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ESTER-CONTAINING LUBRICANT COMPOSITIONS

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The present invention relates to new and useful compositions of matter and pertains more particularly to novel compositions containing a major proportion of an oil of lubricating viscosity. This application is a continuation-in-part of my earlier copending application Serial No. 416,428, filed March 15, 1954, now abandoned, which in turn was a continuation of my applications Serial Nos. 261,905, 261,906 and 261,907, all filed December 15, 1951, now abandoned.

For various purposes, esters of aliphatic mono- and poly-hydric alcohols with aliphatic or aromatic mono- or poly-basic acids have been heretofore proposed as addends to oils such as turbine oils, steam engine lubricants, transformer oils, crankcase lubricants for internal combustion engines, etc. For example, glycerol esters such as glyceryl monoricinoleate are said to inhibit the emulsifying tendency of certain polyacrylate viscosity index improvers in lubricating oils; certain carboxylic acid esters of partially dehydrated aliphatic polyhydric alcohol such as sorbitan monostearate are added to slushing oils to prevent rusting or to prevent corrosive attack on steel by sulfur dioxide and water vapor; esters of saccharoses such as pentastearyl glycose are proposed as wax suppressors for waxy lubricating oils, etc.

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. It is also a function of the lubricant to prevent the deposition of solid products on the piston walls and other surfaces of the engine coming in contact with the lubricant. Such deposits seriously interfere with efficient engine operation for they accelerate piston ring and cylinder wall wear and also increase oil losses by plugging the oil ring grooves. The troublesome deposits which form on the face of the piston and on the other walls of the combustion chamber, as well as on valves and spark plugs are also partially attributable in many cases to the lubricant. 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 form an ash which is partially deposited out on the various surfaces of the combustion chamber and on those of the spark plugs and valves.

Accordingly, it is a particular object of this invention to provide a lubricant composition which is compounded with metal- or mineral-free detergents and wear-reducing additives.

While certain of the additives heretofore employed in oils (and to a lesser degree the oil itself) are partially responsible for deposits which form on engine surfaces, it is now recognized that the major source of such deposits or their precursors lies in the various aldehydes, acids, oxy-acids and other similarly reactive, partially-oxidized combustion products of the fuel. These products are formed both under pre-ignition conditions as well as during the combustion step proper, particularly during the period before the engine has reached operating temperature. Accordingly, under city driving conditions where the engine is repeatedly started in the cold condition and is seldom driven for a distance sufficient to reach the most efficient operating temperatures, the formation of partial oxidation products is particularly severe. Many of these partial oxidation products are carried down into the crankcase of the engine along with other blow-by gases, and since most are insoluble or only sparingly soluble in lubricating oils, they tend to separate from the oil and adhere to engine surfaces or form large droplets. In either case, under the elevated temperature conditions prevailing in the engine, these reactive monomers quickly polymerize to form solid masses which readily deposit out on the engine wall surfaces.

It is the practice in the art to prevent the formation of such deposits by adding to the lubricant a material normally referred to as a detergent. Insofar as is known, all the detergent additives which have heretofore been successfully employed on a commercial scale are organic, metal-containing compounds such as calcium petroleum sulfonate, calcium cetyl phosphate, calcium octyl salicylate, calcium phenyl stearate, the barium salt of wax-substituted benzene sulfonate, or the potassium salt of the reaction product of phosphorus pentasulfide and polybutene. Various of these detergents act by reacting chemically with deposit precursors to form harmless compounds. Others act to prevent flocculation or coagulation of solid particles in the oil and maintain the same in a state of suspension as finely divided particles. It has been found that detergents can be designed not only to perform this dispersant function but also to 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 larger 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. For this purpose certain esters of higher polyhydric alcohols have been found to be quite effective. The detergent action of the polyhydric alcohol esters appears to depend on unesterified free hydroxyl groups since, for example, in the series of pentaerythritol esters, the detergent action increases as the degree of esterification decreases. Similarly detergent efficiency is increased in going from sorbitan trioleate to sorbitan monooleate. At least one esterifying acid radical is required to impart sufficient oil-solubility to the molecule.

