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EXTREME PRESSURE LUBRICANT

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This invention relates to extreme pressure lubricants capable of withstanding high pressures at elevated temperatures under severe and adverse operating conditions. More specifically this invention pertains to improvement of extreme pressure lubricants by enhancing their extreme pressure properties and at the same time rendering them substantially non-corrosive and stable, by addition of a novel additive thereto, in relatively minor amounts.

Natural and/or synthetic lubricants per se are not capable of withstanding extreme pressures at high temperatures, high speeds and under severe loading conditions as generally encountered in present-day lubricating such as internal combustion engines of various types, transmission devices, certain types of gears, e. g. hypoid gears, metal fabrication such as in cutting and drawing and the like. Under such conditions of lubrication, the protective film formed between contacting surfaces, by the lubricant, so as to prevent direct metal-to-metal contact, breaks down or ruptures and seizure or even welding of metal parts occurs, resulting in serious damage to the elements being lubricated. To overcome this serious weakness generally inherent in undoped lubricants, extreme pressure agents are added which form protective films between contacting surfaces and which possess among their properties the function of imparting film strength and oiliness to lubricants, thus preventing their breakdown and rupture under the above-described lubricating conditions.

The action of extreme pressure agents is largely a physiochemical phenomenon and this accounts primarily for their effectiveness as extreme pressure agents. These agents or materials, in addition to increasing the film strength of lubricants, become reactive with contacting surfaces forming thereon an alloying protective coating or film of great strength and thermal stability. This tenaciously adhering adsorbed protective film not only reduces friction between relatively moving parts such as encountered in internal combustion engines but also acts as an impermeable film which prevents corrosive acids and other contaminants from attacking the metal surface and the like. To be effective, therefore, extreme pressure agents must, to a degree, be reactive with contacting surfaces and form thereon a protective film which prevents welding of moving parts and aids lubrication. Since the reaction is normally between the additives in the lubricants and contacting surfaces at elevated temperatures of around about 150° C. and higher, the performance of a given lubricant must depend upon its composition, the composition of the contacting surface being lubricated, as well as the conditions to which the combination is subjected.

Although extreme pressure additives to be

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effective should be reactive with contacting surfaces, this reactivity should not be corrosive to the reactive surface. This is generally a serious draw-back of known extreme pressure agents, for serious damage to metal surfaces, particularly such as alloy bearings and the like, might result. Such additive should also not tend to promote oxidation which generally prompts formation of corrosive acidic materials, sludge, lacquer and varnish which results in sticking and fouling of movable engine parts and the like.

Numerous compounds and mixtures of compounds have been proposed and tried as extreme pressure agents for lubricants, the best of which have only moderately improved the extreme pressure properties of the lubricant and generally at the expense of increased corrosiveness and instability of the lubricant. Among such compounds may be mentioned organic oxygen-containing compounds such as fatty acids, esters, ketones, oxidized petroleum fractions; organic compounds containing sulfur or oxygen and sulfur such as sulfurized fatty oils, acids, etc.; organic compounds containing chlorine usually obtained by chlorinating organic compounds or petroleum fractions; organic compounds containing phosphorus; organic compounds containing lead and especially such compounds when in conjunction with an active sulfur compound.

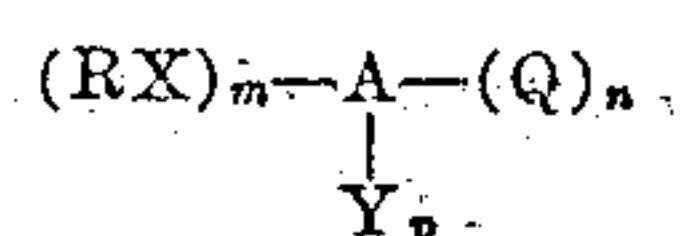
Of the general classes of extreme pressure compounds enumerated, sulfur and/or halogen-containing compounds appear to be most effective and are therefore preferred. However, these have serious defects in that most sulfur compounds to be effective must contain a major amount of sulfur in an active state which is highly corrosive and has a tendency to separate out and form sludge. Materials of this type, when in combination with halogen-containing compounds, have a deleterious effect by liberating highly corrosive acids from the halogenated compounds and also interfere with their function as an extreme pressure dope. Halogen-containing compounds when used alone, become highly corrosive to alloy metals such as cadmium-silver, copper-lead, etc., so as to render them useless after short periods of use.

