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MIXED SALTS OF PHOSPHORUS ACIDS AND HYDROCARBON-SUBSTITUTED SUCCINIC ACIDS

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15 Claims

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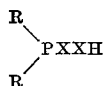
ABSTRACT OF THE DISCLOSURE

Metal salts of mixtures of organic phosphorus acids (especially phosphinodithioic acids) and hydrocarbon-substituted succinic acids improve oxidation stability and extreme pressure and frictional characteristics of lubricating oils, especially automatic transmission fluids and trans-axle lubricants. Mixtures of these salts with a basic metal salt of an organic (sulfonic, carboxylic or phosphorus-containing) acid are particularly useful.

This application is a continuation-in-part of copending application Ser. No. 543,013, filed Apr. 18, 1966, now abandoned, which is a continuation-in-part of application Ser. No. 359,031, filed Sept. 8, 1964, now U.S. Patent 3,271,310.

This invention relates to new compositions of matter, and more particularly to metal salts of acidic mixtures comprising

- (A) one equivalent of a hydrocarbon-substituted succinic acid having at least about 50 aliphatic carbon atoms in the hydrocarbon substituent, and
- (B) about 0.1–1.5 equivalents of a phosphorus acid of the formula



wherein

R is an organic radical and
X is oxygen or sulfur,

the metal of said metal salt being a Group I metal, a Group II metal, aluminum, tin, cobalt, lead, molybdenum, manganese or nickel.

Lubricating compositions are susceptible to oxidation upon prolonged exposure to air at elevated temperatures. Such oxidation results in the formation of organic acids, alcohols, ketones, aldehydes, etc. These products are corrosive to metal, and this corrosive action is the principal cause of excessive wear of the metal parts coming into contact with the oils. It is thus a common practice to incorporate into the mineral lubricating oils, chemical additives which are capable of inhibiting oxidation of the oil. As the internal combustion engines and power transmitting units increase in complexity and effectiveness, the needs for improved lubricants, and the requirements placed upon the additives contained in the lubricants, are correspondingly increased.

The automatic transmission associated with today's internal combustion engines and automotive systems is a good example of a unit which requires specialized lubricants and where the requirement has increased over recent years, placing a heavy burden on the additives contained in the lubricant. The so-called "transaxle" unit which combines the traditionally separate units of transmission and

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axle presents particularly difficult requirements for the lubricant additives. These two units have widely different operating characteristics, and, consequently, a unique problem of lubrication is created when they are combined. Lubricating compositions suitable for such units must possess not only a high viscosity index but also detergency, anti-wear properties under extreme pressure operating conditions, non-corrosiveness, resistance to foam, resistance to deterioration by heat and oxidation, and appropriate frictional characteristics. Furthermore, the additives must not attack or modify the characteristics of the various fibrous, rubbery or plastic components of the transaxle. Additionally, the additives contained in the compositions must be soluble in the lubricant base to the desired extent, and must be compatible with each other. Attempts to formulate mineral oil lubricating compositions which accomplish all of these purposes have not been entirely successful.

Accordingly, a principal object of this invention is to provide novel compositions of matter suitable for use as lubricant additives.

Another object is to provide novel metal salts of mixtures of acids.

A further object is to provide metal salts of mixtures of succinic and phosphorus acids which are soluble in hydrocarbon oils.

Still another object is to provide an improved lubricating composition for use in transaxles and automatic transmissions.

Other objects will in part be obvious and will in part appear hereinafter.

As indicated above, the compositions of this invention are metal salts of a mixture of a hydrocarbon-substituted succinic acid and a phosphorus acid. The hydrocarbon-substituted succinic acid is readily obtainable by the reaction of maleic anhydride or maleic acid and a high molecular weight olefin or a chlorinated hydrocarbon or other high molecular weight hydrocarbon containing an activating polar substituent, i.e., a substituent which is capable of activating the hydrocarbon molecule with respect to the reaction with maleic acid or anhydride. This reaction involves heating equivalent portions of maleic anhydride and the hydrocarbon, for example, at a temperature of about 100–200° C. The resulting product is the hydrocarbon-substituted succinic anhydride, which may be hydrolyzed to the corresponding acid by treatment with water or steam. The hydrocarbon-substituted succinic acid is preferred for the purposes of this invention.

The principal sources of the hydrocarbon radical include the high molecular weight petroleum fractions and olefin polymers, particularly polymers of mono-olefins having about 2–30 carbon atoms. Especially useful polymers are those of 1-mono-olefins such as ethylene, propene, 1-butene, isobutene, 1-hexene, 1-octene, 2-methyl-1-heptene, 3-cyclohexyl-1-butene, and 2-methyl-5-propyl-1-hexene. Polymers of medial olefins, i.e., olefins in which the olefinic linkage is not at the terminal position, are likewise useful. Such medial olefins include 2-butene, 3-pentene, and 4-octene, etc.

Also useful are the interpolymers of the olefins such as those illustrated above with other interpolymerizable olefinic substances such as aromatic olefins, cyclic olefins, and polyolefins. Such interpolymers include those prepared by polymerizing isobutene with styrene, isobutene with butadiene, propene with isoprene, ethylene with piperylene, isobutene with chloroprene, isobutene with p-methylstyrene, 1-hexene with 1,3-hexadiene, 1-octene with 1-hexene, 1-heptene with 1-pentene, 3-methyl-1-butene with 1-octene, 3,3-dimethyl-1-pentene with 1-hexene, isobutene with styrene and piperylene, etc.

The relative proportions of the mono-olefins to the

other monomers in the interpolymers influence the stability and oil-solubility of the products of this invention. Thus, for reasons of oil-solubility and stability, the interpolymers contemplated for use in this invention should be substantially aliphatic and substantially saturated, i.e., they should contain at least about 80%, and preferably at least 95%, on a weight basis, of units derived from the aliphatic mono-olefins and no more than about 5% of olefinic linkages based on the total number of carbon-to-carbon covalent linkages. In most instances, the percent of olefinic linkages should be less than about 2% of the total number of carbon-to-carbon covalent linkages.

Specific examples of such interpolymers useful in this invention include the following (percent by weight): copolymer of 95% isobutene with 5% styrene, terpolymer of 98% isobutene with 1% piperylene and 1% chloroprene, terpolymer of 95% isobutene with 2% 1-butene and 3% 1-hexene, terpolymer of 60% isobutene with 20% 1-pentene and 20% 1-octene, copolymer of 80% 1-hexene and 20% 1-heptene, terpolymer of 90% isobutene with 2% cyclohexene and 8% propene, and copolymer of 80% ethylene and 20% propene.

Another source of the hydrocarbon substituent radical includes saturated aliphatic hydrocarbons derived from highly refined high molecular weight white oils or synthetic alkanes such as are obtained by hydrogenation of the high molecular weight olefin polymers illustrated above or high molecular weight olefinic substances.

In addition to the pure hydrocarbon radicals described above, it is intended that the term "hydrocarbon radical," as used in the specification and claims, include substantially hydrocarbon radicals. For example, the hydrocarbon radical may contain substituents provided, however, that the substituents are not present in proportions sufficiently large as to alter significantly the hydrocarbon character of the radical. The substituents contemplated are those exemplified by chloro, bromo, keto, aldehyde, ether, nitro, etc.

Another important aspect of this invention is that the hydrocarbon radical of the hydrocarbon-substituted succinic compound should be substantially saturated, i.e., at least about 95 percent of the total number of carbon-to-carbon covalent linkages are saturated linkages. An excessive proportion of unsaturated linkages renders the molecule susceptible to oxidation, deterioration, and polymerization and results in products unsuitable for use in hydrocarbon oils in many applications.