The effectiveness of these partial esters to prevent engine deposits is illustrated by the results shown in the following table of FL-2 Chevrolet engine tests of crankcase lubricants containing various esters as the sole compounding agent. Given for comparison are tests on the

base oil alone and a commercial type compounded motor oil of heavy duty grade. In this and subsequent tests the lubricating oil employed was that commonly used in the preparation of compounded automotive crankcase lubricants, namely, a mineral lubricating oil obtained as a solvent refined S.A.E. 30 paraffin base oil from a California waxy crude.

Table I

Test No.	Additive	Piston Rating
1	None	3.0
2	Commercial type compounding	3.5
3	10% Pentaerythritol tetraoleate	3.5
4	10% Pentaerythritol dioleate	7.3
5	10% Pentaerythritol monooleate	9.7
6	5% Pentaerythritol monooleate	7.4
7	10% Sorbitan monooleate	9.4
8	10% Sorbitan trioleate	5.2
9	10% Glyceryl monooleate	8

The above tests illustrate the corrosivity imparted to the base oils by the addition of the partial esters.

Surprisingly, it was found that the corrosion promoting effect of the partial esters is uniquely difficult to counteract. In fact, it was discovered that various agents effective to decrease the oxidation corrosion of usual lubricating oil compositions are not appreciably effective in oils containing partial ester detergents. In other words, agents which might be called "conventional" corrosion inhibitors are not appreciably effective in oils containing partial esters. Actually, in many cases this so-called "corrosion inhibitor" further increases the corrosion rather than behaving as an inhibitor. This unexpected phenomenon is illustrated in the following table of results obtained by subjecting oil compositions containing the corrosive partial esters plus various conventional inhibitors to the strip corrosion test.

Table III

Compounding:	Weight loss (mgs.)
None (base oil alone, average of several runs)	38
10% pentaerythritol monooleate	66.0
10% pentaerythritol monooleate +0.1% quinizarin	46.2
10% pentaerythritol monooleate +0.1% alizarin	50.0
10% pentaerythritol monooleate +6 mm./kg. zinc dicetyl-phenyl dithiophosphate	58.7
10% pentaerythritol monooleate +1% sulfurized olefin inhibitor A	91.9
10% pentaerythritol monooleate +1% sulfurized di-paraffin wax sulfide	99.6
10% pentaerythritol monooleate +1% dilauryl selenide	100.7
10% pentaerythritol monooleate +1% phenyl alpha naphthylamine	195.2
10% pentaerythritol monooleate +0.5% phenothiazine	142.5
10% pentaerythritol monooleate +1% 2,2'-methylene bis(4-methyl 6-ter. butyl phenol)	170.8
10% pentaerythritol monooleate +0.5% p-hydroxy diphenylamine	197.0
10% pentaerythritol monooleate +2% zinc dibutyl dithiocarbamate	169.8
10% pentaerythritol monooleate +1% aromatic amine inhibitor B	136.6
10% pentaerythritol monooleate +1% 2,6-di-tertiary-butyl 4-methyl phenol	213.0
10% pentaerythritol monooleate +2% pinene-P_2S_5 condensation product	116.0
10% sorbitan monooleate	142.4
10% sorbitan monooleate +2% pinene-P_2S_5 reaction product	133.2
10% sorbitan monooleate +0.15% catechol	96.1
10% glyceryl monooleate	59.3
10% glyceryl monooleate +2% pinene-P_2S_5 reaction product	49.7
10% glyceryl monooleate +2% sulfurized olefin inhibitor A	62.8

Other partial esters as described below will give similar results.

While these partial esters impart satisfactory detergency to oils and do not appear to have any adverse effects when employed under quite mild service conditions, we have found that the free hydroxyl groups in the partial esters act at elevated temperatures to promote corrosion of sensitive bearing metals such as copper-lead, cadmium-silver, cadmium-nickel, the so-called high lead bearing alloys, and the like. These sensitive bearing metals are susceptible to attack by acidic and/or peroxidic materials; this phenomenon has been designated as "acid or oxidation corrosion." To illustrate the corrosivity at elevated temperature, oil compositions containing the partial esters were subjected to a strip corrosion test which indicates the relative corrosivity at actual engine operating conditions. The results of the 20-hour 300° F. corrosion test (subsequently described in more detail) are given in the following table:

Table II

Compounding:	Weight loss (mgs.)
None (base oil alone, average of several runs)	38
5% pentaerythritol monooleate	60.4
10% pentaerythritol monooleate	66.0
5% pentaerythritol dioleate	117.1
5% pentaerythritol tetraoleate	40.1
5% monoester of pentaerythritol and soya bean oil fatty acids	64.6
5% inositol pentanaphthenate	71.1
5% pentaerythritol dinaphthenate	67.3
5% pentaerythritol monostearate	97.2
5% sorbitan monostearate	120.0
5% sorbitan trinaphthenate	169.0
5% sorbitan tristearate	124.0
5% sorbitan monooleate	77.4
10% sorbitan monooleate	142.4
5% sorbitan trioleate	61.8
10% glyceryl monooleate	59.3

Of the various agents employed in the test reported in the foregoing table, the sulfurized olefin inhibitor A is a product marketed by Enjay Company, Inc., under the trademark "Paranox 12." The sulfurized diparaffin wax sulfide was prepared substantially in accordance with Example 1 of Clausen and Rutherford Patent 2,514,625. The aromatic amine inhibitor B is a product marketed by E. I. du Pont de Nemours & Company, Inc., under the trademark "Ortholeum 300." The pinene-P_2S_5 reaction product was prepared in accordance with May Patent 2,486,188 and contained approximately 3.35% phosphorus and 8.71% sulfur.

In light of the foregoing negative results with the addition of various agents to the corrosive partial ester-containing oils, it was particularly unexpected to discover that the oxidation corrosion attack on hard bearing metals such as copper-lead alloys at elevated temperatures by these corrosive partial ester-containing oils could be greatly reduced, to the desired minimum, by the combination of certain vicinal dihydroxy aryl compounds with oil-soluble reaction products of olefins and sulfur or phosphorus sulfide. The effect of this combination is particularly surprising since neither one alone has a marked effect on the corrosion of the ester-containing oils. The combination of agents is synergistic in the compositions of the present invention.

The inhibitor combination will find ready use not only in those partial ester-containing oils which are "extremely corrosive" but also in such oils which are "mildly corrosive." Not only the elevated temperatures to which such oils are subjected but also other factors such as improvements in the mechanical arts come into play and contribute to the seriousness and importance of the oxidation corrosion problem and the need for a counteractant. Thus, modern internal combustion engines and other mechanisms employing oil of lubricating viscosity are so carefully designed and built and the clearances so small that they cannot tolerate even relatively mildly

corrosive oils which were satisfactorily used in the past. Because of these low tolerances the inhibition of "mildly corrosive" oils by means of our agents can be the most important aspect of the present invention, and such inhibition will be, under some circumstances, the more difficult problem to overcome in the absence of our agents. That is, reducing the corrosivity to the extremely low minimum is often more difficult than just reducing the corrosivity from "extremely corrosive" to "mildly corrosive." By "extremely corrosive" oils is meant those oils characterized by a corrosivity of greater than about 40 mgs. weight loss of a 2½-inch by 3/16 inch by 1 inch section of a copper-lead bearing insert in a 20-hour 300° F. corrosion test (subsequently described in more detail). A "mildly corrosive" oil is characterized by a bearing weight loss in the same test of from 20 to 40 mgs. The foregoing 40 mgs. and 20 mgs. bearing weight losses can be designated as corrosion indices of 40 and 20 respectively.

To illustrate the corrosion-inhibitory properties of the inhibitor combination in the new oil compositions of the present invention, a section of a copper-lead bearing insert having the dimensions of about 2½ inches by 3/16 inch by 1 inch was first cleaned with a wire brush until the strip was highly polished. The strip was weighed and the weight recorded. The highly polished strip was completely immersed in the test oil. The oil was stirred at a temperature of 300° F. for 20 hours, at which time the strip was removed and cleaned, first with chloroform, and then with petroleum ether. The strip was then weighed and the difference in weight of the original strip and the strip after the solvent wash was noted and recorded as the weight loss due to corrosion by the oil composition. Oils which are noncorrosive as shown by this test are admirably suited for use as inhibited electrical insulating oils, cable oils, etc. Also, oils passing this test, and when otherwise satisfactory, can be employed for other purposes. Thus, for example, the oils containing the partial esters in sufficient amount to impart detergency, i.e., to decrease engine deposits satisfactorily as shown in the Chevrolet FL–2 test, can be rated in the corrosion test with respect to their tendency to corrode sensitive bearing metals and thereby clearly indicate their acceptability for actual engine lubrication.

In the following table are given the data from the above tests for various oil compositions containing partial esters with and without the agents of the present inhibitor combination, the same base oil being used throughout the test.

