

1

3,489,682

METAL SALT COMPOSITIONS

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15 Claims

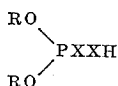
ABSTRACT OF THE DISCLOSURE

Metal salts of mixtures of organic phosphorus acids (especially phosphorodithioic acids) and hydrocarbon-substituted succinic acids improve oxidation stability and extreme pressure and frictional characteristics of lubricating oils, especially automatic transmission fluids and transaxle 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 in turn is a continuation-in-part of application Ser. No. 395,031, 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 equivalent 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 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

2

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 for use as lubricant additives.

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

A further 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 poly-olefins. 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

3

at least about 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 radicals 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.

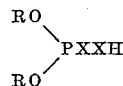
The most common sources of these substantially aliphatic hydrocarbon radicals are the polyolefins such as polyethylene, polypropylene, polyisobutene, etc. A preferred polyolefin is polyisobutene having a molecular weight of about 1,000.

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 include polypropene 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

4

reaction of itaconic acid with a high molecular weight olefin or a polar-substituted hydrocarbon at a temperature of 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-octylbutylnaphthyl, cyclopentyl, cyclohexyl, phenyl, chlorophenyl, o-dichlorophenyl, bromophenyl, naphthyl, 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.

The phosphorodithioic [(RO)₂PSSH] acids are readily obtainable from the reaction of phosphorus pentasulfide and an alcohol or phenol. The reaction involves mixing, at a temperature of about 20-200° C., 4 moles of the alcohol or phenol with one mole of phosphorus pentasulfide. Hydrogen sulfide is liberated as the reaction takes place.

The phosphorodithioic acids can be converted to the phosphoric acids [(RO)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 phosphorodithioic acid is preferred for rust inhibiting purposes while the phosphoric 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 form 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 mixture comprising one equivalent of the hydrocarbon-substituted succinic acids 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.

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

In some instances, the incorporation of certain ingredients such as small amounts of the metal acetate in combination with the metal oxide, or a small amount of acetic 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% of zinc acetate 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 zinc 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 zinc salt of a mixture of phosphorus acids is prepared by adding 779 parts (2 equivalents) of di-(isooctyl)phosphorodithioic acid to a slurry of 1090 parts of mineral oil and 166 parts (4.09 equivalents) of zinc oxide at 30° C. After heating to 90–105° C. and maintaining the mixture at this temperature for 2 hours, 494 parts (0.9 equivalent) of di-(chlorophenyl)phosphoric acid is added over a period of 2 hours at this temperature. The mixture is stirred an additional 2 hours at this temperature and filtered. The filtrate is heated at 130° C./

10–15 mm. to remove the volatile components. The residue is the desired salt having a zinc content of 4.49% and a phosphorus content of 3.62%.

A mixture of 833 parts (1 equivalent) of a 40% oil solution of the polyisobutenyl succinic acid having an acid number of 62.6 and an average of about 72 carbon atoms in the polyisobutenyl substituent, 81 parts (2 equivalents) of zinc oxide and 200 parts of mineral oil is heated and maintained at a temperature of 95–105° C. for 2 hours whereupon 1017 parts (1 equivalent) of the above zinc salt mixture is added. This mixture is heated for an additional hour at 95–105° C. and at 135° C./28 mm. to remove the volatile components. The residue is filtered and the filtrate is the desired product.

EXAMPLE 2

A mixture of 1108 parts (2 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), 300 parts of toluene, 104 parts of mineral oil and 90 parts of water is heated to 95° C. and maintained at this temperature for three hours. Zinc oxide (164 parts, 4 equivalents) is added and the mixture is maintained at 95° C. for three hours. Di-(isopropyl)-phosphorodithioic acid (411 parts, 1.8 equivalents) prepared from isopropyl alcohol and phosphorus pentasulfide, is added at 85° C., maintained at 95° C. for an additional hour, and then at 120° C./20 mm. to remove the volatile components. Mineral oil (1473 parts) is added to the mixture which is then filtered. The filtrate is the desired product having a phosphorus content of 1.06% and a zinc content of 2.93%.