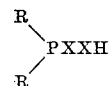
The size of the hydrocarbon radical appears to determine the effectiveness of the additive of this invention as an additive in lubricating oils. It is critically important that the radical be large, that is, that it have at least about 50 aliphatic carbon atoms in its structure. The molecular weight of the hydrocarbon radical should be about 700-100,000. Olefin polymers having a molecular weight of about 750-5,000 are preferred. However, higher molecular weight olefin polymers having molecular weights of about 10,000-100,000 are also useful and have been found to impart viscosity index improving properties to the metal salt compositions of this invention. In many instances, the use of such higher molecular weight olefin polymers is desirable.

The most common sources of these substantially aliphatic hydrocarbon radicals are the polyolefins such as polyethylene, polypropylene, polyisobutene, etc. A preferred polyolefin is polyisobutene having a molecular weight of about 1,000.

As indicated earlier, in lieu of the high molecular weight olefin polymers or chlorinated hydrocarbons, other high molecular weight hydrocarbons containing an activating polar substituent, i.e., a substituent which is capable of activating the hydrocarbon molecule in respect to reaction with maleic acid or anhydride, may be used in the above reaction for preparing the succinic compounds. Such polar substituents are illustrated by the sulfide, disulfide, nitro, mercapto, bromo, keto and aldehyde radicals. Examples of such polar-substituted hydrocarbons in-

clude polypropylene sulfide, di-(polyisobutene disulfide), nitrated mineral oil, di-(polyethylene sulfide), brominated polyethylene, etc. Another method useful for preparing the succinic acids and anhydrides involves the reaction of itaconic acid with a high molecular weight olefin or a polar-substituted hydrocarbon at a temperature about 100-200° C.

The phosphorus acid has the formula



wherein X is oxygen or sulfur and R is an organic radical, generally containing about 3-30 carbon atoms. These organic radicals can be alkyl, aryl, alkaryl, aralkyl or cycloalkyl radicals. It is contemplated that these organic radicals may also contain substituents such as the chloro, bromo and nitro. Specific examples of the R radicals include isopropyl, isobutyl, n-butyl, sec-butyl, n-hexyl, heptyl, 2-ethylhexyl, diisobutyl, isooctyl, decyl, dodecyl, tetradecyl, hexadecyl, octadecyl, butylphenyl, o,p-dipentylphenyl, octylphenyl, polyisobutene (molecular weight 350) - substituted phenyl, tetrapropylene - substituted phenyl, α -octylbutylmethyl, cyclopentyl, cyclohexyl, phenyl, chlorophenyl, o-dichlorophenyl, bromophenyl, naphthenyl, 2-methylcyclohexyl, benzyl, chlorobenzyl, chloropentyl, dichlorophenyl, nitrophenyl, dichlorodecyl and xenyl radicals. Alkyl radicals having about 3-30 carbon atoms, and aryl radicals having about 6-30 carbon atoms, are preferred.

Phosphinodithioic acids (R_2PSSH) can be prepared by the reaction of a Grignard reagent (e.g., butylmagnesium bromide, cyclohexylmagnesium iodide) with phosphorus pentasulfide (see *Organophosphorus Compounds*, G. M. Kosolapoff, p. 135, John Wiley and Sons, New York, 1960). The diaromatic phosphinodithioic acids can also be prepared by reacting, in the presence of a Friedel-Crafts catalyst, an aromatic compound (e.g., benzene, xylene, and chlorobenzene) with a phosphorus sulfide. The latter reaction can be illustrated by mixing, at about 150-180° C., and in the presence of aluminum trichloride, four moles of chlorobenzene and one mole of phosphorus pentasulfide. As the reaction takes place, hydrogen sulfide is emitted.

The preparation of alkyl aryl phosphinodithioic acids is illustrated by the reaction of an alkyl thionophosphine sulfide [e.g., $(RPS_2)_2$] with an aromatic compound in the presence of aluminum chloride as described by Newallis et al. in vol. 27, *Journal of Organic Chemistry*, page 3829. For example, phenylmethylphosphinodithioic acid is easily prepared by the reaction of methylthionophosphine sulfide with benzene in the presence of aluminum chloride.

The phosphinodithioic acids can be converted to the phosphinic acids (R_2POOH) by treating them with water or steam which, in effect, replaces the sulfur atoms with oxygen atoms. Either one or both of the sulfur atoms can be replaced. The phosphinodithioic acid is preferred for rust inhibiting purposes while the phosphinic acid is preferred when the salt is to be used as a detergent.

The metal salts which are useful in this invention include those salts containing metals selected from the class consisting of Group I metals, Group II metals, aluminum, lead, tin, molybdenum, manganese, cobalt, and nickel. Examples of metal compounds which may be reacted with the acid mixture include

lithium oxide,
lithium hydroxide,
lithium carbonate,
lithium pentylate,
sodium oxide,
sodium hydroxide,
sodium carbonate,
sodium methylate,
sodium propylate,

sodium phenoxide,
 potassium oxide,
 potassium hydroxide,
 potassium carbonate,
 potassium methylate,
 silver oxide,
 silver carbonate,
 magnesium oxide,
 magnesium hydroxide,
 magnesium carbonate,
 magnesium ethylate,
 magnesium propylate,
 magnesium phenoxide,
 calcium oxide,
 calcium hydroxide,
 calcium carbonate,
 calcium methylate,
 calcium propylate,
 calcium pentylate,
 zinc oxide,
 zinc hydroxide,
 zinc carbonate,
 zinc propylate,
 strontium oxide,
 strontium hydroxide,
 cadmium oxide,
 cadmium hydroxide,
 cadmium carbonate,
 cadmium ethylate,
 barium oxide,
 barium hydroxide,
 barium hydrate,
 barium carbonate,
 barium ethylate,
 barium pentylate,
 aluminum oxide,
 aluminum propylate,
 lead oxide,
 lead hydroxide,
 lead carbonate,
 tin oxide,
 tin butylate,
 cobalt oxide,
 cobalt hydroxide,
 cobalt carbonate,
 cobalt pentylate,
 nickel oxide,
 nickel hydroxide and
 nickel carbonate.

The metal salts of this invention can be prepared by mixing, at a temperature between about 20° C. and the reflux temperature, the metal reactant and a mixture of the hydrocarbon-substituted succinic acid and one or more of the above-described phosphorus acids. The hydrocarbon-substituted succinic acid can be replaced by the anhydride but if this is done, it is necessary to incorporate water in an amount up to about 15% of the weight of the succinic compound. In any event, it is necessary to mix the metal compound and the acidic mixture for a sufficient period of time to complete the reaction, e.g., from about 2 to about 10 hours. After the mixing period, the mixture is dried, generally under vacuum, and the residue is filtered.

Alternatively, the metal salt of this invention can be prepared by mixing the metal reactant and the hydrocarbon-substituted succinic acid to first form the metal salt of the succinic acid which is then further reacted with the phosphorus acid to give the desired metal salt. This latter method is the preferred method since larger amounts of metal can be incorporated into the salt, and the resulting salt is generally more soluble in lubricating oils.

The ratio of the phosphorus acid to succinic acid in the mixture will vary depending on the particular properties desired, for example, oil solubility, dispersancy and oxidation inhibition. The metal salt may be derived from an acidic mixtures comprising one equivalent of the hy-

drocarbon-substituted succinic acid and about 0.1–1.5 equivalents of the phosphorus acid. The equivalent weight of the succinic acid compound is one-half its molecular weight whereas the equivalent weight of the phosphorus acid is its molecular weight. The preferred mixture of the acidic components is about 0.3–1.0 equivalent of the phosphorus acid per equivalent of the hydrocarbon-substituted succinic compound. Generally, compositions having greater proportions of the succinic radical will be more oil-soluble and have better dispersancy properties.

At least about one equivalent of the metal is used in the preparation of the metal salts for each equivalent of acid. Generally, about 1.05–1.5 or more equivalents of the metal reactant are used per equivalent of acid. The upper limit of metal reactant which can be incorporated in the form of the metal salt must be determined in individual instances. The upper limit is reached when the metal salt becomes insoluble in lubricating oil since such a salt is no longer useful as a lubricant additive. Hence, the upper limit is determined to some degree by the relative solubilities of the reactants used in the preparation of the metal salts of this invention. Where the components of the acidic mixture are highly soluble in mineral oil, the mixture can tolerate larger amounts of metal and still remain soluble.