Table IV

Compounding:	Weight loss (mgs.)
No compounding (base oil alone, average of several runs)	38
10% sorbitan monooleate	142.4
10% sorbitan monooleate +2% pinene-P_2S_5	133.2
10% sorbitan monooleate +2% pinene-P_2S_5 +0.15% alizarin	1.8
10% sorbitan monooleate +1% pinene-P_2S_5 +0.15% alizarin	12.9
10% sorbitan monooleate +2% pinene-P_2S_5 +0.10% alizarin	27.5
10% sorbitan monooleate +2% sulfurized terpene inhibitor C +0.15% alizarin	0.7
10% sorbitan monooleate +2% sulfurized olefin inhibitor A +0.15% alizarin	10.2
10% sorbitan monooleate +2% sulfurized mixed olefin polymer +0.15% alizarin	+13
10% sorbitan monooleate +0.15% catechol	96
10% sorbitan monooleate +2% pinene-P_2S_5 +0.15% catechol	2.6
10% sorbitan monooleate +2% pinene-P_2S_5 +0.10% catechol	14.7
10% sorbitan monooleate +2% pinene-P_2S_5 +0.05% catechol	25.5
10% sorbitan monooleate +2% pinene-P_2S_5 +0.15% pyrogallol	18.5
10% sorbitan monooleate +2% sulfurized mixed olefin polymer +0.15% catechol	+30
5% sorbitan trioleate	61.8
5% sorbitan trioleate +2% pinene-P_2S_5 +0.15% alizarin	23.3
5% sorbitan trioleate +2% pinene-P_2S_5 +0.15% catechol	16.4
5% pentaerythritol monostearate	97.2
5% pentaerythritol monostearate +2% pinene-P_2S_5 +0.15% catechol	24.1
5% sorbitan monostearate	120
5% sorbitan monostearate +2% pinene-P_2S_5 +0.15% catechol	3.8
10% glyceryl monooleate	82.4
10% glyceryl monooleate + 2% pinene-P_2S_5 +0.15% catechol	17.4

In the foregoing table the commercial sulfurized terpene inhibitor C is a product marketed by E. I. du Pont de Nemours & Company, Inc. under the trademark "Ortholeum 202." The sulfurized mixed olefin polymer was prepared by heating a mixture of about 200 parts of heavy propylene polymer (average molecular weight= approximately 180), 200 parts of butylene polymer (average molecular weight=about 530), 25 parts of C.P. oleic acid and 75 parts of C.P. flowers of sulfur, to a temperature of 375–380° F. for 2 hours, hydrogen sulfide being evolved during the reaction; during the heating and cooling down nitrogen was bubbled through the mixture; clay was added when the temperature reached 130° F.; the reaction mixture was filtered through a clay cake at 90° F., yielding a product of clear dark red-brown color and having an average molecular weight of 395, a gravity of 22.4° A.P.I. at 60° F., a bromine number of 50, and 13.0% sulfur. Other partial esters as described below will give similar results.

The above results illustrate that the addition of the inhibitor combination of the present invention in every case clearly lowered the oxidation corrosion, whereas in contrast thereto the addition of the organic sulfur inhibitor alone was relatively ineffective.

When the vicinal polyhydroxy aryl compounds are replaced with polyhydroxy aryl compounds in which the hydroxy groups are not on adjacent carbon atoms of the benzene ring, an adverse effect results. Thus, as shown in the following table, the substitution of quinizarin for alizarin, 1,3-dihydroxy benzene for catechol-(1,2-dihydroxy benzene), and like substitutions bring about an increase in the corrosivity of the oil compositions.