It is an object of the present invention to provide an improved extreme pressure type lubricant capable of effective lubrication under high pressures at elevated temperatures and adverse operating conditions. Still another object of this invention is to provide an improved, stable, sludge-free, non-corrosive extreme pressure lubricant. Also, it is an object of this invention to provide an improved extreme pressure lubricant by addition to any lubricating carrier or base a minor amount of a novel reaction product of this invention. Still another object is to form an improved non-corrosive extreme pressure additive

from the reaction products of this invention. Other objects of this invention will appear as the description proceeds.

To the accomplishment of the foregoing and related ends, this invention consists of features which will be hereinafter fully described and particularly pointed out in the claims, the following description setting forth in detail certain embodiments of the invention, these being illustrative of but a few variations in which the principle of the invention may be employed.

Broadly stated, this invention is directed to the use in liquid hydrocarbon compositions such as lubricants, fuels, greases, rust-inhibiting compositions and the like, as well as synthetic lubricating bases, of a reaction product obtained by reacting alkylene oxide, sulfide and/or imines, the preferred class being the epoxy-type compounds with an organic polyacidic compound containing at least one —CXXR acidic radical, and the other acidic radicals being also the —CXXR radical or oxy-inorganic acids and derivatives thereof such as sulfonic, nitric or acids of phosphorus, said organic compound also containing at least one —XR radical, which compound can be represented by the general formula:



wherein A is an organic radical selected from the class consisting of aliphatic, cycloaliphatic, aromatic and heterocyclic organic radicals; n is an integer of at least 2 and represents the number of acidic radicals Q which are attached to A; one of the acid radicals represented by a —CXXR radical and the other acid radicals represented by Q can be the same as —CXXR or may be selected from oxy-inorganic acids such as sulfonic, sulfinic, nitric and acids of phosphorus; X is an element selected from the group consisting of O, S, Se and Te and in the radical —CXXR the X's can be the same or different; R can be hydrogen, alkyl, cycloalkyl, aralkyl, alkylaryl, aryl radicals or a cationic portion of a molecule such as Na, Li, Ca, Ba, Sr, Sn, Ni, Al, Zn, Pb or organic amines, at least one of the R's in either the acid or polar radical —XR being hydrogen; Y is a polar selected from the group consisting of nitro, nitroso, amino, sulfo and halo groups; m is an integer of at least 1 and preferably 1 to 3; and p can be a whole number varying from zero to one.

Specific compounds which are embraced within the scope of the above general formula and of which any and all as well as mixtures thereof can be used to form the reaction products of this invention include: hydroxy malonic acid, hydroxy succinic acid, tartaric acid, octyl tartaric acid, citric acid, hydroxy glutaric acid, hydroxy adipic acid, chloromalic acid, mercapto succinic acid, hydroxy-glutamic acid, chloro hydroxy succinic acid, hydroxy phthalic acid, mercapto phthalic acid, sulfo hydroxy phthalic acid, methylene, disalicylic acid, hydroxy dithio-sebacic acid, hydroxy phenylene dithiodicarboxylic acid, S-phenylthiomalic acid, dihydroxy dithiostearic acid, naphthol dicarboxylic acid, 2-propyl-5-hydroxy thiophene-3,4-dicarboxylic acid, 2-propyl dihydroxy thiophene-3,4-dicarboxylic acid, thio and dithio tartaric acid, B-sulfonic acid of ω-hydroxy octyl carboxylic acid, B-sulfonic acid of ω-hydroxy decyl carboxylic acid, Na salt of B-sulfonic acid of ω-hydroxy hexyl carboxylic acid, naphthol 3-carboxylic 6-

sulfonic acid, etc. Any of these acids can be partially esterified to form partial esters, which partial esters can be used to form the condensation reaction product of this invention. Esters which are particularly preferred to form condensation reaction products of this invention include acid ester of oleyl malate, acid ester of oleyl tartarate, acid ester of oleyl citrate, acid ester of stearyl citrate, acid ester of cetyl citrate, 9,10 octa-decenyl acid citrate, dodecyl acid hydroxy succinate, octyl mercapto acid phthalate, acid ester of methylene disalicylate, dihydroxy dithiomonostearate of butyl alcohol, acid ester of oleyl dihydroxyl thiophene carboxylate, B-sulfonic acid of oleyl ω-hydroxyl decanate, etc. In addition, the full esters can be used to form condensation products of this invention, among which can be mentioned dioleyl tartarate, dioctyl tartarate, dibenzyl tartarate, diphenyl tartarate, dioleyl malate, tri-oleyl citrate, dioleyl ester of methylene salicylic acid, distearyl ester of methylene salicylic acid, dioleyl ester of propyl dihydroxy thiophene dicarboxylic acid, etc. The acids or the esters or mixtures thereof can be partially neutralized with a metal compound or organic bases to form salts, which salts can be used to form condensation products of this invention. Preferred examples of such salts are sodium salt of acid ester of oleyl malate, sodium or potassium salt of acid ester of oleyl tartarate, calcium salt of acid ester of oleyl citrate, calcium salt of methylene disalicylate, triethanolamine salt of acid ester of stearyl citrate, dibutylamine salt of acid ester of octyl tartarate, etc. If desired, the salts of this invention can be produced after the condensation products of this invention have been formed.

