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2,785,128

METAL SALTS OF ORGANIC ACIDS OF
PHOSPHORUS

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No Drawing. Application September 20, 1954,
Serial No. 457,298

16 Claims. (Cl. 252—32.7)

This invention relates to a novel method for preparing metal salts of acidic phosphorus-containing organic compounds and is especially concerned with the preparation of salts of weakly basic metals with acidic phosphorus- and sulfur-containing organic compounds such as for example the zinc, tin, cobalt and nickel salts of phospho-

sulfurized hydrocarbons. The invention also relates to the metal salts themselves which are useful in lubricating oil compositions, insecticides, fungicides and the like, and to such compositions containing the metal salts. The utilization of metallo-organic additives in lubricating oil compositions for internal combustion engines is well known. The addition of these materials to lubricating oils enhances their performance and produces lubricating oil compositions having among other desirable properties lower combustion chamber deposit-forming tendencies. Recently it has been found that the nature of the lubricating oil compositions employed and the additives incorporated therein has a substantial effect on the octane requirement of motor gasoline engines. More specifically, it has been found that after a new automobile has been driven for several thousand miles, the octane requirement of the car has increased. After a time, the octane requirement of the automobile reaches an equilibrium value, and it has been determined that the nature of both the gasoline and the lubricating oil employed contributes to this octane requirement increase of the automobile. Because of the severity of present-day engine operation and because of the criticality of octane requirement for automobiles, there is a need for improved lubricating oil compositions and for improved additives for these compositions.

One particular type of lubricating oil additive which has been extensively employed is a metal salt of a phosphosulfurized organic material. Such additives have been utilized as detergents in lubricating oil compositions to prevent the formation of engine crankcase deposits and thus to improve the operation of the engines. These additives have been prepared in the past by treating a phosphosulfurized organic material at an elevated temperature with a basic reagent containing a metal constituent such as a metal oxide, a metal hydroxide, or a metal carbonate. Although this method has been employed to produce phosphorus-containing metallo-organic compounds of potassium and barium, for example, this particular method has not been effective for producing good yields of the compounds of weakly basic metals such as zinc, tin, nickel, cobalt, etc. There has thus been a need for an effective process for producing such salts since these phosphorus- and sulfur-containing salts are exceedingly effective as detergent additives and in addition have various other uses in such fields as insecticides, fungicides and the like. Heretofore it is not believed that there was such a method.

A novel method has now been found for preparing phosphorus-containing metallo-organic compounds of weakly basic metals, such as zinc, tin, cobalt, nickel and the like. Briefly, the method of the present invention comprises reacting an acidic phosphorus-containing

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organic compound with an aqueous acidic solution of a metal halide at an elevated temperature for a period of time sufficient to produce a substantially dry metal salt of the acidic phosphorus-containing organic compound. The metal which may be used in this method is one having an electrode potential in the electromotive series in the range of about 0 to 2.0 volts. A sufficient amount of the metal halide is employed in the reaction to form a salt of the phosphorus-containing organic compound. The method of this invention is unique and unexpected, involving the replacement in a salt of a strong acid by a weak acid. More particularly, the halogen atoms of the metal halide are replaced by the acidic phosphorus-containing organic compound. The reaction is carried out at an elevated temperature, preferably in the range of about 140° to 300° F., until most of the water has been driven off from the reaction mixture, after which the temperature may be raised to as high as about 500° F. to assure substantial completion of the reaction. It has been found that the method of this invention may be best carried out by employing an aqueous solution of the metal halide and a small amount of preferably a halogen acid which is believed to act as a catalyst in the reaction. The metallo-organic compounds so formed may be employed as additives in lubricating oil compositions in concentrations of about 0.5 to 12%.

The acidic phosphorus-containing organic materials of this invention may in general be prepared by treating an organic material with a sulfide or oxide of phosphorus by procedures well known to the art. Sulfides of phosphorus such as P_2S_3 , P_2S_5 , P_4S_3 , P_4S_7 , and preferably phosphorus pentasulfide, P_2S_5 , may be employed. It will be understood of course that mixtures of elemental sulfur and phosphorus may also be utilized for this purpose. When the organic material is treated with an oxide of phosphorus, P_2O_3 , P_2O_5 , P_4O_3 , P_4O_7 and preferably phosphorus pentoxide, P_2O_5 , may be employed. The phosphorization or phospho-sulfurization reaction is generally carried out at a temperature of about 200° to about 600° F. and preferably from about 300° to about 550° F., using from about 1 to about 10, and preferably about 2 to about 5, molecular proportions of the organic material to 1 molecular proportion of the oxide or sulfide of phosphorus. It is usually desirable to use an amount of the oxide or sulfide of phosphorus which will react substantially completely with the organic material such that further purification of the product is unnecessary. The reaction time is generally not critical, the time required being that necessary for substantial completion of the reaction, that is to cause substantially a maximum amount of the sulfide or oxide used to react under the temperature conditions employed. A reaction time from 2 to 10 hours in the preferred temperature range of 300° to 550° F. is generally necessary. Catalysts such as organic or inorganic peroxides may be employed in the reaction. If desired, the reaction product may be further treated by blowing with steam, alcohol, ammonia, or the like, at an elevated temperature in the range of about 200° to about 600° F. to improve the odor thereof.