Table V

Compounding:	Weight loss (mgs.)
No compounding, base oil alone (average of several runs)	38
10% sorbitan monooleate	142.4
10% sorbitan monooleate +2% pinene-P_2S_5 reaction product	133.2
10% sorbitan monooleate +2% pinene-P_2S_5 reaction product +0.15% quinizarin	133.1
10% sorbitan monooleate +2% pinene-P_2S_5 reaction product +0.15% 1,8-dihydroxyanthraquinone	122.4
10% sorbitan monooleate +2% pinene-P_2S_5 reaction product +0.15% para-tertiary butyl catechol	246
10% sorbitan monooleate +2% pinene-P_2S_5 reaction product +0.15% bis-1,4-(2,3-dihydroxy-phenyl)-2,3-dimethylbutane	89.8
10% sorbitan monooleate +2% pinene-P_2S_5 reaction product +0.15% 1,3-dihydroxy benzene	118.7
10% sorbitan monooleate +2% pinene-P_2S_5 reaction product +0.15% 1,4-dihydroxy benzene	213.9
10% sorbitan monooleate +2% pinene-P_2S_5 reaction product +0.15% 1,3,5-trihydroxy benzene	190.6
10% sorbitan monooleate +2% pinene-P_2S_5 reaction product +0.15% 1,5-dihydroxynaphthalene	116.5
10% sorbitan monooleate +2% pinene-P_2S_5 reaction product +0.15% 2,6-di-tertiary butyl 4-methyl phenol	215.1
10% sorbitan monooleate +2% pinene-P_2S_5 reaction product +0.15% naphthol	195.1

It will be seen from the data of the foregoing Table V that the combinations of the sulfur-containing inhibitor with non-vicinal polyhydroxy benzene compounds are not effective to reduce the oxidation corrosivity of oil compositions containing partial esters. Thus, the effective inhibitor combinations are those in which the benzene compounds have at least two hydroxyl groups on adjacent carbon atoms of the ring (see Table IV). It will be further noted from Table V that bis-1,4-(2,3-dihydroxyphenyl)-2,3-dimethylbutane in the combination gives borderline results but that increasing the ratio of aliphatic carbons in alkyl substituents to aromatic carbons, as with paratertiary butyl catechol, brings about an adverse effect.

Thus, the vicinal polyhydroxy aryl compounds in the inhibitor combination of the present normally-corrosive partial ester-containing oils can be defined as polyhydroxy benzenes and anthraquinones having at least two hydroxy groups on adjacent carbon atoms of a benzene ring. The vicinal polyhydroxy benzenes are exemplified by catechol (1,2-dihydroxybenzene), pyrogallol (1,2,3-trihydroxybenzene), 1,2,4-benzenetriol (1,2,4-trihydroxybenzene), apionol (1,2,3,4-tetrahydroxybenzene), etc. The benzene ring can be substituted with methyl groups or other short chain alkyl groups or two benzene rings can be linked together with short alkylene groups. In such substituted dihydroxybenzenes, there should be no more than half as many aliphatic carbon atoms as aromatic. Preferably there should be besides the hydroxyl groups no more ring substituents than two alkyl groups of no more than three carbon atoms. Ordinarily the unsubstituted vicinal polyhydroxybenzenes are preferred.

The vicinal dihydroxyanthraquinones are exemplified by alizarin (1,2-dihydroxyanthraquinone), hystazarin (2,3-dihydroxyanthraquinone), etc. and various substituted derivatives thereof including those containing additional hydroxy groups such as in alizarin RG (1,2,7-trihydroxyanthraquinone), alizarin SG (1,2,9-trihydroxyanthraquinone), anthragallol (1,2,3-trihydroxyanthraquinone), quinalizarin (1,2,5,8-tetrahydroxyanthaquinone), alizarin garnet (1,2-dihydroxy-4-amino-anthraquinone), etc. The vicinal dihydroxy anthraquinones may be substituted with one or two short chain alkyl groups such as methyl, propyl, etc. but not such which by their structure and/or position substantially decrease the reactivity of the vicinal hydroxy groups by stearic hindrance or resonance. Ordinarily it is preferred to use the unsubstituted vicinal dihydroxyanthraquinones.

The other component of the inhibitor combination is a reaction product of an olefin with elemental sulfur or preferably a phosphorus sulfide such as P_2S_5. The olefin is of sufficient chain length (usually of at least 8 carbon atoms) and character to impart enough oleophilic properties to make the reaction product oil-soluble to the extent desired for incorporation in the final oil composition. Suitable sulfurized olefins include sulfurized ethylene-propylene copolymers, sulfurized polybutenes, sulfurized terpenes such as Du Pont's "Ortholeum 202," and the like. The reaction products of terpenes and phosphorus sulfides are described, for example, in May Patent 2,486,188.