EXAMPLE 3

A mixture of 2,216 (4 equivalents) of the polyisobutenyl succinic anhydride described in Example 2, 180 parts of water, 509 parts of mineral oil and 600 parts of toluene is heated to 95° C. and maintained at this temperature for 3 hours whereupon 937 parts (8.4 equivalents) of lead oxide is added. The mixture is maintained at 90° C. for 3 hours, and 1512 parts (4 equivalents) of di-(isooctyl)phosphorodithioic acid is added over a period of 15 minutes. The mixture is maintained at this temperature for 2 hours, heated to 130° C./20 mm. to remove the volatile components and filtered using a filter aid. The filtrate is the desired product containing 2.47% phosphorus and 16.06% lead.

EXAMPLE 4

A mixture of 1098 parts (2 equivalents) of the polyisobutenyl succinic anhydride of Example 2, 90 parts of water, 300 parts of toluene and 237 parts of mineral oil is heated to 95° C. and maintained at this temperature for 3 hours. Barium oxide (323 parts, 4.2 equivalents) is added slowly at 80° C. over a period of 1 hour, and the mixture is maintained at 90° C. for an additional 0.5 hour whereupon 746 parts (2-equivalents) of di-(isooctyl)phosphorodithioic acid is added. The mixture is maintained at 95° C. for 2 hours, heated to 120° C./20 mm. to remove the volatile components and filtered using a filter aid. The filtrate is the desired product having a phosphorus content of 2.61% and a barium content of 11.66%.

EXAMPLE 5

A mixture of 1662 parts (3 equivalents) of the polyisobutenyl succinic anhydride described in Example 2, 421 parts of mineral oil, 450 parts of toluene and 135 parts of water is heated to 95° C. and maintained at this temperature for 3 hours. Zinc oxide (258 parts, 6.3 equivalents) is added, and the mixture is maintained for 1.5 hours at 95° C. whereupon 1908 parts (3 equivalents) of di(tetrapropylene - substituted phenyl)phosphorodithioic acid (obtained by reacting 12 equivalents of tetrapropyl-

ene-substituted benzene with phosphorus pentasulfide) is added slowly at 90° C. and maintained at 95° C. for 3 hours. The mixture is heated to 130° C./20 mm. to remove the volatile components, and is filtered using a filter aid. The filtrate is the desired product having a phosphorus content of 2.17% and a zinc content of 4.98%.

EXAMPLE 6

A mixture of 1662 parts (3 equivalents) of the polyisobutenyl succinic anhydride of Example 2, 382 parts of mineral oil, 450 parts of toluene and 135 parts of water is heated to 95° C. and maintained at this temperature for 3 hours. Zinc oxide (258 parts, 6.3 equivalents) is added and the mixture is maintained for 1.5 hours at 95° C. whereupon 1556 parts (3 equivalents) of di-(heptylphenyl)phosphorodithioic acid (prepared from heptylphenol and phosphorus pentasulfide) is added slowly at 90° C. The mixture is maintained at 95° C. for an additional 3 hours, heated to 125° C./15 mm. to remove the volatile components and filtered using a filter aid. The filtrate is the desired product having a phosphorus content of 2.50% and a zinc content of 5.35%.

EXAMPLE 7

A mixture of 1108 parts (2 equivalents) of the polyisobutenyl succinic anhydride described in Example 2, 90 parts of water, 264 parts of mineral oil and 300 parts of toluene is heated to 95° C. and maintained at this temperature for 3 hours. Zinc oxide (172 parts, 4.2 equivalents) is added at 90° C. and the mixture is maintained for an additional 3 hours at 95° C. To this mixture there is added 1120 parts (2 equivalents) of a phosphorodithioic acid obtained by reacting phosphorus pentasulfide with a commercial mixture of fatty alcohols consisting of 2% decyl alcohol, 65% of dodecyl alcohol, 26% of tetradecyl alcohol and 7% of hexadecyl alcohol. The mixture is maintained at 95° C. for an additional hour, heated to 120° C./15 mm. to remove the volatile components and filtered using a filter aid. The filtrate is the desired product having a phosphorus content of 2.71% and a zinc content of 5.13%.