The above polar-substituted organic polyacidic compounds, their ester and/or salts are reacted with alkylene oxide, sulfide and/or imine to form the desired condensation reaction product of this invention. The alkylene oxides which can be used are: ethylene oxide, propylene oxide, butylene oxide, amylene oxide, epichlorhydrin, glycidol, alkyl glycidols, glycidyl compounds, e. g., glycidyl isopropyl ether, and the like. Instead of the alkylene oxides as enumerated above, the sulfide and imine analogues can be used, of which particularly preferred are ethylene sulfide, propylene sulfide, ethylene imine, propylene imine and the like.

The mole ratio of the alkylene oxide, sulfide or imine to the polar-containing organic polyacidic compound can vary over wide limits in order to produce the desired reaction product. The preferred ratio of oxide to the polyacidic organic compound or its derivative is 4:1 to 12:1, respectively. The reaction temperature can be varied over wide limits and primarily depends upon the reactants used in forming the condensation product of this invention. Broadly, the reaction temperature lies between 50° C. and 350° C., and generally the reaction temperature lies between 75° C. and 200° C. The reaction can be carried out under pressure in a suitable reaction vessel, with the pressure varying from 50-pound gauge pressure to over 1,000-pound gauge pressure. The condensation reaction, however, need not be carried out under pressure, but it is preferred that it be carried out in an enclosed vessel. Catalysts may be used in carrying out the condensation reaction, and the catalyst may be either acid or basic. A few examples of such catalysts are boric acid, caustic

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alkalies, alkali alcoholates, e. g., sodium methylate, sodium ethylate; sodium oleate, di-sodium phosphate, sodium di-hydrogen phosphate, organic amines, e. g., ethylene diamine, etc. The reaction can be carried out in a suitable solvent or diluent. The diluents can be light or heavy hydrocarbons such as benzene, kerosene, gas oil, mineral oil or dioxane (purified by distillation with alkylene reagents), or any other suitable organic diluent which is substantially non-reactive with the constituents comprising the condensation reaction product of this invention and from which products of this invention can be easily removed. One method of preparing lubricants of this invention is to form the condensation reaction product directly in the base lubricant such as a mineral lubricating oil, alkylated naphthalene, and the like; filtering and purifying the compounded lubricant, if necessary, and using said compounded lubricant for its intended purpose.

The mechanism of the present invention is complex. Generally, mixtures of condensation products form in which the alkylene oxide, sulfide or imine attaches to both the carboxyl and hydroxyl radicals, provided both are free, although the reaction can be controlled so that only the carboxyl or hydroxyl groups are attacked. In view of the complexity of the reaction, it is desired to cover within the scope of the present invention all possible condensation products and mixtures thereof which are formed from reaction products of this invention.

The reaction is carried out under conditions set forth above until the base organic polyacidic compound has increased in average molecular weight by at least 44 weight units and up to a 1,000 or higher. The sole controlling factor as to the degree of condensation to which products of this invention are carried out is their solubility in base lubricants. Products which are too highly condensed tend to lose their oil solubility, which can be overcome, however, by addition or use of oil solubilizers.

Broadly stated, the method of preparing condensation reaction products of this invention can be accomplished by employing the following procedure. About one mole of an organic polar-containing polycarboxylic acid or derivative thereof such as tartaric acid, oleyl tartarate, acid ester of methylene disalicyclic acid, etc., is slowly heated in a suitable reaction vessel, such as an autoclave, and the product heated to above about 75° C. and higher, depending upon the organic polyacidic material used. The material can be heated per se or dispersed in a diluent such as mineral oil and heated therein. To the heated mixture is then added from 1 to 30 and generally 2 to 12 moles of an alkylene oxide, sulfide or imine and the reaction allowed to proceed, varying the reaction temperature by either cooling or heating above the temperature indicated above, in order to form a smooth reaction, and the ingredient allowed to react for from 4 to 48 hours. The reaction is preferably carried out under pressure and in the presence of a basic catalyst and is regarded as being completed when the average molecular weight of the organic polyacidic starting material has increased by at least 44 weight units and higher.

