer product is precipitated from the reaction mixture by the addition of a sixfold volume of methanol. Analysis of the polymeric product shows 0.33% nitrogen. The copolymer thus obtained is the copolymer of octadecyl methacrylate, 2-ethylhexyl methacrylate, N-dodecyl methacrylamide and methacrylic acid in an approximately 6/9/1/1 molar ratio.

The copolymers of this invention as illustrated by the above examples are oil-soluble. That is to say, they are soluble to the extent of at least 2% by weight in oil. Lubricating oil concentrates containing up to 75% by weight of the copolymers are particularly useful in the preparation of the superior detergent and wear inhibiting lubricant compositions, and such concentrates are, therefore, considered to be another embodiment of the compositions according to this invention.

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 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. For example, from about 0.1 to 10% by weight of alkaline earth metal higher alkyl phenate detergent and wear reducing agents such as the calcium alkyl phenates, preferably those having an average of approximately 14 carbon atoms in the alkyl group, may be employed in combination with the copolymer of the invention to provide highly effective lubricant compositions. Other suitable additives for such use include the organic thiophosphate corrosion and high temperature oxidation inhibitors such as the reaction product of pinene and P_2S_5 and the bivalent metal dihydrocarbyldithiophosphates, namely, zinc butyl hexyl dithiophosphate, zinc tetradecyl phenyl dithiophosphate and the like.

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 13.2 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 deoiled 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."

Table II

Lubricant composition	Ratio of (1) Monomer to (2) monomer to (3) monomer, etc.	Lacquer deposit (milligrams)
Base oil alone		850
2.8% copolymer of (1) dodecyl acrylate, (2) N-2-ethylhexyl methacrylamide and (3) acrylic acid in base oil	15/1/1	554
2.8% copolymer of (1) dodecyl methacrylate, (2) methacrylamide and (3) methacrylic acid in base oil	15/1/1	502
2.8% copyolymer of (1) octadecyl methacrylate, (2) 2-ethylhexyl acrylate, (3) N-dodecyl methacrylamide and (4) methacrylic acid	6/9/1/1	538

From the above test results it will be seen that the lubricant compositions of the present invention are excellent detergents in lubricating oils. In the tests the base oil alone gives a lacquer deposit of 850 mg. On the other hand, lubricant compositions containing representative copolymers according to the invention provide greatly reduced lacquer deposition in the order of 500 mg. This is a better than 40% improvement over the base alone.

The wear inhibiting properties of lubricant compositions containing representative copolymers according to the present invention are also illustrated by a number of tests. In these tests, the well-known Falex wear test is employed. A description of this test, which is generally familiar to those skilled in the art, may be found, for example, in the "Journal of the Institute of Petroleum," volume 32, April 1946. The base oil of the compositions is a solvent refined 150 neutral mineral lubricating oil. The polymeric detergents illustrative of the compositions of the invention are employed in amounts of about 5% by weight, based on the total lubricant composition. The compositions also contain 6mK./kg. of an illustrative organic thiophosphate corrosion and high temperature oxidation inhibitor, namely, zinc butyl hexyl dithiophosphate. In carrying out the test, the following specific conditions are observed: speed, 300 r.p.m.; load, 1100 pounds; time, 30 minutes; specimens, steel-on-steel. The weight of the shaft before and after the test is noted and the loss in weight in milligrams indicates the amount of wear.

Table III

Lubricant composition	Ratio of (1) Monomer to (2) monomer to (3) monomer, etc.	Falex test (wear, mg.)
5% copolymer of (1) dodecyl acrylate and (2) N-2-ethylhexyl methacrylamide in base oil	15/1	45.4
5% copolymer of (1) dodecyl acrylate, (2) N-2-ethylhexyl methacrylamide and (3) acrylic acid in base oil	15/1/1	9.1
5% copolymer of (1) dodecyl methacrylate and (2) methacrylamide in base oil	15/1	42.8
5% copolymer of (1) dodecyl methacrylate, (2) methacrylamide and (3) methacrylic acid in base oil	15/1/1	11.2
5% copolymer of (1) octadecyl methacrylate, (2) 2-ethylhexy acrylate and (3) N-dodecyl methacrylamide in base oil	6/9/1	50.2
5% copolymer of (1) octadecyl methacrylate, (2) 2-ethylhexyl acrylate, (3) N-dodecyl methacrylamide and (4) methacrylic acid in base oil	6/9/1/1	10.0

From the illustrative test results set out above, it is readily seen that all of the lubricant compositions containing the acidic copolymers in accordance with the present invention are outstanding wear inhibitors. In the "back-to-back" comparison of the above examples, in each case, the acid-containing copolymers give wear rates which are one-fourth or less of the wear rate encountered with the corresponding nonacid copolymer.