EXAMPLE 8

A mixture of 1098 parts (2 equivalents) of a polyisobutenyl succinic anhydride prepared as in Example 2, 90 parts of water, 300 parts of toluene and 215 parts of mineral oil is heated to 95° C. and maintained at this temperature for 3 hours. Calcium hydroxide (155 parts, 4.2 equivalents) is added slowly at 80° C. and the mixture is maintained at 95° C. for an additional 2 hours. Di-(isooctyl)phosphorodithioic acid is added to the mixture at 90° C., and the mixture is maintained at this temperature for 2 hours. The mixture is then heated to 120° C./20 mm. to remove the volatile components and filtered using a filter aid. The filtrate is the desired product having a phosphorus content of 3.26% and a calcium content of 4.39%.

EXAMPLE 9

The procedure of Example 8 is repeated except that calcium hydroxide is replaced by an equivalent amount of aluminum isopropoxide.

EXAMPLE 10

A mixture of 264 parts (0.47 equivalent) of the polyisobutenyl succinic anhydride of Example 2 and 53 parts of mineral oil is heated to 110° C. and blown with steam for 2 hours. To the product is added 13.2 parts of isooctyl alcohol and 37.5 parts (0.92 equivalent) of zinc oxide. The mixture is agitated for 3 hours at 94° C., after which time 179 parts (0.497 equivalent) of di-(isooctyl)phosphorodithioic acid is added over 30 minutes at 89–94° C. Mixing is continued for 1 hour at 94° C., after which the mixture is heated at 120° C./15 mm. for about 4 hours to remove volatile material. To the residue is added 67

parts of mineral oil. A filter aid is added and the material is filtered. The product, an 80% solution of the desired metal salt in mineral oil, contains 2.58% phosphorus and 5.33% 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 of 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 comprises (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 naphthalene sulfonic acid, dodecylbenzenesulfonic acid, didodecylbenzenesulfonic acid, dinonylbenzenesulfonic acid, di-(octadecylphenyl)ether sulfonic acid, di-(octadecylphenyl)amine sulfonic acid, cetylchlorobenzenesulfonic acid, biscetylphenyl 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, laurylcyclohexanesulfonic acid, and polyethylene(molecular weight of 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 at 210° F. 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 acids. They are exemplified by palmitic acid, stearic acid, myristic acid, oleic acid, hydrolyzed sperm oil, linoleic acid, behenic acid, hexatricontanoic acid, tetrapropylene-substituted glutaric acid, polyisobutene (molecular weight of 5000)-substituted succinic acid, polypropylene- (molecular weight of 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-decahydronaphthylene carboxylic acid, didodecyl-tetralin carboxylic acid, dioctyl-cyclohexane carboxylic 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, do-decanol, 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 refer-

ence 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 hydroxyl 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 and calcium bromide. Of these, ammonium chloride, 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.

Tables I and II list a number of illustrative oil concentrates and lubricating compositions containing the metal salts of this invention. Examples A, B, F and J are concentrates; the remainder of the examples are finished lubricants or automatic transmission fluids. Examples G and K were prepared from the concentrates of Examples F and J, respectively. The compositions in Table I are primarily for general lubricant use; those in Table II are primarily for use as automatic transmission fluids.