One of the advantages of the compositions of this invention is that they furnish a means for increasing the effective solubility of a phosphorus acid salt in oil. For example, salts of many aromatic phosphinodithioic acids are only slightly soluble in oil, and therefore cannot be used in additive concentrates. However, analogous salts of this invention can be prepared which are much more oil-soluble and which therefore can be used to form concentrates, as well as furnishing greater amounts of the phosphinodithioic acid radical in a lubricant to improve the properties thereof.

The use of solvents in the preparation of the metal salts of this invention is generally desirable. Salts of which have been found useful for this purpose include toluence, mineral oil, higher alcohols, dimethylformamide and xylene.

In some instances, the incorporation of certain ingredients such as small amounts of a metal carboxylate in combination with the metal oxide, or a small amount of carboxylic acid used in conjunction with the metal reactant, will facilitate the reaction and result in an improved reaction. For example, the use of up to about 5% (based on the total weight of the reactants) of zinc acetate or acetic acid, in combination with the required amount of zinc oxide, results in the formation of a zinc salt containing a higher amount of zinc than when the acetate is omitted. An oil solution of the product obtained in this manner also appears to be more stable on standing in that no haze or sediment develops.

The following examples are illustrative of the preparation of the metal salts of this invention. All parts, unless otherwise indicated, are by weight.

EXAMPLE 1

A mixture of 2,176 parts (4 equivalents) of a polyisobutenyl succinic anhydride (having an acid number of 103 and prepared by the reaction at about 200° C. of maleic anhydride with a chlorinated polyisobutene having an average chlorine content of 4.3% and an average of 67 carbon atoms), 112 parts of isooctyl alcohol and 1404 parts of mineral oil is heated and blown with steam at a temperature of from about 95° C. to about 105° C. for 2 hours. Zinc oxide (342 parts, 8.4 equivalents) is added at 105° C., and the reaction mixture is maintained at this temperature for 2 hours. To this mixture, there is added 2,959 parts (3.6 equivalents) of di-(isopropylphenyl)phosphinodithioic acid obtained by reacting isopropyl benzene with phosphorus pentasulfide in the presence of aluminium trichloride catalyst. The mixture is maintained at 95°–105° C. for 2 hours whereupon the volatile materials are removed by heating at 125° C./32 mm. The

residue is filtered using a filter aid and 1500 parts of mineral oil is added. The filtrate is the desired product having a phosphorus content of 1.41% and a zinc content of 3.53%.

EXAMPLE 2

To 73 parts (1.8 equivalents) of zinc oxide in 583 parts of mineral oil at a temperature of 100°–110° C., there is added a mixture of 560 parts (1 equivalent) of a polyisobutenyl succinic anhydride prepared as in Example 1 and having an acid number of 100, and 606 parts (0.8 equivalent) of di-(chlorophenyl)phosphinodithioic acid (prepared by mixing, at 140°–155° C., chlorobenzene and phosphorus pentasulfide in the presence of aluminum trichloride as a catalyst). The mixture is maintained at this temperature for an additional 0.5 hour, and the volatile components are removed by heating to 150° C./38 mm. The residue is filtered using a filter aid. The filtrate is the desired product.

EXAMPLE 3

A mixture of 977 parts (1 equivalent) of a 40% oil solution of the polyisobutenyl succinic acid having a saponification number of 57.4, 231 parts of mineral oil, 70 parts of dimethyl formamide and 81 parts (2 equivalents) of zinc oxide is heated to 95°–105° C. and maintained at this temperature for 2 hours. To this mixture there is added 681 parts (0.9 equivalent) of di-(chlorophenyl)phosphinodithioic acid at 95° C. over a period of 1.5 hours. The mixture is maintained at this temperature for an additional hour, and then heated to 150° C./28 mm. to remove the volatile components. The residue is filtered using a filter aid. The filtrate is the desired product having a phosphorus content of 0.82% and a zinc content of 3.51%.

EXAMPLE 4

The procedure of Example 1 is repeated except that only 1645 parts (2.0 equivalents) of di-(isopropylphenyl)phosphinodithioic acid is used.

EXAMPLE 5

The procedure of Example 2 is repeated except that the zinc oxide is replaced by an equivalent amount of lead oxide.

EXAMPLE 6

The procedure of Example 3 is repeated except that the zinc oxide is replaced by an equivalent amount of cadmium oxide.

EXAMPLE 7

A mixture of 1095 parts (1.22 equivalents) of a 40% oil solution of a polyisobutenyl succinic acid having an acid number of 62.6 and an average of about 72 carbon atoms in the polyisobutenyl substituent, 142 parts (3.48 equivalents) of zinc oxide and 359 parts of mineral oil is heated to and maintained at a temperature of 95°–105° C. for 2 hours. Di-p-dichlorophenyl-phosphinodithioic acid (910 parts, 1.1 equivalents) is added at this temperature over a period of 2 hours and the mixture is maintained at this temperature for an additional hour. The mixture is heated to 150° C./22 mm. to remove the volatile components and then filtered twice using a filter aid. Mineral oil (500 parts) is added to facilitate the filtration. The filtrate is the desired product having a phosphorus content of 0.74% and a zinc content of 3.35%.

EXAMPLE 8

Di-(o-dichlorophenyl)phosphinodithioic acid is prepared by mixing, at 95° C., 1940 parts (13.2 moles) of orthodichlorobenzene, 666 parts (3 moles) of phosphorus pentasulfide and 998 parts (7.5 moles) of aluminum trichloride. The mixture is heated for an additional 10 hours at 165°–170° C. to remove the hydrogen sulfide formed in the reaction. The mixture is cooled to room temperature, 2328 parts of toluene is added, and the mixture hydrolyzed with water. The organic and aqueous layers are

separated, and the organic layer is filtered using a filter aid. The filtrate is the desired phosphinodithioic acid which is found to have a phosphorus content of 2.77% and a sulfur content of 4.98%.

A mixture of 2,980 parts (3.33 equivalents) of a 40% oil solution of the polyisobutenyl succinic acid described in Example 7, 385 parts (9.48 equivalents) of zinc oxide and 779 parts of mineral oil is heated to 95° C. and maintained at this temperature for 2 hours. The phosphinodithioic acid prepared above (1806 parts, 3 equivalents) is added over a 2 hour period at 95°–105° C. and maintained at this temperature for an additional hour. After heating to 150° C./25 mm. the residue is filtered using a filter aid. The filtrate is the desired product having a phosphorus content of 0.44% and a zinc content of 2.28%.

EXAMPLE 9

A mixture of 225 parts (0.237 equivalent) of a 40% oil solution of the polyisobutenyl succinic acid described in Example 7 and 74 parts of mineral oil is heated to 35° C. and 24.4 parts (0.6 equivalent) of zinc oxide is added in 20 minutes. The mixture is heated to 95° C. and maintained at this temperature for 2.5 hours whereupon 196 parts (0.244 equivalent) of di-(chlorophenyl)phosphinodithioic acid is added in 2 hours at 95°–101° C. The mixture is heated to 152° C./20 mm. (2.3 hours) to remove the volatile components and filtered. The filtrate is the desired product having a phosphorus content of 1.31% and a zinc content of 4.62%.

EXAMPLE 10

A mixture of 833 parts (1 equivalent) of a 40% oil solution of the polyisobutenyl succinic acid described in Example 7, 235 parts of mineral oil, 81 parts (2 equivalents) of zinc oxide and 28 parts of zinc acetate is heated for 2 hours at 95°–105° C. whereupon 725 parts (0.9 equivalent) of di-(chlorophenyl)phosphinodithioic acid is added over a 0.5-hour period. The mixture is maintained at this temperature for an additional hour, and then heated to 150° C./38 mm. to remove the volatile components. The residue is filtered with a filter aid, and the filtrate is the desired product having a phosphorus content of 1.48% and a zinc content of 4.78%.