To more clearly illustrate the present invention, the following examples are presented. It is understood, however, that various modifications can be resorted to without departing from the spirit of the invention.

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Example I

Approximately 1 mole of tartaric acid was slowly heated to a temperature between 75° C. and 100° C. with constant stirring and about 2 to 8 moles of ethylene oxide was slowly added together with a catalytic amount of sodium methylate and the mixture was allowed to react under pressure for 48 hours at the above temperature. At the end of the reaction period, the tartaric acid indicated an increase in average molecular weight between 90 and 135 weight units. The condensation product when added to mineral oil in minor amounts imparted extreme pressure properties to the oil.

Example II

Approximately 1 mole of tartaric acid was dispersed in purified dioxane and between 2 and 10 moles of ethylene oxide was added slowly and the mixture reacted under pressure at between 75° and 100° C. in the presence of ethylene diamine catalyst for about 48 hours. At the end of the reaction period, the condensation product was removed from the dioxane and the acid indicated an average increase in molecular weight between 360 and 450 weight units. The condensation product when added to mineral oil imparted extreme pressure properties to said oil.

Example III

Following the procedure and conditions as outlined in Example II, malic acid was reacted with ethylene oxide. The condensation product thus formed had good extreme pressure properties.

Example IV

Approximately 1 mole of hydroxy glutamic acid was reacted with 4 to 10 moles of propylene oxide under conditions set forth in Example I. At the end of the reaction period, the hydroxy glutamic acid indicated an average increase in molecular weight between 348 and 580 weight units. The condensation product when added to an oil imparted extreme pressure properties thereto.

Example V

Approximately 1 mole of methylene disalicyclic acid was reacted with 4 to 10 moles of ethylene oxide in the presence of sodium methylate in alcohol at between 100° and 150° C. The condensation product formed indicated an average molecular weight increase over the acid of from 176 to 352 weight units. The condensation product when added to oil imparted extreme pressure properties and rendered the compounded oil non-corrosive.

Example VI

Approximately 1 mole of 2-propyl dihydroxythiophene 3-4 dicarboxylic acid was reacted with 5 to 15 moles of ethylene oxide in the presence of sodium methylate in purified dioxane at between 100° and 150° C. for about 48 hours. At the end of the reaction, the condensation product was removed from the solvent and on analysis indicated an increase in average molecular weight over the acid of from 220 to 660 weight units.

Example VII

Approximately 1 mole of tartaric acid was reacted with 4 to 10 moles of ethylene sulfide under conditions set forth in Example II. On analysis, the tartaric acid indicated an average molecular weight increase between 240 and 600 weight units. The condensation product was soluble in oil.

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Example VIII

Malic acid was used in place of tartaric acid to form a condensation product as set forth in Example VII. The sulfur-containing condensation product when added to oil imparted extreme pressure properties to it. On analysis, the malic acid indicated an average molecular weight increase between 240 and 600 weight units.

Example IX

Approximately 1 mole of tartaric acid was heated with 4 to 10 moles ethylene imine under conditions as set forth in Example VII. On analysis, the tartaric acid indicated an increase in molecular weight between 168 and 420 weight units. The nitrogen-containing condensation product was oil-soluble and possesses good anti-oxidant properties.

Example X

Approximately 1 mole of acid ester of oleyl malate was dispersed in purified dioxane and between 4 and 15 moles of ethylene oxide were slowly added and the mixture reacted between 75° and 125° C. in the presence of sodium methylate for about 48 hours. At the end of the reaction period, the condensation product was removed and the acid ester indicated an average increase in molecular weight between 176 and 440 weight units. The condensation product when added to oil imparted extreme pressure properties.

Example XI

Following the procedure of Example X, approximately 1 mole of octyl mercapto acid phthalate and 4 to 15 moles of ethylene oxide were reacted under conditions set forth in Example X but the reaction temperature being maintained at above 100° C. The ester indicated an average increase in molecular weight between 132 and 352 weight units.

Example XII

Approximately 1 mole of dibenzyl tartarate and between 2 and 10 moles of amylene oxide were reacted under conditions set forth in Example X, while maintaining the reaction temperature above 125° C. The ester indicated an average increase in molecular weight between 175 and 345 weight units.

Example XIII

Approximately 1 mole of dihydroxydithiobutyl monostearate was reacted with 4 to 10 moles of ethylene sulfide under conditions set forth in Example X. The ester indicated an average increase in molecular weight of around 240 weight units. The condensation product contained a substantial increase in sulfur content and the product possessed good extreme pressure properties.