For the purpose of further illustration other representative lubricant compositions containing copolymers of (A) oil-solubilizing monomers, (B) nitrogenous monomers and (C) acidic monomers in accordance with the present invention are given in the following table:

Table IV

Percent by weight copolymer in base oil	Copolymer	Ratio of (1) monomer to (2) monomer to (3) monomer, etc.	Base oil
1.5	(1) vinyl 2-ethylhexyl ether, (2) octadecyl methacrylate, (3) N-2-ethylhexyl methacrylamide and (4) methacrylic acid.	5/15/1/1	Di(2-ethylhexyl)sebacate.
5	(1) allyl stearate, (2) N-dodecyl methacrylamide and (3) methacrylic acid.	15/1/1	Hexa(2-ethylhexoxy)di-siloxane.
5	(1) allyl stearate, (2) didodecyl maleate, (3) N,N'-didodecyl maleamide and (4) N-dodecyl maleamic acid.	10/1/1/1	Mineral lubricating oil.
75	(1) vinyl 2-ethylhexyl ether, (2) N-dodecyl methacrylate (salt) and (3) acrylic acid.	15/1/1	Do.
5	(1) octadecene-1, (2) methacrylamide and (3) methacrylic acid	20/1/1	Do.
75	(1) dodecyl methacrylate, (2) N-dodecyl acrylamide and (3) acrylic acid.	15/1/1	Do.

This application is a continuation-in-part of Stewart, Stuart and Lowe application Serial No. 329,138, filed December 31, 1952, and Lowe, Stewart and Stuart application Serial No. 363,679, filed June 23, 1953, both parent applications now abandoned.

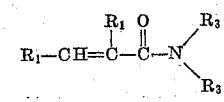
We claim:

1. A copolymer of monomers selected from each of the classes consisting of (A) dodecyl acrylate, (B) N-2-ethylhexyl methacrylamide, and (C) acrylic acid, said components being present in the copolymer in the ratio of from about 1 to 20 monomer units of the A component for each monomer unit of said B and C components, there being present at least one monomer unit of each of said B and C components in the copolymer, said copolymer having an apparent molecular weight of at least 2,000 and a solubility in oil of at least 2% by weight.

2. A copolymer of monomers selected from each of the classes consisting of (A) dodecyl methacrylate, (B) methacrylamide, and (C) methacrylic acid, said components being present in the copolymer in the ratio of from about 1 to 20 monomer units of the A component for each monomer unit of said B and C components, there being present at least one monomer unit of each of said B and C components in the copolymer, said copolymer having an apparent molecular weight of at least 2,000 and a solubility in oil of at least 2% by weight.

3. A copolymer of monomers selected from each of the classes consisting of (A) a mixture of octadecyl methacrylate and 2-ethylhexyl acrylate, (B) N-dodecyl methacrylamide, and (C) methacrylic acid, said components being present in the copolymer in the ratio of from about 1 to 20 monomer units of the A component for each monomer unit of said B and C components, there being present at least one monomer unit of each of said (B) and C components in the copolymer, said copolymer having an apparent molecular weight of at least 2,000 and a solubility in oil of at least 2% by weight.

4. A copolymer of monomers selected from each of the classes consisting of (A) 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 each, (B) amides of α,β-unsaturated monocarboxylic acids of from 3 to 6 carbon atoms having the formula:



wherein the R_1's are members selected from the group consisting of hydrogen atoms and alkyl groups and the R_3's are members selected from the group consisting of hydrogen atoms and alkyl radicals of from 1 to 18 carbon atoms and (C) α,β-unsaturated monocarboxylic acids of from 3 to 6 carbon atoms, said components being present in the copolymer in the ratio of from about 1 to 20 monomer units of the A component for each monomer unit of said B and C components, there being present at least one monomer unit of each of said B and C components in the copolymer, said copolymer having an apparent molecular weight of at least 2,000 as determined by the standard light scattering method and a solubility in oil of at least 2% by weight.

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