The foregoing combination of agents of this invention are not limited to their applicability to any particular base stock which contains an ester. The advantages herein disclosed can be obtained with various corrosive ester-containing oils of the lubricating class, the selection of which will be determined by conditions and services which the compounded oil is to encounter. Ordinarily the oil alone will not be appreciably corrosive, and of concern here is the substantial increase in corrosivity brought about by the addition of the partial esters. The compounding ingredients are useful not only in Pennsylvania oils or highly refined naphthenic oils, but also in moderately-refined naphthenic base oils or in lubricating oils from Mid-Continent stocks, as well as in synthetic hydrocarbon oils such as hydrogenated polymers of olefin hydrocarbons or synthetic non-hydrocarbon oils of lubricating viscosity such as condensation products of chlorinated alkyl hydrocarbons with aryl compounds, polyether oils, etc. Suitable polyether synthetic oils are obtained by the polymerization of lower molecular weight (e.g., C_2 to C_5) alkylene oxides, such as propylene and/or ethylene oxides, and derivatives and mixtures thereof to liquid products of lubricating oil viscosity; included in the term "polyether oils" are the derivatives obtained by etherification and/or esterification of the hydroxy groups in the alkylene oxide polymer, such as for example, the acetate of the 2-ethyl hexanol initiated polymer of propylene oxide. Various polyether oils are described in Patents 2,425,755; 2,448,664; 2,480,185; 2,520,614; and others.

Synthetic oils of the dicarboxylic acid ester type include those which are prepared by esterifying such dicarboxylic acids as adipic acid, azelaic acid, suberic acid, sebacic acid, alkenyl succinic acid, fumaric acid, maleic acid, etc., with alcohols such as butyl alcohol, hexyl alcohol, 2-ethylhexyl alcohol, dodecyl alcohol, etc. Examples of such ester oils are dibutyl adipate, dihexyl adipate, di-2-ethylhexyl sebacate, etc.

The esters in the oil compositions in which my inhibitor combination is incorporated are the higher polyhydric aliphatic alcohols partially esterified with an aliphatic carboxylic acid having an oil-solubilizing chain of at least 8 carbon atoms. Since as indicated above the effectiveness of the esters to inhibit deposit formation in engines depends at least in part upon unesterified hydroxyl groups, it is preferred that at least two, and most desirably all but one, of the hydroxyl groups remain unesterified. For appreciable effectiveness as a detergent additive, the alcohol should contain at least three, preferably four or five, and including six hydroxyl groups. Suitable alcohols which may be employed in forming the esters are exemplified by glycerol, tetrahydric alcohols such as erythritol, pentaerythritol, etc., the pentahydric alcohols such as penitol, tetramethylol cyclohexanol, etc., hexahydric alcohols such as sorbitol, mannitol, inositol, etc., ether alcohols including polyglycols such as diethylene glycol, polypentaerythritols such as dipentaerythritol, etc., anhydro alcohols such as sorbitan, mannitan, etc., derivatives of anhydro alcohols such as the polyoxyalkylene derivatives of sorbitan and mannitan, and the like. For some uses, the tetra- or higher poly-hydric alcohols are preferred. When the esters are employed primarily to prevent rusting, as in an aircraft engine preservative oil, the inhibitor combination therewith is required to counteract the corrosive attack on sensitive bearing metals at the elevated temperatures encountered when the engine is operated.

Representative higher aliphatic carboxylic acids which can be employed to form the above-described esters include capric, undecylic, lauric, myristic, palmitic, stearic, arachidic, behenic, and melissic as well as the higher naphthenic acids and naphthenic acid mixtures of the type derived from petroleum. Also, mixtures of acids derived from natural sources such as coconut oil, lard oil, tallow, cottonseed oil, soyabean oil and palm oil can be used. Among the higher aliphatic acids, a preferred group comprises those containing 10 or more carbon atoms and a single olefinic carbon-to-carbon double bond, as exemplified by 9-undecylenic, 4-tetradecylenic, oleic, palmitoleic, ricinoleic, elaidic and brassidic acids.

While the acids and alcohols employed in forming the esters of the present invention have been referred to as "aliphatic" in character, such term is also intended to include acids of the type defined above which are substituted by one or more of various groups such as amino, hydroxyl, alkoxy, chloro, phenyl, and the like, particularly when the number, nature and position of such substituent groups is not sufficient to alter the essentially aliphatic character and stability under the se-

lected conditions of use of the ester. The term also includes higher cyclic aliphatic acids and alcohols as exemplified, respectively, by the naphthenic acids and sorbitan.

Of the various partial esters indicated above, the monooleates of pentaerythritol and sorbitan are preferred for their outstanding effectiveness as detergents.