Example XIV

Approximately 1 mole of dioleyl malate was dispersed in purified dioxane and between 4 and 12 moles of ethylene oxide added and the mixture slowly reacted in the presence of sodium methylate at between 75° and 125° C. for about 48 hours. At the end of the reaction period, the condensation product was recovered and the ester indicated an average increase in molecular weight between 176 and 440 weight units. The condensation product was oil soluble and imparted extreme pressure properties to the oil.

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Example XV

Following the procedure set forth in Example XIV but using glycidyl isopropyl ether, the condensation product formed indicated that the ester increased in average molecular weight by about 1,000 weight units.

Example XVI

Approximately 1 mole of tartaric acid was dispersed in purified dioxane and between 4 and 12 moles of ethylene oxide added and the mixture slowly reacted in the presence of sodium methylate at between 75° and 125° C. for about 48 hours. At the end of the reaction period, the condensation product was recovered and the ester indicated an average increase in molecular weight between 176 and 440 weight units. The condensation product was oil soluble and imparted extreme pressure properties to the oil.

Example XVII

Following the procedure set forth in Example XIV but using ethylene sulfide, the condensation product formed contained substantial amount of sulfur and the ester indicated an average increase in molecular weight of over 240 weight units.

Example XVIII

Following the procedure set forth in Example XIV but using ethylene imine, the condensation product formed contained substantial amount of nitrogen and the ester indicated an average increase in molecular weight of over 168 weight units.

Example XIX

A condensation product was prepared by reacting potassium salt of acid ester of oleyl tartarate with ethylene oxide under the reaction condition set forth in Example XIV. The product obtained indicated an average molecular weight increase over the salt of around 220 weight units.

Example XX

A condensation product was prepared by reacting calcium methylene disalicylate with ethylene oxide under conditions set forth in Example XIV except that the reaction temperature was increased to 150 to 200° C. The product obtained indicated an average molecular weight increase over the salt of around 900 weight units.

Example XXI

Approximately 1 mole of B-sulfonic acid of ω -hydroxy decyl carboxylic acid was dispersed in purified dioxane and between 4 and 12 moles of ethylene oxide added and the mixture slowly reacted in the presence of sodium methylate at between 75° and 125° C. for about 48 hours. At the end of the reaction period, the condensation product was recovered and the ester indicated an average increase in molecular weight between 176 and 440 weight units. The condensation product was oil soluble and imparted extreme pressure properties to the oil.

Condensation reaction products of this invention can be halogenated and/or sulfurized, sulfo-phosphorized, phosphorized and the like with such reagents as chlorine, sulfur, sulfur chloride, inorganic polysulfides, e. g., sodium polysulfide; phosphorus sulfide such as P_2S_5 , P_4S_3 ; phosphorus oxides, e. g., P_2O_5 ; phosphorus oxychlorides, e. g., $POCl_3$, elemental phosphorus and the like.

Example XXII

About 1 mole of the condensation product of

Example XIV and 4 to 8 moles of P_2S_5 were reacted at 125° to 250° C. for about 24 hours. The phosphorized-sulfurized condensation product was extracted with a ketone and the solvent thereafter removed. On analysis, the product indicated the presence of reacted sulfur and phosphorus in the molecule.

Example XXIII

About 1 mole of the condensation product of Example XIV and 4 moles of sulfur were reacted at about 160° C. for about 24 hours. The sulfurized product was isolated by means of toluene to yield a product containing sulfur in the molecule. Any of the above condensation products can be admixed with from 1 to 8 parts of the acid or acid ester from which the condensation products are derived. Thus, for example, one part of the condensation product of Example II when admixed with four parts of tartaric acid and the mixture added to a base mineral oil the resultant composition (A) possesses excellent extreme pressure properties.

Base lubricants which may be improved by addition of minor amounts of condensation reaction products of this invention may be selected from a wide variety of natural oils such as mineral oil, vegetable oil, animal oil, marine oil and mixtures thereof. In addition, synthetic lubricants may be used such as polymerized olefins, organic esters, e. g., 2-ethylhexyl sebacate, dioctyl phthalate, trioctyl phosphate, silicon polymers, e. g., dimethyl silicone polymer; mixtures of natural and synthetic lubricants; lubricating emulsion bases and the like.