EXAMPLE 11

Di-(1,2,4-trichlorophenyl)phosphinodithioic acid is prepared by heating a mixture of 1,2,4-trichlorobenzene, phosphorus pentasulfide and aluminum chloride to a temperature of 195°–215° C. while removing the hydrogen sulfide formed in the reaction. Toluene (2742 parts) is added and the mixture is hydrolyzed. The phosphinodithioic acid is separated from the organic layer and is found to have a phosphorus content of 2.70% and a sulfur content of 8.02%.

A mixture of 1790 parts (2 equivalents) of a 40% oil solution of the polyisobutenyl succinic acid of Example 7, 220 parts, (5.4 equivalents) of zinc oxide and 1265 parts of mineral oil is heated for 2 hours at 95°–105° C. whereupon 1810 parts (1.6 equivalents) of the di-(1,2,4-trichlorophenyl)phosphinodithioic acid prepared above is added over a 2-hour period. The mixture is stirred an additional hour at this temperature, heated to 150° C./30 mm. and filtered. The filtrate is the desired product.

EXAMPLE 12

A mixture of 448 parts (0.5 equivalent) of a 40% oil solution of the polyisobutenyl succinic acid described in Example 7, 110 parts (1.9 equivalents) of manganese carbonate, and 287 parts of mineral oil is heated for 2 hours at 95°–105° C. whereupon 310 parts (0.45 equivalent) of di-(chlorophenyl)phosphinodithioic acid is added over a 3-hour period. The mixture is mixed for an additional hour at 95°–105° C. and filtered with a filter aid. The filtrate is heated to 150° C./30 mm. to remove the volatile components and the residue is filtered. The filtrate is the desired product.

EXAMPLE 13

The procedure of Example 12 is repeated except that the manganese carbonate is replaced by an equivalent amount of cobalt propylate.

EXAMPLE 14

A mixture of 396 parts (3.52 moles) of chlorobenzene, 137 parts (0.88 mole) of diphenyl and 222 parts (1 mole) of phosphorus pentasulfide is heated to 95° C. and 333 parts (2.5 moles) of aluminum chloride is added. The mixture is heated to and maintained at a temperature of 135–160° C. for 6 hours while removing the hydrogen sulfide formed in the reaction. Toluene is added to improve the viscosity of the mixture which is then hydrolyzed. The organic layer is separated and filtered using a filter aid. The filtrate is heated to remove the toluene and the residue is the desired phosphinodithioic acid having a phosphorus content of 3.54% and a sulfur content of 7.58%.

A mixture of 895 parts (1 equivalent) of a 40% oil solution of the polyisobutenyl succinic acid described in Example 7, 122 parts (3 equivalents) of zinc oxide, 17 parts of hydrated zinc acetate and 473 parts of mineral oil is heated to 95° C. and maintained at this temperature for 2 hours whereupon 438 parts (0.5 equivalent) of the phosphinodithioic acid prepared above is added over a period of 3 hours. The mixture is maintained an additional hour at 95°–105° C., and then filtered with a filter aid. The filtrate is heated to 160° C./30 mm. to remove the volatile components and then refiltered. The filtrate is the desired product containing 0.66% phosphorus and 3.39% zinc.

EXAMPLE 15

The procedure of Example 14 is repeated except that the zinc oxide:zinc acetate is replaced with an equivalent amount of lithium hydroxide monohydrate.

EXAMPLE 16

A mixture of 834 parts (1 equivalent) of a 40% oil solution of the polyisobutenyl succinic acid described in Example 7, 213 parts (5.7 equivalents) of lithium hydroxide monohydrate and 480 parts of mineral oil is heated to 95° C. and maintained at this temperature for 2 hours. Di-(chlorophenyl)phosphinodithioic acid (620 parts, 0.9 equivalent) is added over a 2-hour period while maintaining the temperature at 95–105° C. The mixture is maintained at this temperature for an additional hour whereupon 1500 parts of toluene is added and the solution is filtered using a filter aid. The filtrate is allowed to stand for 2 days during which time a salt precipitates. This salt was removed by filtration and the filtrate heated to 185° C./26 mm. to remove the volatile components. The residue is refiltered and the filtrate is the desired product having a lithium content of 0.76% and a phosphorus content of 1.51%.

EXAMPLE 17

The procedure of Example 16 is repeated except that the lithium hydroxide monohydrate is replaced by an equivalent amount of nickel carbonate.

EXAMPLE 18

A mixture of 1000 parts (1.22 equivalents) of a polyisobutenyl succinic acid prepared as in Example 7 and 430 parts of mineral oil is heated to 50° C. whereupon 112 parts (2.75 equivalents) of zinc oxide is added. The mixture is heated to 105° C. and maintained at this temperature for 2 to 3 hours. To this solution there is added 335 parts (0.61 equivalent) of di-(chlorophenyl)-phosphinic acid (obtained by the hydrolysis of the corresponding phosphinodithioic acid) over a period of 2 to 2.5 hours. The mixture is heated for an additional 3 hours at 95–108° C. and filtered with filter aid. Toluene (225 parts) is added to flush the filter aid. The filtrate is heated to 122° C./15 mm. to remove the volatile

components. The residue is the desired product having a phosphorus content of 0.39% and a zinc content of 2.10%.

EXAMPLE 19

Polyisobutene (1200 parts, having an average of 71 carbon atoms) is heated to 90° C. and 120 parts of maleic anhydride is added. The mixture is heated to 200° C. in 5 hours, maintained at this temperature for an additional 4 hours, heated to 238° C. in 3 hours and maintained at this temperature for 9 additional hours. The mixture is then cooled and maintained at a temperature about 195° C./50 mm. for 2 hours. The residue is filtered, and the filtrate is the desired polyisobutene-substituted succinic anhydride.

A mixture of 680 parts (1 equivalent) of the above-prepared succinic anhydride, 460 parts of mineral oil and 10 parts of water is heated to 90–100° C. whereupon 108 parts (2.65 equivalents) of zinc oxide is added in 5 minutes. The mixture is maintained for an additional 0.5 hour at this temperature, and 505 parts (0.75 equivalent) of di-(chlorophenyl)phosphinodithioic acid is added in 2 hours. The mixture is stirred an additional hour at this temperature, and then heated to 150° C. to remove the volatile components. The residue is filtered using a filter aid, and the filtrate is the desired product having a phosphorus content of 1.46% and a zinc content of 5.04%.

EXAMPLE 20

The procedure of Example 7 is repeated except that the zinc oxide is replaced by an equivalent amount of stannous oxide.

EXAMPLE 21

Water, 19 parts (1 mole), is added to a solution of 1122 parts (2 equivalents) of a polyisobutenyl succinic anhydride in 379 parts of mineral oil, and the mixture is heated for two hours at 99–105° C. An additional 683 parts of oil is added, followed by 6.7 parts of acetic acid. Then 179 parts (4.4 equivalents) of zinc oxide is introduced over a 10-minute period at 90–94° C. The mixture is agitated for 30 minutes at 94° C., after which time 1056 parts (1.55 equivalents) of a 51% solution of di(chlorophenyl)phosphinodithioic acid in toluene is added at 90–96° C. The mixture is agitated for 1 hour and the toluene and water is removed by distillation at 150° C./20 mm. An additional 340 parts of mineral oil is added and the mixture is filtered, yielding a 56% solution in oil of the desired product containing 1.48% phosphorus and 4.47% zinc.

The metal salts of this invention are useful as detergents, oxidation inhibitors and rust inhibitors. When used as lubricating additives, they are usually present in the lubricating oil in amounts of about 0.1–20 parts (by weight) per 100 parts oil. The optimum amount of the metal salt present in the lubricant is governed by the character of service to which the lubricating composition is to be subjected. For example, lubricating compositions for use in gasoline internal combustion engines may contain about 0.5–5.0 parts of the product of this invention per 100 parts of oil. When the lubricating composition is to be used in differential housing or diesel engines, the concentration of said salt may range as high as about 20 parts or even more.