A wide variety of organic materials may be reacted with the oxides or sulfides of phosphorus. Especially preferred organic materials are hydrocarbon polymers, oxygen-containing hydrocarbon polymers and complex organic esters and ethers. More specifically, monocolefin polymers having molecular weight ranges from about 100 to 50,000 and obtained by the polymerization of low molecular weight olefins such as ethylene, propylene, isobutylene, amylene and the like, may be employed. The polymerization reaction is carried out by methods well known to the art.

Oxygen-containing hydrocarbon polymers, having molecular weight ranges from about 100 to 50,000 and such

ratio of carbon-hydrogen to oxygen as to be oil-soluble, which are obtained by the polymerization of oxygen-containing olefins such as vinyl ethers, vinyl esters, maleate and fumarate esters, and copolymers of such materials may also be employed. Specific oxygen-containing compounds of this type include the polymers or copolymers of the following:

Vinyl acetate
 "Lorol B" fumarate¹
 "Lorol B" maleate¹
 Tridecyl itaconate
 Vinyl lauryl ether
 Butoxyethyl vinyl ether

¹ Derived from "Lorol B" alcohol which is a commercially available saturated straight chain monohydric alcohol product having an average of about 13.5 carbon atoms per molecule, made by hydrogenation of coconut oil.

As examples of the complex esters and ethers which may be treated with an oxide or sulfide of phosphorus, the following may be mentioned:

Polyalkylene oxide mono alkyl ethers
 Polyalkylene oxide dialkyl ethers
 Polyalkylene oxide mono ester mono ethers
 Diesters of polyalkylene oxide
 Complex formals

Specific complex esters and ethers include the following:

Polypropylene oxide mono butyl ether
 Polyethylene oxide methyl butyl ether
 Polypropylene oxide isodecyl ether acetate
 Dioctanoic ester of polypropylene oxide
 Bis tridecoxy tetradecaisopropoxy methylene

Although a preference has been expressed for certain particular organic materials, it will be understood that this invention is applicable to all of those organic materials which form an acidic compound when treated with an oxide or sulfide of phosphorus. These organic materials include hydrocarbons such as olefins, diolefins, acetylenes, aromatics, alkyl aromatics, alicyclics, petroleum fractions such as lubricating oil distillates, petrolatums, cracked cycle stocks or condensation products of petroleum fractions, solvent extracts, petroleum fractions and the like.

The metal halides of this invention are preferably the chlorides although it will be understood that other halides such as bromide and iodide may be employed if desired. The metal of the halides is one which acts as a weak base. More particularly, the metal is a weakly basic one which has an electrode potential in the range of about 0 to 2.0 volts in the electromotive series. These metals, for example, are listed on pages 915 to 916 of Lange's Handbook of Chemistry, 4th edition, published in 1941 by Handbook Publishers, Inc., Cincinnati, Ohio. Of the metals having the aforedescribed electrode potentials, certain metals are preferred. These include tin, zinc, cobalt, and nickel. Other metals in this range of electrode potentials include magnesium, aluminum, manganese, chromium, iron, cadmium, and lead. Generally, the metals useful in the present invention are those weakly basic metals from lead to magnesium, inclusive, in the electromotive series of the metals.

The method of this invention is carried out by reacting the acidic phosphorus-containing organic compound with an aqueous acidic solution of the metal halide at an elevated temperature for a period of time sufficient to produce a substantially dry metal salt of the acidic phosphorus-containing organic compound. It has been found that it is necessary in order to obtain substantially complete conversion to the metal salt to add a small amount of an acid which is preferably a halogen acid such as HCl to the reaction mixture of the metal halide and the acidic phosphorus-containing organic compound. It is believed that the acid may serve as a catalyst in the reaction. Also the presence of the acid probably prevents

the precipitation of undesirable metal sulfides and metal oxides in the reaction.