General formulation of compositions of invention can be represented by:

	Amount (percent by weight)
Primary additive: Condensation reaction product of this invention	0.01 to 10% (0.1-5%)
Secondary additive: Detergents, e. g., sulfonates, solubilizers, e. g., esters of polyhydric acids (sorbitan monooleate, glycerol monooleate, etc.), corrosion inhibitors, etc.	0 to 2% (0.01 to 1%)
Base: Nature oil such as mineral oil and/or fixed oils and derivatives thereof and/or synthetic lubricants	Balance

The following table illustrates compositions of this invention:

Components ¹	Compositions																			
	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20
Composition of Ex. II	x												x				x			
Composition of Ex. III		x													x					
Composition of Ex. XIV			x	x							x	x				x	x			x
Composition of Ex. XV					x													x		
Composition of Ex. XVII						x														
Composition of Ex. IX							x													
Composition of Ex. V								x											x	
Composition of Ex. XIX									x											
Composition of Ex. XXII										x										
Ca petroleum sulfonate					x				x	x				x	x	x		x	x	
Sorbitan monooleate				x							x				x				x	x
Sorbitol monooleate							x						x							
Glycerol monooleate						x			x											
High molecular wt. aliphatic amine										x										x
Mineral oil	x	x	x	x	x	x	x	x	x	x	x						x	x	x	x
Mineral oil + alkyl naphthalene												x	x							
Dimethyl silicone fluid ²														x						

¹ The additives were present in amounts varying from 0.5 to 5%.

² Manufactured by Dow Corning Corporation and identified as DC oils.

Compositions of this invention were evaluated for their extreme pressure properties on a spur-gear machine, which essentially consists of two geometrically similar pairs of gears connected by two parallel shafts. The gear pairs are placed in separate gear boxes, which also contain the supporting ball bearings. One of the shafts consists of two sections connected by a coupling. Loading is accomplished by locking one side of the coupling and applying torque to the other. The conditions of the test were:

Speed: 7100 R. P. M.

Test duration: 5 mins. running at each load

Specimen: involute spur gear (SAE 3312 steel)

Composition:	Score load (lbs.)
Mineral oil	5
Mineral oil containing 1% sorbitol	25
Mineral oil containing 1% sorbitan monooleate	25
Mineral oil containing 2% salicylic acid	20
Mineral oil containing 5% polyethylene oxide polymer (M. W. 1500)	10
Mineral oil containing 1% methylene disalicylic acid	20
Mineral oil containing 1% glycerol monooleate	25
Composition 3 (as in table)	70+
Composition 4 (as in table)	70+
Composition 1 (as in table)	70+
Composition 2 (as in table)	70+
Composition 6 (as in table)	70+
Composition 7 (as in table)	60+
Composition 13 (as in table)	70+
Composition 17 (as in table)	75+
Composition A	75+

Because of its synergistic effect the reaction product of this invention can be combined with other additives in lubricants, such as blooming agents, pour point depressants or viscosity improvers, extreme pressure agents, antifoaming agents and the like. Among the specific additives which can be used are oil-soluble detergents which include oil-soluble salts of various bases with detergent forming acids. Such bases include metal as well as organic bases. Metallic bases include those of the alkali metals and of Cu, Mg, Ca, Sr, Ba, Zn, Cd, Al, Sn, Pb, Cr, Mn, Fe, Ni, Co, etc. Organic bases include various nitrogen bases as primary, secondary and tertiary amines and quaternary ammonium bases.

Examples of detergent forming acids are the various fatty acids of, say, 10 to 30 carbon atoms, wool fat acids, paraffin wax acids (produced by oxidation of paraffin wax), chlorinated fatty

acids, rosin acids, aromatic carboxylic acids including aromatic fatty acids, aromatic hydroxy fatty acids, paraffin wax benzoic acids, various alkyl salicylic acids, phthalic acid monoesters, aromatic keto acids, aromatic ether acids, diphenols as di-(alkyl-phenol) sulfides and disulfides, methylene bis alkyl phenols; sulfonic acids such as may be produced by treatment of alkyl aryl hydrocarbons or high boiling petroleum oils with sulfuric acid; sulfuric acid monoesters; phosphoric, arsonic and antimony acid mono and diesters, including the corresponding thiophosphoric, arsonic and antimony acids, phosphonic and arsonic acids and the like.

Additional detergents are the alkaline earth phosphate diesters, including the thiophosphate diester; the alkaline earth diphenolates, specifically the calcium and barium salts of diphenol mono and poly sulfides.

Non-metallic detergents include compounds such as the phosphatides, such as lecithin and cephalin; certain fatty oils as rapeseed oils, voltolized fatty or mineral oils and the like.