This invention also contemplates the use of other additives in combination with the salts of this invention. Such additives include, for example, other detergents and dispersants of the ash-containing or ashless type, oxidation inhibiting agents, corrosion inhibiting agents, viscosity index improving agents, pour point depressing agents, extreme pressure agents, color stabilizers and anti-foam agents. Additives of these kinds are well known in the art; many suitable ones are described in Chapter 1 of "Lubricant Additives" by Calvin V. Smalheer and R. Kennedy Smith (Cleveland: Lezius-Hiles Co., 1967).

A particularly advantageous additive composition com-

prises (I) one part of a metal salt of the type described above and illustrated in the previous examples, and (II) about 0.1–3.0 parts of a basic alkali or alkaline earth metal salt of a sulfonic, carboxylic, or organic phosphorus acid having at least about 12 aliphatic carbon atoms wherein said salt has a metal ratio of at least about 1.1. Examples of alkali or alkaline earth metal salts (hereinafter referred to as "component II") which are useful in the preparation of this component include the salts of lithium, sodium, potassium, magnesium, calcium, strontium, and barium with a long chain sulfonic, carboxylic, or organic phosphorus acid. Mixtures of said salts are also useful. The acid should contain at least about 12 aliphatic carbon atoms in the molecule. The sulfonic acids include the aliphatic and the aromatic sulfonic acids illustrated by the petroleum sulfonic acids or the acids obtained by treating an alkylated aromatic hydrocarbon with a sulfonating agent, e.g., chlorosulfonic acid, sulfur trioxide, oleum, sulfuric acid, or sulfur dioxide and chlorine. The sulfonic acids obtained by sulfonating alkylated benzene, naphthalene, phenol, phenol sulfide, or diphenyl oxide are especially useful.

Specific examples of the sulfonic acids are mahogany sulfonic acids, mono-wax(eicosane)-substituted naphthalenesulfonic acid, dodecylbenzenesulfonic acid, didodecylbenzenesulfonic acid, dinonylbenzenesulfonic acid, di(octadecylphenyl)ether sulfonic acid, di(octadecylphenyl)amine sulfonic acid, cetyl chlorobenzenesulfonic acid, bis-cetylphenyl disulfide sulfonic acid, the sulfonic acid derived by the treatment of polyisobutene having a molecular weight of 1500 with chlorosulfonic acid, nitronaphthalenesulfonic acid, paraffin wax sulfonic acid, lauryl-cyclohexanesulfonic acid, and polyethylene (molecular weight 750) sulfonic acid.

Particularly useful salts are those obtained from bright stock sulfonic acids. Bright stock is the relatively viscous petroleum fraction obtained by dewaxing and treatment with, e.g., fuller's earth, of the distillation residue after the volatile petroleum fractions have been separated. It usually has a viscosity value of at least about 80 SUS (Saybolt Universal Seconds) at 210° F., especially about 85–250 SUS. Its molecular weight may range from about 500 to 2000 or even greater. Sulfonic acids can be obtained by the treatment of bright stock with any of the above-illustrated sulfonating agents.

The carboxylic acids likewise may be aliphatic or aromatic. They are exemplified by palmitic acid, stearic acid, myristic acid, oleic acid, hydrolyzed sperm oil, linoleic acid, behenic acid, hexatriacontanoic acid, tetrapropylene-substituted glutaric acid, polyisobutene(molecular weight 5000)-substituted succinic acid, polypropylene(molecular weight 10,000)-substituted succinic acid, octadecyl-substituted adipic acid, chlorostearic acid, 9-methylstearic acid, dichlorostearic acid, stearylbenzoic acid, poly-wax(eicosane)-substituted naphthoic acid, dilauryl-decahydronaphthalenecarboxylic acid, didodecyl-tetralincarboxylic acid, dioctyl-cyclohexanecarboxylic acid, and the anhydrides of such acids.

The metal salts of organic phosphorus acids useful in the compositions of this invention are those obtained from phosphorus acids having at least one direct carbon-to-phosphorus bond such as those prepared by the treatment of an olefin polymer (e.g., polyisobutene having a molecular weight of 1000) with a phosphorizing agent such as phosphorus trichloride, phosphorus heptasulfide, phosphorus pentasulfide, phosphorus trichloride and sulfur, white phosphorus and a sulfur halide, or phosphorothioic chloride.

An important aspect of these salts is that they have a metal ratio of at least about 1.1. The term "metal ratio" is used herein to designate the ratio of the total chemical equivalents of the metal in the salt to the chemical equivalents of the metal which is in the form of a normal salt, i.e., a neutral salt of the organic acid. To illustrate, a salt containing 5 equivalents of the metal per equivalent of

the organic acid radical has a metal ratio of 5; and a neutral salt has a metal ratio of 1. The use of carbonated salts having a metal ratio between about 4.5 and 20 has been found to be most advantageous, although salts having still higher metal ratios likewise are effective.

A convenient process for preparing the metal salts of component II comprises carbonating a substantially anhydrous mixture of the acid with at least about 1.1 chemical equivalents of an alkali or alkaline earth metal base per equivalent of the acid in the presence of a promoting agent. Carbonation of the mixture, though desirable for the preparation of the more basic salts, is not required for the preparation of all salts. The metal base may be an alkali or alkaline earth metal oxide, hydroxide, bicarbonate, sulfide, mercaptide, hydride, alcoholate, or phenate. It is preferably an oxide, alcoholate, or hydroxide of lithium, barium, or calcium. The carbonation is carried out in a solvent which is preferably mineral oil. The solvent may be n-hexane, naphtha, n-decane, dodecane, benzene, toluene, xylene, or any other fluid hydrocarbon.

The promoting agent is preferably an alcohol or a phenol; it may be a mercaptan, amine, aci-nitro compound, or an enolic compound. The alcohols and phenols useful as the promoting agent include, for example, methanol, isopropanol, cyclohexanol, dodecanol, behenyl alcohol, ethylene glycol, diethylene glycol, monomethyl ether of ethylene glycol, glycerol, pentaerythritol, benzyl alcohol, phenol, catechol, p-tert-butylphenol, etc.

It will be noted that upon mixing with large amounts of metal base, the acid forms a metal salt so that the process mixture before carbonation contains a metal salt of the acid and a large excess of the metal base. Such a mixture is heterogeneous primarily because of the presence of the large excess of the insoluble metal base. As carbonation proceeds, the metal base becomes solubilized in the organic phase and the carbonated product eventually becomes a homogeneous composition containing an unusually large amount of the metal. In many instances a homogeneous product is obtained when as little as 75% of the excess metal base is carbonated. For the sake of convenient reference in the specification and the claims of this invention, the term "carbonated, basic alkaline earth metal salt" of the oil-soluble acid designates the homogeneous, carbonated product without specific reference to the degree of conversion of the excess metal base by carbonation.

Formation of a carbonated, basic metal salt having a metal ratio of at least about 4.5 requires the presence in the carbonation step of a promoting agent such as described previously. The amount of the promoting agent to be used is best defined in terms of its chemical equivalents per equivalent of the long chain sulfonic or carboxylic acid used. The amount may be as little as 0.1 equivalent or as much as 10 equivalents or even more per equivalent of acid. The preferred amount is 0.25–5.0 equivalents per equivalent of acid. It will be noted that the equivalent weight of the promoting agent is based upon the number of functional radicals in the molecule. To illustrate, the equivalent weight of an alcohol or a phenol is based upon the number of hydroxy radicals in the molecule; that of an amine is based upon the number of amine radicals in the molecule; etc. Thus, methanol has one equivalent per mole; ethylene glycol has two equivalents per mole; a bis-phenol has two equivalents per mole; phenylenediamine has two equivalents per mole; nitropropane has one equivalent per mole; acetylacetone has one equivalent per mole; etc.