Since the reaction proceeds very slowly if the metal halide is added as a dry salt, it is preferable to utilize the metal halide in an aqueous solution. In general, therefore, a preferred procedure in carrying out this reaction comprises heating an oil solution of the phosphorus-sulfide reaction product to an elevated temperature between about 220° F. and 300° F. and adding slowly to such heated solution an aqueous acidic solution of the metal halide. Water is driven off during the course of the reaction and when all of the aqueous solution has been added, the temperature of the resultant solution is raised to a temperature in the range of 350° to 500° F. to assure completion of the reaction and elimination of substantially all of the water.

An alternate procedure to the above-described method is one wherein a mixture is initially formed comprising the aqueous solution of the metal halide, the acidic phosphorus-containing organic material, and a small amount of a halogen acid. This mixture is heated at an elevated temperature in the range of about 140° to 300° F. to commence the reaction and to remove water from the reaction mixture. Because of the presence of water in the reaction mixture, care must be observed to prevent excessive foaming during the initial stages of the reaction in this procedure. For this reason it is preferred to raise the temperatures of the reaction mixture slowly in the range of about 140° to 300° F. until a substantial portion of the water has been driven off from the reaction mixture. Thereafter the reaction mixture may be further heated up to a temperature in the range of about 350° to 500° F. to assure substantial completion of the reaction between the metal halide and the acidic phosphorus-containing organic material. During the heating steps, halogen acids originally present in the reaction mixture and those formed in the reaction as well as the water originally present will be essentially removed by vaporization. A small amount of the halogen atoms derived from the metal halide or acid may remain in the final product.

The reaction time is generally not critical, the time required being that necessary for substantially completion of the reaction. A reaction time in the range of about 1 to 10 hours will generally be sufficient. The proportions of the ingredients are selected to give the desired metal salt of the acidic phosphorus-containing organic material. It is generally preferred to employ stoichiometric equivalents such that the acid groups are substantially completely converted to salt groups. However, where the acidic phosphorus-containing compounds are polybasic, the proportion of metal halide employed can be such that acid salts are obtained. When an excess of a polyvalent metal halide is employed, mixed salts can be formed which contain both halogen and the phosphorus-containing group joined to the metal. In general, the acidic phosphorus-containing organic compound is reacted with a sufficient amount of the metal halide to effect the neutralization of at least about 1% of the titratable acidity. If the reaction is permitted to be substantially completed, the metal content of the resultant product will be approximately equivalent to its concentration in the original mixture. Although not essential, it is preferable for ease of reaction and handling of the finished product to use a diluent such as a petroleum lubricating oil base. In a preferred embodiment of this invention the reactants involved are phosphosulfurized polyolefins and metal chlorides, in which reaction the preferred acid catalyst is concentrated aqueous HCl. The amount of aqueous HCl utilized may be about 0.02 to 0.1 wt. percent, based on the total reaction mixture.

The following specific examples of the invention are presented to set forth the invention in greater detail, but it will be understood that it is not intended that these examples limit the invention in any way.

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Example 1.—Preparation of the zinc salt of P₂S₅-treated polybutene

To 500 grams of a P₂S₅-treated polybutene (made by reacting a polybutene having a Staudinger average molecular weight of about 1200 with 10% by weight of P₂S₅ in a 4-liter beaker at 360° F.) was added a solution of 38 grams of zinc chloride, 50 cc. of water and 15 drops of concentrated aqueous hydrochloric acid. The addition required 2 hours, and foaming occurred during the addition. During the addition of the aqueous acidic zinc chloride solution, the temperature of the contents of the beaker was maintained at a temperature of 400 to 440° F. After the aqueous acidic zinc chloride solution had been added, the temperature of the reaction mixture in the beaker was 440° F. and the temperature was then maintained at 420 to 440° F. for a period of 2 hours. A clear liquid product resulted which was blended into a 50% concentrate with a solvent extracted and de-waxed mineral lubricating oil base to form a concentrate which had the following inspections by weight:

	Percent
Zinc	1.8
Phosphorus	1.31
Sulfur	0.28
Chlorine	0.20

This concentrate was then utilized in preparing the following lubricating oil composition:

Component:	Weight percent
1. Concentrate containing zinc salt	10.0
2. Oil solution of polymerized isobutylene (M. W.=14,000)	9.0
3. P ₂ S ₅ -treated α pinene	0.2
4. Mineral lubricating oil base	80.8
	100.0

This lubricating oil composition had an SSU viscosity of 190.2 at 100° F. and 52.1 at 210° F. and a viscosity index of 149.