An excellent metallic detergent for the present purpose in the calcium salt of oil-soluble petroleum sulfonic acids. This may be present advantageously in the amount of about 0.025% to 0.2% sulfate ash. Also alkaline metal salts of alkyl phenol-aldehyde condensation reaction products are excellent detergents.

Antioxidants comprise several types, for example, alkyl phenols such as 2,4,6-trimethyl phenol, pentamethyl phenol, 2,4-dimethyl-6-tertiarybutyl phenol, 2,4-dimethyl-6-octyl phenol, 2,6-ditertiary-butyl-4-methyl phenol, 2,4,6-tritertiary-butyl phenol and the like; amino phenols as benzyl amino phenols; amines such as dibutyl-phenylene diamine, diphenyl amine, phenyl-beta-naphthylamine, phenyl-alpha-naphthylamine, dinaphthyl amine.

Corrosion inhibitors or anti-rusting compounds may also be present, such as dicarboxylic acids of 16 and more carbon atoms; alkali metal and alkaline earth salts of sulfonic acids and fatty acids; organic compounds containing an acidic radical in close proximity to a nitrile, nitro or nitroso group (e. g. alpha cyano stearic acid).

Extreme pressure agents which may be used comprise: esters of phosphorus acids such as tri-aryl, alkyl hydroxy-aryl, or aralkyl phosphates, thiophosphates or phosphites and the like; neutral aromatic sulfur compounds of relatively high-boiling temperatures such as diaryl sulfides, diaryl disulfides, alkyl-aryl disulfides, e. g. diphenyl sulfide, diphenol sulfide, dicresol sulfide, dixylenol sulfide, methyl butyl diphenol sulfide, dibenzyl sulfide, corresponding di- and tri-sulfides, and the like; sulfurized fatty oils or esters of fatty acids and monohydric alcohols, e. g. sperm oil, jojoba oil, etc.; in which the sulfur is strongly bonded; sulfurized long chain olefins such as may be obtained by dehydrogenation or cracking of wax; sulfurized phosphorized fatty oils or acids, phosphorus acid esters having sulfurized organic radicals, such as esters of phosphoric or phosphorus acids with sulfurized hydroxy fatty acids; chlorinated hydrocarbons, such as chlorinated paraffin, aromatic hydrocarbons, terpenes, mineral lubricating oil, etc.; or chlorinated esters of fatty acids containing the chlorine in position other than alpha position.

Additional ingredients may comprise oil-soluble urea or thiourea derivatives, e. g. urethanes, allophanates, carbazides, carbazones, etc.; polyisobutylene polymers, unsaturated polymerized

esters of fatty acids and monohydric alcohols and other high molecular weight oil-soluble compounds.

Depending upon the additive used and conditions under which it is used, the amount of additive used may vary from 0.1 to 2% or higher.

The novel reaction products of this invention, in addition to being excellent lubricating oil improving agents, are potent oxidation inhibitors for fuels, natural and synthetic rubber, wax coating compositions and other organic materials.

It is to be understood that while the features of the invention have been described and illustrated in connection with certain specific examples, the invention, however, is not to be limited thereto or otherwise restricted, except by the prior art and the broad scope of the disclosed invention.

The invention claimed is:

1. A lubricating composition comprising a major amount of a liquid organic lubricating base having incorporated therein from about 0.01 to 10% of a reaction product obtained by reacting an aliphatic compound selected from the group consisting of C_2-C_5 alkylene oxide, C_2-C_5 alkylene sulfide, and C_2-C_5 alkylene imine with an organic poly acidic compound containing from 1 to 3 free carboxylic acid groups and at least one hydroxy group, said reaction being carried out at a temperature of at least $75^\circ C.$ in the mole ratio of from 4:1 to 12:1 respectively.

2. A lubricating composition comprising a major amount of liquid organic lubricating base having incorporated therein from 0.01% to 10% of a reaction product obtained by reacting C_2-C_5 alkylene oxide with an organic polyhydroxy carboxylic acid containing from 1 to 3 carboxylic acid groups at a temperature of at least $75^\circ C.$ and in the mole ratio of 4:1 to 2:1 respectively.

3. A lubricating composition comprising a major amount of liquid organic lubricating base having incorporated therein from 0.01% to 10% of a reaction product obtained by reacting ethylene oxide with an organic polyhydroxy carboxylic acid containing from 1 to 3 carboxylic acid groups at a temperature of at least $75^\circ C.$ and in the mole ratio of 4:1 to 2:1 respectively.