TABLE I.—PARTS BY WEIGHT

Ingredient	Example						
	A	B	C	D	E	F	G
SAE 10 mineral oil.....		5.0					
SAE 20 mineral oil.....	5.0						
SAE 30 mineral oil.....				91.75	93.72		
SAE 40 mineral oil.....			90.0				91.88
Neutral diluent oil (100 SUS at 100° F.).....						32.73	2.66
Product of Example 1.....		10.0					
Product of Example 2.....	9.5						
Product of Example 4.....			9.0				
Product of Example 10.....				2.42	2.42	24.87	2.02
Reaction product of polyisobutenyl succinic anhydride with polyethylene polyamine mixture.....				2.5		11.6	0.94
Mono-(pentaerythritol) ester of polyisobutenyl succinic acid.....						10.6	0.86
Basic calcium salt of polyisobutenylphenol sulfide (metal ratio 2.4).....				2.78			
Basic calcium salt of polyisobutenyl salicylic acid sulfide.....						20.2	1.64
Reaction product of basic calcium petroleum sulfonate (99.2%) with anthranilic acid (0.8%).....					2.85		
Basic barium petroleum sulfonate.....					0.66		
Reaction product of basic barium salt of sperm oil acid (98%) with anthranilic acid (2%).....			2.0				
Basic strontium mahogany sulfonate.....		3.0					
Formaldehyde condensation product of calcium 4-methyl-2-amylphenate.....					0.35		
Zinc salt of mixed isobutyl- and primary amylphosphorodithioic acids.....				0.55			
Silicone anti-foam agent.....			0.08	0.009	1.14	0.037	0.003

TABLE II.—PARTS BY WEIGHT

Ingredient	H J K L			
	H	J	K	L
Neutral diluent oil (100 SUS at 100° F.).....		28.09	2.77	
Automatic transmission mineral base oil.....	89.61		86.21	91.37
Product of Example 10.....	2.02	20.00	1.97	2.02
Basic calcium bright stock sulfonate (metal ratio 20).....	1.08	12.77	1.26	1.08
Reaction product of basic barium petroleum sulfonate (98%) with anthranilic acid (2%).....	0.54			
Reaction product of basic barium salt of sperm oil acid (98%) with anthranilic acid (2%).....		3.54	0.35	0.54
Zinc isooctylphosphorodithioate.....				0.64
Sulfurized hydrocarbon seal-swelling agent.....	3.00	35.60	3.51	
Copolymer of N-vinylpyrrolidone with C ₁₄ -alkyl methacrylates.....	3.75		3.93	4.35
Red dye.....	0.033		0.025	0.03
Silicone anti-foam agent.....	0.02	0.203	0.02	0.02

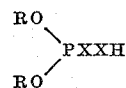
The effectiveness of the compositions of this invention as additives for automatic transmission fluids is evaluated by means of the Merc-O-Matic Transmission Oxidation Test. In this test, a 3-speed Merc-O-Matic automatic transmission is operated for 300 hours at a sump temperature of 325 ± 2° F., using 5 quarts of the transmission fluid being tested. The speed of the motor operating the transmission is maintained at 2150 ± 50 r.p.m. At the

end of the 300-hour operating period, the transmission is dismantled and the parts are examined for varnish and sludge. The evaluation ratings for the overall condition the transmission are from 0 to 50, with 50 representing a completely clean transmission. Separate ratings are recorded for varnish and for sludge.

When evaluated by this method, the automatic transmission fluid of Example H gave a varnish rating of 46.0 and a sludge rating of 49.1.

What is claimed is:

1. 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 phosphorous 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 alkyl radical and X is sulfur.

4. The metal salt of claim 3 wherein the metal is zinc.

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 a 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.

13

10. A composition according to claim 9 wherein component II has been reacted with up to about 0.1 part, per 10 parts of component II, of anthranilic acid.

11. A composition according to claim 1 which additionally contains about .001-30.0 parts of a lubricating 5 oil per part of metal salt.

12. A composition according to claim 9 which additionally contains about .001-30.0 parts of a lubricating oil per part of component I.

13. A composition according to claim 10 which additionally contains about .001-30.0 parts of a lubricating oil per part of component I.

14. A composition comprising 100 parts of a lubricating oil and about 0.01-30 parts of the product of claim 1.

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

14

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