In other related experiments, it was found that the reaction between the zinc chloride and the P₂S₅-treated polybutene proceeded very slowly if the zinc chloride was added as a dry salt rather than in an aqueous solution. It was also found that if zinc oxide was used instead of zinc chloride, apparently no reaction at all took place and the unreacted zinc oxide was left in the reaction mixture. When zinc oxide was employed, it was also found that the addition of an aqueous hydrochloric solution appeared to initiate a reaction but it was also found that substantial quantities of unreacted zinc oxide were present after a considerable period of heating.

Example 2.—Preparation of the tin salt of P₂S₅-treated polybutene

About 500 grams of the P₂S₅-treated polybutene of Example 1 were blended with about 333 grams of a mineral lubricating oil in a beaker. To this was added a solution of 44.6 grams of SnCl₂·2H₂O, 90 cc. of water, and 15 drops of concentrated aqueous hydrochloric acid. The addition of the acidic aqueous tin chloride solution required about 2 hours, and foaming occurred during the addition. During the step of adding this acidic aqueous tin chloride solution, the temperature of the reaction mixture in the beaker was maintained at a temperature of about 275° to 300° F. After the tin chloride solution had been added, the temperature of the reaction mixture was maintained at a temperature of about 300° F. for a period of ½ hour. A clear liquid product was obtained which had good solubility in oil.

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Example 3.—Preparation of the cobalt salt of P₂S₅-treated polybutene

The reaction was carried out with 1010 grams of a 60% solution by weight of P₂S₅-treated polybutene in a mineral oil and an aqueous solution comprising 57.0 grams of CoCl₂·6H₂O in 100 cc. of water to which was added 15 drops of concentrated hydrochloric acid. The oil solution of P₂S₅-treated polybutene was heated to 260° F. and the aqueous cobalt chloride solution was then added over a period of 4.5 hours. During this reaction period, the temperature was maintained between 235° and 300° F. When all of the aqueous solution had been added, the reaction mixture was maintained for 3.5 hours at a temperature in the range of 240° to 400° F. A nitrogen gas blanket was maintained over the reaction system during the entire reaction. The weight of the resultant product was 970 grams and the product had the following elemental analysis:

	Percent
Cobalt	1.37
Phosphorus	1.58
Sulfur	0.88

When the metal salts of this invention are utilized as lubricating oil additives, they are usually added to the lubricating oil compositions in proportions in the range of about 0.5 to 12% by weight and preferably in the range of about 1.5 to 5% by weight. For commercial purposes, it is convenient to prepare concentrated oil solutions in which the amount of the metal salts of this invention in the composition ranges from about 20 to 75% by weight and to transport and store them in such form. In preparing a lubricating oil composition for use as a crankcase lubricant, the additive concentration is merely blended with the lubricating oil base stock in the required amount.

The lubricating oil base stocks used in the compositions of this invention may be straight mineral lubricating oils or distillates derived from paraffinic, naphthenic, asphaltic, or mixed base crudes, or, if desired, various blended oils may be employed as well as residuals, particularly those from which asphaltic constituents have been carefully removed. The oils may be refined by conventional methods using acid, alkali and/or clay or other agents such as aluminum chloride, or they may be extracted oils produced, for example, by solvent extraction with solvents of the type of phenol, sulfur dioxide, furfural, dichlorodiethyl ether, nitrobenzene, crotonaldehyde, etc. Hydrogenated oils, white oils, or shale oil may be employed as well as synthetic oils, such as those prepared, for example, by the polymerization of olefins or by the reaction of oxides of carbon with hydrogen or by the hydrogenation of coal or its products.

Other lubricating oil base stocks which may be employed include synthetic lubricating oils having a viscosity of at least 30 SSU at 100° F. such as esters of mono-basic acids (e. g. ester of C₈ Oxo alcohol with C₈ Oxo acid, ester of C₁₃ Oxo alcohol with octanoic acid, etc.), esters of dibasic acids (e. g. di-2-ethyl-hexyl sebacate, di-nonyl adipate, etc.), esters of glycols (e. g. C₁₃ Oxo acid diester of tetraethylene glycol, etc.), complex esters (e. g. the complex ester formed by reacting one mole of sebacic acid with two moles of tetraethylene glycol and two moles of 2-ethyl-hexanoic acid, complex ester formed by reacting one mole of tetraethylene glycol with two moles of sebacic acid and two moles of 2-ethyl hexanol, complex ester formed by reacting together one mole of azelaic acid, one mole of tetraethylene glycol, one mole of C₈ Oxo alcohol, and one mole of C₈ Oxo acid), esters of phosphoric acid (e. g. the ester formed by contacting three moles of the mono methyl ether of ethylene glycol with one mole of phosphorus oxychloride, etc.), halocarbon oils (e. g. the polymer of chlorotrifluoroethylene containing twelve recurring units of chloro-