4. A lubricating composition comprising a major amount of liquid organic lubricating base having incorporated therein from 0.01% to 10% of a reaction product obtained by reacting C_2-C_5 alkylene oxide with an aliphatic polyhydroxy poly-carboxylic acid, said carboxylic acid radical being not more than three in number, at a temperature of from $75^\circ C.$ to $200^\circ C.$ and in the mole ratio of 4:1 to 2:1 respectively.

5. A lubricating composition comprising a major amount of mineral oil having incorporated therein in an amount sufficient to impart extreme pressure properties of a condensation reaction product obtained by reacting ethylene oxide and tartaric acid at a temperature of from 75 to $100^\circ C.$ in the mole ratio of about 10:1, respectively.

6. A lubricating composition comprising a major amount of mineral oil having incorporated therein in an amount sufficient to impart extreme pressure properties of a condensation reaction product obtained by reacting ethylene oxide and malic acid at a temperature of from 75 to $100^\circ C.$ in the mole ratio of about 10:1, respectively.

7. A lubricating composition comprising a major amount of mineral oil having incorporated therein in an amount sufficient to impart extreme pressure properties of a condensation reaction product obtained by reacting ethylene sulfide and

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tartaric acid at a temperature of from 75 to 100° C. in the mole ratio of about 10:1, respectively.

8. A lubricating composition comprising a major amount of a liquid organic lubricating base having incorporated therein from about 0.01 to 10% of a reaction product obtained by reacting an organic compound selected from the group consisting of C₂—C₅ alkylene oxide, C₂—C₅ alkylene sulfide, and C₂—C₅ alkylene imine with an organic poly acidic compound containing from 1 to 3 free carboxylic acid groups and at least one hydroxy group, said reaction being reacted at a temperature of at least 75° C. in the mole ratio of from 4:1 to 12:1 respectively and re-treating about one mole of the reaction product thus formed with about four moles of a sulfurizing, sulfo-phosphorizing and phosphorizing agent at a temperature of at least 125° C.

9. A lubricating composition comprising a major amount of a liquid organic lubricating base having incorporated therein from about 0.01 to 10% of a reaction product obtained by reacting an organic compound selected from the group consisting of C₂—C₅ alkylene oxide, C₂—C₅ alkylene sulfide, and C₂—C₅ alkylene imine with an organic poly acidic compound containing from 1 to 3 free carboxylic acid groups and at least one hydroxy group, said reaction being carried out at a temperature of at least 75° C. in the mole ratio of from 4:1 to 12:1 respectively and treating about 1 mole of the condensation product thus formed with about 4 moles of a sulfurizing agent at a temperature of around 160° C.

10. A lubricating composition comprising a major amount of a liquid organic lubricating base having incorporated therein from about 0.01 to 10% of a reaction product obtained by reacting an organic compound selected from the group consisting of C₂—C₅ alkylene oxide, C₂—C₅ alkylene sulfide, and C₂—C₅ alkylene imine with an organic poly acidic compound containing from 1 to 3 free carboxylic acid groups and at least one hydroxy group, said reaction being carried out at a temperature of at least 75° C. in the mole ratio of

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from 4:1 to 12:1 respectively and treating about 1 mole of the condensation product thus formed with about 4 moles of a phosphorous sulfide at a temperature of around 250° C.

11. A lubricating composition comprising a major amount of a liquid organic lubricating base having incorporated therein from about 0.01 to 10% of a reaction product obtained by reacting a C₂—C₅ alkylene oxide with an organic poly acidic compound containing from 1 to 3 carboxylic acid groups and at least one hydroxy group, said reaction being carried out at a temperature of at least 75° C. in the mole ratio of from 4:1 to 12:1, respectively.

12. A lubricating composition comprising a major amount of a liquid organic lubricating base having incorporated therein from about 0.01 to 10% of a reaction product obtained by reacting an ethylene oxide with an organic poly acidic compound containing from 1 to 3 carboxylic acid groups and at least one hydroxy group, said reaction being carried out at a temperature of at least 75° C. in the mole ratio of from 4:1 to 12:1, respectively.

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REFERENCES CITED

The following references are of record in the file of this patent:

UNITED STATES PATENTS

Number	Name	Date
1,463,092	Pelly	July 24, 1923
1,810,318	Loehr	June 16, 1931
2,134,736	Reuter	Nov. 1, 1938
2,341,846	Meincke	Feb. 15, 1944
2,370,300	Farrington	Feb. 27, 1945
2,457,139	Pife	Dec. 28, 1948
2,481,278	Ballard	Sept. 6, 1949
2,491,432	White	Dec. 13, 1949
2,536,684	Harman et al.	Jan. 2, 1951
2,542,550	McDermott	Feb. 20, 1951