An inorganic halide may be incorporated into the mixture to help the efficient utilization of the sulfonic acid reactant and the alkali or alkaline earth metal base reactant. It is generally a halide such as ammonium chloride, ammonium bromide, ammonium iodide, sodium chloride, sodium bromide, sodium iodide, potassium bromide, potassium iodide, calcium chloride, barium chloride or calcium bromide. Of these, ammonium chlo-

ride, sodium chloride, barium chloride and calcium chloride are especially effective.

These halides, for the most part, are soluble in water. It is often convenient to introduce this component to the process mixture in the form of an aqueous solution or a slurry. Hydrates of such halides are also useful. As little as about 0.1% (based on the weight of the sulfonic or carboxylic acid) of the halide is sufficient to bring about the desired effects of this process. Ordinarily, no more than about 5% is required.

The carbonation temperature depends to a large measure upon the promoting agent used. When a phenol is used as the promoting agent the temperature usually ranges from about 80° C. to 300° C. and preferably from 100° C. to 200° C. When an alcohol or a mercaptan is used as the promoting agent, the carbonation temperature usually will not exceed the reflux temperature of the reaction mixture.

After carbonation, the promoting agent, if it is a volatile substance, may be removed from the product by distillation. If it is a non-volatile substance, it is usually allowed to remain in the product.

The methods of preparing the carbonated basic metal salts useful as component II in the compositions of this invention include (but are not restricted to) those described in U.S. Patents 2,616,905; 2,616,924; 2,616,911; 2,971,014; and 3,027,325.

It is frequently advantageous to react component II with anthranilic acid, by heating the two at about 140–200° C. The amount of anthranilic acid used is generally less than about 1 part (by weight) per 10 parts of component II, preferably 1 part per 40–200 parts of component II. The presence of anthranilic acid improves the oxidation- and corrosion-inhibiting effectiveness of the compositions of this invention.

The lubricating compositions of this invention may be prepared by merely adding the additives in the desired proportions to a lubricating oil. Alternatively, a concentrate may be prepared in which the additive compositions are diluted with a minimum amount of a mineral lubricating oil to produce a fluid concentrated composition, and the concentrate may then be blended with additional oil to give the final lubricant.

The concentrates prepared from the metal salt and other additives of this invention usually contain about 0.01–30 parts by weight of a mineral oil per part of the metal salt. The oil is, for the most part, a lubricating oil having a viscosity value at 210° F. of 50–500 SUS. Especially useful is a mineral oil from SAE 5 to SAE 120 grade. The sources of the oils are not critical although carefully refined oils having viscosity index values above 80 are preferred. A mineral lubricating oil which is particularly suited for use in the well-known "Type A" automatic transmission fluids is one having a viscosity of 116 SUS at 100° F. and 40 SUS at 210° F. and a viscosity index of 82.

The following examples are illustrative of the oil concentrates and lubricating compositions containing the metal salts of this invention.

EXAMPLE A

	Parts by weight
Product of Example 1	9
SAE 5 mineral lubricating oil	1

EXAMPLE B

Product of Example 1	1
SAE 5 mineral lubricating oil	9

EXAMPLE C

Product of Example 9	10
Sulfurized mixture of the methyl ester of tall oil acid (57%) and lard oil (43%) having a sulfur content of 7.8%	3
SAE 20 mineral lubricating oil	2

EXAMPLE D

	Parts by weight
Product of Example 9	10
Basic barium sulfonate prepared by carbonating a mixture of oil, mahogany sulfonic acid (1 equivalent), heptylphenol (0.6 equivalent) and barium hydroxide (3 equivalents) at 150° C.	5
Mineral oil for Type A automatic transmission fluid	5

EXAMPLE E

Product of Example 14	10
Basic barium sulfonate of Example D	1
Polyacrylate pour point depressant	1
Silicone anti-foam agent	.001
SAE 20 mineral lubricating oil	2

EXAMPLE F

Product of Example 18	10
Basic calcium sulfonate prepared by carbonating a mixture of a neutral calcium bright stock sulfonate having a molecular weight of 1100 (0.5 equivalent) mineral oil, calcium hydroxide (8 equivalents), a mixture of methyl alcohol, iso-octyl alcohol and water, and a small amount of calcium chloride (to a base number of 43; phenolphthalein indicator). This sulfonate has a calcium sulfate ash content of 19.7% and a metal ratio of 10.7	5
Decyl stearate	2
Dodecenyl succinic acid (anti-rust agent)	0.01
SAE 30 mineral lubricating oil	90

EXAMPLE G

Product of Example 9	28.47
Carbonated basic calcium sulfonate obtained by carbonating a mixture of a neutral calcium bright stock sulfonate having a molecular weight of 1100 (1 equivalent), mineral oil, calcium hydroxide (15.5 equivalents), a small amount of calcium chloride, and an alcohol mixture consisting of 100 parts of ethyl alcohol, 75 parts of iso-octyl alcohol, and 2.5 parts of water. The filtered product has a calcium sulfate ash content of 27% and a metal ratio of 16	25.96
Reaction product of 2 parts of anthranilic acid with 98 parts of a basic barium salt obtained by carbonating a mixture of sperm oil (1 equivalent), heptylphenol (0.602 equivalent), mineral oil, water and barium oxide (8 equivalents)	8.7
Fatty acid amide mixture consisting of, by weight, 91% oleamide, 6% stearamide, and 3% linoleamide	2.19
SAE 20 mineral lubricating oil	4.51
Aromatic hydrocarbon oil distillate having a viscosity value of 100 SUS at 100° F. and a value of 36 at 210° F.	30.19
Silicone anti-foam agent	0.174

EXAMPLE H

Product of Example 9	46.54
Basic calcium sulfonate of Example G	37.42
SAE 20 mineral lubricating oil	3.38
Reaction product of 1 part of anthranilic acid with 50 parts of a carbonated basic barium petroleum sulfonate obtained by carbonating a mixture of neutral barium petroleum sulfonate, heptylphenol, and barium oxide. The product has a barium content of 27.25% and a sulfate ash content of 38.5%	12.66
Silicone anti-foam agent	0.256

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EXAMPLE J

	Parts by weight
Concentrate of Example H	6.75
SAE 20 mineral lubricating oil	86.22
C ₆ -C ₁₄ alkyl polymethacrylate	4
Aromatic hydrocarbon distillate of Example G ..	3.0
Red dye	0.03

EXAMPLE K

Mineral lubricating oil having a viscosity of 81.5 SUS at 100° F. and a value of 37.8 SUS at 210° F. and a viscosity index value of 100	85.93
Product of Example 9	3.83
Anthranilic acid-barium salt product of Example G	1.03
Carbonated basic barium sulfonate obtained by carbonating a mixture of barium oxide and a sulfonic acid obtained by treating wax-substituted phenol with chlorosulfonic acid. This basic salt has a sulfate ash content of 18.2% and a barium content of 10.65%	0.75
Silicone anti-foam agent	0.02
Polyacrylate VI improver	8.46

EXAMPLE L

Mineral lubricating oil of Example K	85.70
Polyacrylate VI improver	8.46
Product of Example 9	3.77
Anthranilic acid-barium salt product of Example G	1.84
Amide mixture of Example G	0.20
Silicone anti-foam agent	0.02

EXAMPLE M

Mineral oil of Example K	85.65
Polyacrylate VI improver	8.46
Product of Example 9	3.83
Anthranilic acid-barium salt product of Example G	2.06

EXAMPLE N

Composition of Example 1	10
Carbonated basic calcium petroleum sulfonate obtained by carbonating a mixture of a sodium petroleum sulfonate having a molecular weight of 480, calcium hydroxide and an alcohol mixture of isobutyl, methyl and amyl alcohols, and having a calcium sulfate ash content of 39.5% and a metal ratio of 12.2	5
SAE 20 mineral lubricating oil	3