The esters of the above-disclosed alcohols and acids will ordinarily be present in the base oil in amounts ranging from about 2 or 3% to 10 or 15%, although in some cases they can be present in amounts as small as 0.5 to 1%. Generally not more than 25% of the esters will be incorporated in the oil compositions. Ordinarily the partial esters, when used to impart detergency characteristics to a crankcase lubricant, will be employed in amounts ranging preferably from about 5% to about 10% of the final lubricant composition. While some esters appear to have limited solubilities in very light mineral oils, they are readily soluble up to 12 to 20% or more in oils normally used as lubricants. Usually the esters can be dispersed in amount greater than their apparent solubility limits.

The inhibitor combination is incorporated into the ester-containing oil in sufficient amount to inhibit substantially against corrosion attack on hard bearing metals. In general, the amount of organic sulfide inhibitor required in the combination for substantial reduction of the corrosion ranges from about 0.05% up to 5% or more by weight of the finished oil; preferably the organic sulfide inhibitor is kept at a minimum below 3.0% but above 0.1%. The vicinal polyhydroxybenzenes are effective for the present purpose when used in amounts as low as about 0.005%, but are ordinarily employed in amounts ranging from 0.03% up to about 1.5%, depending on the limits of solubility, although amounts greater than 0.5% are not usually required. The higher amounts of the inhibitor usually will be required for crankcase lubricants for internal combustion engines. The minimum amount of the sulfur inhibitor for this purpose ordinarily will be 1%. The lower proportions of the inhibitor combination will be satisfactory where the conditions of use of the compounded oil are less rigorous, though at elevated temperature, than encountered in internal combustion engines. Thus, where the desired life of the oil or the temperature is not as high as in an internal combustion engine, the combination of the inhibitors at the lower percentages will be effective and satisfactory. In any event, an effective amount of each in the inhibitor combination will be employed.

To illustrate further the present invention, some oil compositions were subjected to the L–4–545 test of the Co-ordinating Research Council, which test employs a Chevrolet engine run for 36 hours at a jacket temperature of 200° F. and a sump temperature of 280° F. The bearings are weighed before and after the test and the average bearing weight loss is recorded as the corrosion. A weight loss of below 50 mgs. is considered excellent, a loss below 300 mgs. is considered satisfactory, but a loss above about 350 mgs. is not ordinarily satisfactory. The results obtained in this so-called "L–4 Chevrolet test" are given in Table VI below. The same base oil was used in all tests and the pinene-P_2S_5 reaction product was the same as used in the corrosion tests set forth hereinabove. Also given for comparison are some piston ratings obtained in tests of the oils as crankcase lubricants in a Chevrolet 6-cylinder engine operated using a low grade gasoline especially prone to cause engine deposits, the conditions being those defined in the standard FL–2 test procedure as described in the June 21, 1948, report of the Co-ordinating Research Council. This procedure requires the maintenance of a jacket temperature of 95° F. and a crankcase oil temperature of 155° F. at 2500 r.p.m. and 45 brake horsepower for 40 hours. At the end of the test, the engine is dismantled and the amount of engine deposits on the piston is determined and expressed as the average piston rating. This value is obtained by visually rating (on a scale of 0 to 10, with 10 representing the absence of any deposit) the amount of deposit on each piston skirt and averaging the individual ratings so obtained for the various pistons.

Table VI

Additive	Bearing Wt. Loss (mgs.)	Piston Rating
10% Sorbitan monooleate+3% pinene-P_2S_5	350	
10% Sorbitan monooleate+3% pinene-P_2S_5+0.15% alizarin	40	9.8
10% Sorbitan monooleate+2% pinene-P_2S_5+0.15% alizarin	109	
10% Sorbitan monooleate+2% pinene-P_2S_5+0.15% catechol	209	10
10% Sorbitan trioleate+1% sulfurized olefin inhibitor	2,691	
10% Sorbitan trioleate+1½% pinene-P_2S_5	958	
10% Pentaerythritol monooleate+1% diamyl phenol disulfide	2,250	

The above tests show that the inhibitor combination is also very effective in inhibiting the corrosion of bearing metals under the conditions of use as a gasoline engine crankcase lubricant. For comparative purposes, a bearing weight loss of about 250 mg. was obtained for a highly satisfactory commercial crankcase lubricant containing a calcium petroleum sulfonate, a sulfurized calcium cetyl phenate and a zinc dicetylphenyl thiophosphate.