trifluoroethylene), alkyl silicates (e. g. methyl polysiloxanes, ethyl polysiloxanes, methyl-phenyl polysiloxanes, ethyl-phenyl polysiloxanes, etc.), sulfite esters (e. g. ester formed by reacting one mole of sulfur oxychloride with two moles of the methyl ether of ethylene glycol, etc.), carbonates (e. g. the carbonate formed by reacting C₈ Oxo alcohol with ethyl carbonate to form a half ester and reacting this half ester with tetraethylene glycol), mercaptals (e. g. the mercaptal formed by reacting 2-ethyl hexyl mercaptan with formaldehyde), formals (e. g. the formal formed by reacting C₁₃ Oxo alcohol with formaldehyde), polyglycol type synthetic oils (e. g. the compound formed by condensing butyl alcohol with fourteen units of propylene oxide, etc.), or mixtures of any of the above in any proportions.

Also, for special applications, animal, vegetable or fish oils or their hydrogenated or voltolized products may be employed in admixture with the synthetic or mineral oils. Also, mixtures of any of the above-mentioned oils in any proportions may be employed.

For the best results the base stock chosen should normally be that oil which without the new additive present gives the optimum performance in the service contemplated. However, since one advantage of the additives is that their use also makes feasible the employment of less satisfactory mineral oils or other oils, no strict rule can be laid down for the choice of the base stock. Certain essentials must of course be observed. The oil must possess the viscosity and volatility characteristics known to be required for the service contemplated. The oil must be a satisfactory solvent for the additive, although in some cases auxiliary solvent agents may be used. The lubricating oils, however they may have been produced, may vary considerably in viscosity and other properties depending upon the particular use for which they are desired, but they usually range from about 40 to 150 seconds Saybolt viscosity at 210° F. For the lubricating of certain low and medium speed diesel engines the general practice has often been to use a lubricating oil base stock prepared from naphthenic or aromatic crudes and having a Saybolt viscosity of 210° F. of 45 to 90 seconds and a viscosity index of 0 to 50. However, in certain types of diesel engine and other gasoline engine service, oils of higher viscosity index are often preferred, for example, up to 75 to 100, or even higher, viscosity index.

In addition to the material to be added according to the present invention, other agents may also be used such as dyes, pour depressors, heat thickened fatty oils, sulfurized fatty oils, organo-metallic compounds, metallic or other soaps, sludge dispersers, anti-oxidants, thickeners, viscosity index improvers, oiliness agents, resins, rubber, olefin polymers, voltolized fats, voltolized mineral oils, and/or voltolized waxes and colloidal solids such as graphite or zinc oxide, etc. Solvents and assisting agents, such as esters, ketones, alcohols, aldehydes, halogenated or nitrated compounds, and the like may also be employed.

In addition to being employed in lubricants, the metal salts of this invention may be also used in motor fuels, hydraulic fluids, torque converter fluids, cutting oils, flushing oils, turbine oils or transformer oils, industrial oils, process oils, gear lubricants, greases and generally as useful additives in oleaginous products. The metal salts are also useful as flotation agents, fungicides, insecticides and the like. When utilized as fungicides or insecticides, the metal salts are preferably dispersed or dissolved in such materials as water, organic solvents such as kerosene, light petroleum gas oils, etc., inert solids such as clay, and the like.

What is claimed is:

1. A method for preparing metallo-organic compounds which comprises reacting a phosphosulfurized hydrocarbon in the presence of a small amount of acid with a metal halide in aqueous solution and in an amount suffi-

cient to form a metal salt of said phosphosulfurized hydrocarbon, the reaction being carried out at a temperature and for a period of time sufficient to complete the resultant reaction and to form an essentially dry metal salt, said metal being one which has an electrode potential in the electromotive series in the range of about 0 to 2.0 volts.