EXAMPLE P

Composition of Example 9	3.25
SAE 20 mineral lubricating oil	84.90
Polyacrylate VI improver	4.10
Aromatic hydrocarbon distillate of Example G ..	3.50
Basic calcium sulfonate of Example G	3.00
Anthranilic acid-barium salt product of Example G	1.00
Fatty acid amide of Example G	0.25

EXAMPLE R

Neutral diluent oil (100 SUS at 100° F.)	27.39
Product of Example 21	37.73
Reaction product of polyisobutenyl succinic anhydride with polyethylene polyamine mixture	16.49
Basic calcium petroleum sulfonate (metal ratio 1.43)	3.79
Basic sulfurized calcium polyisobutenyl salicylate ..	14.60
Silicone anti-foam agent	0.03

EXAMPLE S

SAE 40 mineral oil	88.63
Concentrate of Example R	11.37

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As mentioned previously, the compositions of this invention impart oxidation resistance to lubricating oils. The oxidation resistance of lubricants containing products of this invention is shown by the results, summarized in the table below, of an Air Oxidation Test which consists of bubbling air at a rate of 1.25-1.3 cubic feet per hour into 350 grams of a lubricant sample having immersed therein an oxidation catalyst (consisting of 120 grams of iron, 120 grams of copper, and 31 grams of lead) at 150° C. and measuring the viscosity change of the lubricant at regular intervals until a sharp increase of the viscosity occurs or haze or sediment develops. The viscosity change is expressed in terms of the percentage of SUS increase. It will be noted that a smaller increase in viscosity indicates a greater oxidation resistance of the lubricant, and that the appearance of haze or sediment indicates the formation of a significant quantity of oxidation products and, therefore, indicates the extent of oxidation resistance of the lubricant. The results of this test on several lubricants are summarized below. (The control is a base oil containing 3.6% of a polyacrylate viscosity index improver and 20 p.p.m. of a silicone anti-foam agent.)

AIR OXIDATION TEST

Lubricant Tested	Test Results				
	Percent Viscosity Increase and/or Sedimentation at the end of (hours)—duplicate				
	64	72	88	112	136
Control.....	(1)				
Control plus 2% of the product of Example 9.	4.7		6.9	8.2	(2)
Control + 2% of the zinc salt of the succinic acid of Example 9.	4.4		6.7	8.2	14.0
Control + 2% of the zinc salt of di-(chlorophenyl) phosphinodithioic acid.*	484		solid		
Example P.....	160		solid		
Example P less product of Example 9.	6.6		7.7	10.5	(2)
	7.7		9.1	11.7	(2)
Example P.....					8

¹ Medium sludge.

² Slight sludge.

³ Haze.

*This phosphinodithioic acid salt is only slightly soluble in mineral oil: 2% is the amount added to the oil but little dissolved. The sample subjected to the test was first filtered to remove the particles of undissolved salt.

In connection with these results, it should be noted that the lubricant containing 2% of the succinic acid salt was severely oxidized, while the lubricant containing less than 2% of the phosphinodithioic acid salt was slightly oxidized. However, the product of Example 9 was more effective as an oxidation inhibitor than either of these salts, even at half the concentration (for each acid) contained in the other two samples. This increased effectiveness is doubtless due, at least in part, to the increased solubility of the compositions of this invention in oil as compared to the phosphinodithioic acid salts taken alone.

The frictional or extreme pressure characteristics of lubricant compositions containing the compositions of this invention are evaluated by means of the Four-Ball Test. In this test, four steel balls are arranged in the form of an equilateral tetrahedron. The three lower balls are held immovable in a cup-shaped clamp to form a cradle in which the fourth ball is caused to rotate about a vertical axis under prescribed conditions of load and speed. The points of contact are lubricated by placing 10 ml. of the lubricant sample in the cup holding the lower three balls. For testing automatic transmission and transaxle fluids, the upper ball is rotated at 600 r.p.m. under a 40 kilogram load, at 93° C., for 2 hours or until the balls are welded together which is an immediate indication of a failure. During the test, circular scars are worn on the surface of the three stationary balls. The wear characteristics of the lubricant are evaluated by measuring the average diameter of the scars. Generally, a maximum diameter of 0.45 mm. is tolerated for an automatic transmission fluid. The results of this test, which demonstrate

the unexpected superiority of the compositions of this invention as extreme pressure additives, are summarized in the following table. (The control is the same as that used in the Air Oxidation Test.)

Four-Ball Test

Test lubricant:	Ave. scar diameter (mm.)
Example J -----	0.36
Control -----	0.84
Control+2% of the product of Example 9 ----	0.41
Control+2% of the zinc salt of the succinic acid of Example 9 -----	0.80
Control 1+2% of the zinc salt of di-(chloro-phenyl)phosphinodithioic acid ¹ -----	0.55, 0.58

¹This phosphinodithioic acid salt is only slightly soluble in mineral oil: 2% is the amount added to the oil but little dissolved. The sample subjected to the test was first filtered to remove the particles of undissolved salt.

8000 Cycle ATF Durability Test

This test provides a method of accelerated transmission endurance testing for evaluation of automatic transmission fluids using a 3-speed Ford automatic transmission. The results reported below were obtained using a specially instrumented and equipped 1965 Ford Galaxie 500 equipped with a 289 2V engine provided with instrumentation sufficient for continuously monitoring transmission sump pump oil temperature and transmission control oil temperature at ambient temperature. The test consists of subjecting a transmission to 8000 cycles, each cycle comprising the following procedure. With the selector level in the Drive position (D₁ or equivalent) and the vehicle speed at 15 m.p.h. (or less) the accelerator pedal is depressed to the floor until both the 1-2 and 2-3 upshifts are completed. After the 2-3 upshift is completed, the accelerator pedal is returned to engine idle throttle position and the selector level is moved to Lo position whereupon the transmission must shift to second gear. The vehicle is decelerated in second gear until an automatic 2-1 zero-throttle downshift occurs. The selector level is moved to the D₁ position and the above sequence repeated. Each sequence constitutes a cycle. The test is carried out for a total of 8000 cycles unless the operator observes slipping or rough shifting in the transmission. The lubricant of Example J successfully passed this test.

Powerglide durability cycling test

This test measures the durability of an automatic transmission fluid with respect to its stability and friction retention. In this test, lubricants are tested in a 1964 Powerglide transmission with a special 1965 transfer plate and clutch spring. The transmission is driven by a 1964, 327 cubic inch 250 H.P. Chevrolet V-8 engine through a series of upshifts and downshifts until the clutch engagement time for the upshift reaches 0.9 second. Each cycle is 40 seconds in duration; 30 seconds open throttle, 10 seconds closed throttle. The cycle begins with the transmission in low gear, and the engine is accelerated to 3200 r.p.m. At this point the upshift occurs, and approximately 25 seconds later the throttle is closed allowing the engine to decelerate and the transmission to shift back to low gear.

The operating conditions are as follows: transmission sump temperature (maximum during cycle) 132-138° C.; engine speed at upshift, 3200±20 r.p.m.; engine idle speed, 900±20 r.p.m.; dynamometer load in high gear at 2300 engine r.p.m., 230±2 ft.-lb.; engine oil temperature, 122° C. (maximum). At the end of the test, the parts are inspected for (1) plate condition and (2) varnish and sludge formation (on a scale of from 0 to 50, 0 being heavy varnish or sludge formation and 50 being no varnish or sludge). When evaluated by this test, a lubricant containing 10 percent by volume of the product of Example G has a varnish rating of 50 and a sludge rating of 48.4 at the end of 283 hours.