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

The compounded oils of this invention may be utilized as turbine oils, cable oils, electric switch oils, transformer oils, hydraulic oils and the like as well as in crankcase lubricants for internal combustion engines including spark-ignition and diesel engines. The compounding agents of this invention can also be added to hydrocarbon and other oils of lubricating viscosity containing additional ingredients, such as metal salt detergents (e.g., polyvalent metal phenates, phenate sulfides, sulfonates, thiophosphates, etc.), pour point depressants, oiliness agents, extreme pressure addition agents, anti-oxidants, blooming agents, compounds for enhancing the viscosity index of the oil, thickening agents and/or metal soaps in grease-forming proportions or in amounts insufficient to form grease, as in the case of mineral castor machine oils or other compounded liquid lubricants. For some purposes, for example, such as to minimize the formation of deposits tending to cause pre-ignition as sometimes occurs in aviation engines, it is desirable to avoid metal-containing compounds, and for this purpose only those additional ingredients of non-metallic character are employed.

I claim:

1. A lubricating oil composition of relatively low corrosivity to sensitive bearing metals, comprising a major proportion of a lubricating oil containing from 5 to 10% by weight of sorbitan monooleate, which ester-containing oil has high detergency but is normally corrosive at elevated temperatures to sensitive bearing metals, together with about 1½% to about 3% of a terpene-P_2S_5 reaction product about 0.03% to about 0.5% of catechol.

2. A lubricating oil composition of relatively low corrosivity to sensitive bearing metals, comprising a major proportion of a lubricating oil containing from 5 to 10% by weight of sorbitan monooleate, which ester-containing oil is normally corrosive at elevated temperatures to sensitive bearing metals, together with about 1½% to about

3% of an oil-soluble terpene-P_2S_5 reaction product and about 0.03% to about 0.5% of alizarin.

3. A lubricating oil composition of relatively low corrosivity to sensitive bearing metals, comprising a major proportion of a lubricating oil containing from 5 to 10% by weight of pentaerythritol monooleate, which ester-containing oil is normally corrosive at elevated temperatures to sensitive bearing metals, together with about 1½% to about 3% of a terpene-P_2S_5 reaction product and about 0.03% to about 0.5% of catechol.

4. A lubricating oil composition of relatively low corrosivity to sensitive bearing metals, comprising a major proportion of a lubricating oil containing about 5 to 10% by weight of pentaerythritol monooleate, which ester-containing oil is normally corrosive at elevated temperatures to sensitive bearing metals, together with about 1½% to about 3% of an oil-soluble terpene-P_2S_5 reaction product and about 0.03% to about 0.5% of alizarin.

5. A lubricating oil composition of relatively low corrosivity to sensitive bearing metals, comprising a major proportion of a lubricating oil containing from 5 to 10% by weight of a monoester of a polyhydroxy aliphatic alcohol having four to six hydroxyl groups, the acid radical in said monoester being that of an aliphatic carboxylic acid with an oil-solubilizing chain of at least 8 carbon atoms which contains a single olefinic carbon-to-carbon double bond, together with about 1½% to about 3% of an oil-soluble terpene-P_2S_5 reaction product and a small amount, greater than 0.03% and up to 1.5% within the limits of solubility, of an unsubstituted vicinal dihydroxy aryl compound selected from the group consisting of dihydroxy benzenes and dihydroxy anthraquinones.

6. A lubricating oil composition of relatively low corrosivity to sensitive bearing metals, comprising a major proportion of a lubricating oil containing from 5 to 10% by weight of a partial ester resulting from the partial esterification of an aliphatic polyhydric alcohol of 3 to 6 hydroxyl groups with an aliphatic carboxylic acid having an oil-solubilizing chain of at least 8 carbon atoms, together with about 1½% to about 3% of an oil-soluble sulfurized olefin inhibitor obtained as a reaction product of an oil-solubilizing olefin and one of the class consisting of elemental sulfur and a phosphorus sulfide, and a small amount, greater than 0.03% and up to 1.5% within the limits of solubility, of a polyhydroxyl aryl compound having benzene ring substituents consisting essentially of hydroxyl groups, at least two of which are vicinal, said aryl compound being selected from the group consisting of polyhydroxy benzenes and polyhydroxy anthraquinones.

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