2. A method for preparing metallo-organic compounds which comprises reacting a phosphosulfurized hydrocarbon in the presence of a small amount of halogen acid with a metal halide in aqueous solution and in an amount sufficient to form a metal salt of said phosphosulfurized hydrocarbon, the reaction being carried out at a temperature in the range of about 140° to 500° F. until the resultant reaction is substantially completed and a substantially dry metal salt is formed, said metal being one which has an electrode potential in the electromotive series in the range of about 0 to 2.0 volts.

3. A method for preparing metallo-organic compounds which comprises reacting a phosphosulfurized hydrocarbon in the presence of a small amount of halogen acid with a metal halide in aqueous solution and in an amount sufficient to form a metal salt of said phosphosulfurized hydrocarbon, the reaction being carried out at a temperature in the range of about 140° to 300° F. until a substantial portion of the water is driven off and thereafter at a temperature in the range of about 350° to 500° F. until the resultant reaction is substantially completed and essentially all of the water present is removed, said metal being one which has an electrode potential in the electromotive series in the range of about 0 to 2.0 volts.

4. A method for preparing metallo-organic compounds which comprises reacting a phosphosulfurized hydrocarbon in the presence of a small amount of hydrochloric acid with a metal chloride in aqueous solution and in an amount sufficient to form a metal salt of said phosphosulfurized hydrocarbon, the reaction being carried out at a temperature in the range of about 140° to 300° F. until a substantial portion of the water is driven off and thereafter at a temperature in the range of about 350° to 500° F. until the resultant reaction is substantially completed and essentially all of the water present is removed, said metal being selected from the group consisting of zinc, tin, nickel and cobalt.

5. Method according to claim 4 wherein said metal is zinc.

6. Method according to claim 4 wherein said metal is tin.

7. Method according to claim 4 wherein said metal is cobalt.

8. Method according to claim 4 wherein said metal is nickel.

9. Method according to claim 4 wherein said phosphosulfurized hydrocarbon is a P₂S₅-treated olefin polymer having a molecular weight in the range of about 100 to 50,000.

10. A method for preparing metallo-organic compounds which comprises reacting a P₂S₅-treated polybutene in the presence of a small amount of hydrochloric acid with a metal chloride in aqueous solution and in an amount sufficient to form a metal salt of said P₂S₅-treated polybutene, the reaction being carried out at a temperature in the range of about 140° to 300° F. until a substantial portion of the water has been driven off and thereafter at a temperature in the range of about 350° to 500° F. until the resultant reaction is substantially completed and essentially all of the water present is removed, said metal being selected from the group consisting of zinc, tin, cobalt and nickel.

11. A halogen-containing metallo-organic product obtained by reacting a phosphosulfurized hydrocarbon in the presence of a small amount of acid with a metal halide in aqueous solution and in an amount sufficient to form a metal salt of said phosphosulfurized hydrocarbon, the reaction being carried out at a temperature and for a

period of time sufficient to complete the resultant reaction and to form an essentially dry metal salt, said metal being one which has an electrode potential in the electromotive series in the range of about 0 to 2.0 volts.

12. A chlorine-containing metallo-organic product obtained by reacting a phosphosulfurized hydrocarbon in the presence of a small amount of hydrochloric acid with a metal chloride in aqueous solution and in an amount sufficient to form a metal salt of said phosphosulfurized hydrocarbon, the reaction being carried out at a temperature in the range of about 140° to 300° F. until a substantial portion of the water is driven off and thereafter at a temperature in the range of about 350° to 500° F. until the resultant reaction is substantially completed and essentially all of the water present is removed, said metal being selected from the group consisting of zinc, tin, nickel and cobalt.

13. As a new product, a polyvalent metal salt having at least one halogen atom joined to said metal and also having at least one acidic group of a phosphosulfurized hydrocarbon joined to said metal, said salt having been prepared by reacting a phosphosulfurized hydrocarbon in the presence of a small amount of halogen acid with a metal halide in aqueous solution and in an amount suf-

ficient to form said metal salt of said phosphosulfurized hydrocarbon, the reaction being carried out at a temperature and for a period of time sufficient to complete the resultant reaction and to form an essentially dry metal salt, said metal being one which has an electrode potential in the electromotive series in the range of about 0 to 2.0 volts.

14. A lubricating oil composition comprising a major proportion of a lubricating oil and in the range of about 0.5 to 12% by weight of a product defined by claim 11.

15. A lubricating oil composition comprising a major proportion of a mineral lubricating oil and in the range of about 0.5 to 12% by weight of a product defined by claim 12.

16. A concentrate consisting essentially of a lubricating oil and about 20% to 75% by weight, based on the total concentrate, of a product defined by claim 11.

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