As indicated previously, modern engines and power transmitting units have severe requirements of lubrication which can be met only by lubricants having many desir-

able properties. This is illustrated by the large number of tests which a lubricant must pass in order to be accepted in the trade for use in automotive engines, automatic transmission, gears, etc. Such tests include, for example, metal corrosion test, heat stability test, oxidation resistance test, extreme pressure test, friction test, and detergency test, many of which are accelerated tests carried out in full size equipment. The following procedures are representative of some well-recognized tests for evaluating automatic transmission and transaxle lubricants.

Copper corrosion test (ASTM test procedure D-130-56)

The test consists of immersing a freshly polished copper strip in the lubricant, heating the lubricant at an elevated temperature for 3 hours, and measuring the extent of corrosion of the strip at the end of the heating period. The measurement of corrosion is accomplished by comparing the strip with a set of ASTM copper strip corrosion standards and is reported on the following scale: (1) for slight tarnish; (2) for moderate tarnish; (3) for dark tarnish; and (4) for corrosion.

Heat stability and compatibility test

The test involves heating and maintaining the lubricant at 150° F. for 2 months. The oxidation resistance and compatibility are measured by the development of haze or sediment.

Rust test (ASTM test procedure D-665)

In this test a mixture of 300 ml. of the lubricant and 30 ml. of water is stirred at 140° F. in the presence of a piece of steel for 24 hours. The steel piece is then inspected for appearance of rust spots.

High energy cycling test

This test is used to evaluate an automatic transmission fluid's effect on clutch durability in an aluminum Powerglide transmission operated under high energy cycling conditions. This test utilizes a 1965 Powerglide transmission which is driven by a Chevrolet 327 cubic inch engine equipped with a 4 bbl. carburetor (215 H.P.) through a series of cycles until the clutch lock-up time exceeds 0.9 second. Each cycle consists of the following steps: (1) full throttle acceleration to 4500 engine r.p.m. against inertia only; (2) a forced down-shift at 1100 engine r.p.m. followed by a second full throttle acceleration to 4500 engine r.p.m. against inertia only; and (3) manual low acceleration.

The operating conditions are as follows: transmission sump temperature, 110-113° C.; clutch applied pressure, 112±1 p.s.i. (maximum). At the end of the test, the transmission is disassembled and inspected for varnish and sludge, clutch band durability and condition of gearing, seals, thrust washers and converter thrust pad.

The difficulty in formulating lubricants which would pass these tests is readily apparent. Thus, the advantages of the additive compositions, in addition to compatibility, are shown by the fact that they are capable of imparting to lubricants the necessary properties which enable the lubricants to pass such tests. To illustrate, the lubricant comprising the mineral lubricating oil for Type A automatic transmission fluids and 10% by volume of the product of Example G is found to pass the following tests with the results summarized below and thus found to qualify for commercial use in automatic transmissions for automobiles.

Tests:

Viscosity index -----	142.
Heat stability and compatibility test (150° F.) -----	Clear.
ASTM copper corrosion test -----	1A.

Results

Tests:—Continued

ASTM rust test ----- Pass.

High energy cycling

test ----- No. of cycles: 24,338. Shift
time (sec.) initial: 0.48;
final: 0.61.

Powerglide durability

cyclic test ----- Test hours: 308. Rating: (50
max.). Varnish: 50.0;
Sludge: 49.5.

Many commonly used oxidation inhibitors for lubricants cause corrosion of copper and silver bearings in the engine. The Silver Strip Test is designed to evaluate the tendency, or lack of it, of a lubricant to corrode such bearings. In this test, a weighed silver strip and a weighed copper strip are each polished with steel wool and immersed in a 300-ml. sample of the oil being tested for 72 hours at 285° F. and at 325° F. The strips are removed every 24 hours for weighing and inspection. At the end of the test, the strips are rinsed in carbon tetrachloride and weighed; the silver strip is then cleaned by immersion in a 10% aqueous solution of potassium cyanide at room temperature, followed by brushing, immersion in acetone and drying. The cleaned strip is again weighed. A portion of the oil sample is filtered through a 100-mesh screen and evaluated for n-pentane insolubles, total base number and total acid number; the pH of the sample is calculated from the acid and base numbers. A second portion is filtered through a 200-mesh screen and the viscosity thereof at 100° F. is measured. Demerits are assigned to the lubricant proportionally according to the following scales:

Viscosity increase -----	3.3 demerits per 100 SUS.
Percent viscosity increase --	3.3 demerits per 10%.
Total acid number and total base number change ----	4 demerits each per 1 num- ber change.
pH change -----	3.3 demerits per 1 pH unit.
n-Pentane insolubles -----	8 demerits per 1% insol- ubles.

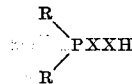
The following table gives the results obtained when the lubricant of Example S was tested by this method. Also given are the specifications required by an automotive manufacturer; these specifications apply at 285° F. only.

Test	285° F.	Results Spec- ifications (285° F.)	325° F.
Weight change after CCl ₄ rinse, mg.:			
Silver strip -----	-0.5	±5.0 max -----	-0.4
Copper strip -----	+0.6	-----	+0.6
Weight change after KCN rinse, mg. (silver strip) -----	-2.0	-5.0 max -----	-2.2
pH -----	7.6	3 min -----	7.1
Total acid number -----	2.08	2.5 max -----	2.06
Viscosity change, percent -----	-0.3	+15 max -----	+3.1
Pentane insolubles, percent -----	0.013	0.25 max -----	0.005
Demerits:			
Viscosity change -----	0.1	-----	1.1
Percent viscosity change -----	0.1	-----	1.0
Acid number change -----	0.8	-----	0.7
Base number change -----	12.6	-----	14.1
pH change -----	1.3	-----	3.0
Pentane insolubles -----	0.1	-----	0.5
Total -----	15.0	30 max -----	20.4

What is claimed is:

- I. A metal salt of an acidic mixture comprising
 - (A) one equivalent of a hydrocarbon-substituted succinic acid having at least about 50 aliphatic carbon atoms in the hydrocarbon substituent, and

(B) about 0.1–1.5 equivalent of a phosphorus acid of the formula



wherein R is an alkyl, aryl, alkaryl, aralkyl or cycloalkyl radical having about 3–30 carbon atoms, and X is oxygen or sulfur,

the metal of said metal salt being a Group I metal, a Group II metal, aluminum, tin, cobalt, lead, molybdenum, manganese or nickel.

2. The metal salt of claim 1 wherein the metal is zinc.

3. The metal salt of claim 1 wherein R is an aryl radical and X is sulfur.

4. The metal salt of claim 2 wherein R is a chlorophenyl radical and X is sulfur.

5. A composition comprising (I) one part by weight of the metal salt of claim 1, and (II) about 0.1–3.0 parts by weight of a basic alkali or alkaline earth metal salt of a sulfonic, carboxylic, or organic phosphorus acid having at least about 12 aliphatic carbon atoms, said salt having metal ratio of at least about 1.1.

6. A composition according to claim 5 wherein the metal of component I is a Group II metal, said composition containing about 0.3–1.0 part of component II.

7. The composition of claim 6 wherein the sulfonic acid of component II is a bright stock sulfonic acid.

8. The composition of claim 6 wherein the alkaline earth metal salt of component II is a metal salt of a fatty acid.

9. The composition of claim 6 wherein the alkaline earth metal salt of component II is a metal salt of a mixture of a fatty acid and a bright stock sulfonic acid.

10. A composition according to claim 9 wherein component II has been reacted with up to about 1 part, per 10 parts of component II, of anthranilic acid.

11. A composition according to claim 1 which additionally contains about 0.001–30.0 parts of a lubricating oil per part of metal salt.

12. A composition according to claim 9 which additionally contains about 0.001–30.0 parts of a lubricating oil per part of component I.

13. A composition according to claim 10 which additionally contains about 0.001–30.0 parts of a lubricating oil per part of component I.

14. A composition comprising a major proportion of a lubricating oil and a minor amount, sufficient to inhibit oxidation, of the product of claim 1.

15. A composition comprising 100 parts of a lubricating oil and about 0.01–20.0 parts of the composition of claim 9.

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