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ONE STEP PREPARATION OF METAL ORGANO DITHIOPHOSPHATES

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ABSTRACT OF THE DISCLOSURE

A metal salt of an organo dithiophosphoric acid is prepared by reaction of P_2S_5 with a slurry comprising a mixture of at least one organic hydroxy compound of from 1 to 30 carbon atoms and at least one metal in powdered form, the metal being above hydrogen in the electromotive series, the quantity of metal in the slurry being at least 90 percent of the amount of metal theoretically required to convert the organic hydroxy compound to a metal diorgano dithiophosphate.

The present invention is concerned with improvements in the preparation of metal salts of organo dithiophosphoric acids. It is particularly directed to the preparation of polyvalent metal salts, and more particularly to the preparation of zinc salts of dialkyl dithiophosphoric acids, such as for use as additives in lubricating oil compositions.

The metal salts of dialkyl dithiophosphoric acids wherein the alkyl groups contain in the range of from about 1 to 20 carbon atoms and more particularly those having from about 3 to about 12 carbon atoms are well known in the art as additives for lubricating oil compositions. Their principal function in such compositions is as antiwear additives and as antioxidants. Zinc salts are usually employed for this purpose, although the nickel salts, as well as those of cadmium and lead, have been similarly used. Other metal salts of organo dithiophosphoric acids have been found to have antioxidant, corrosion inhibiting, or detergent properties in lubricants, fuels, and related oleaginous compositions. Also, some of the salts of organo dithiophosphoric acids, e.g., the tin salts, have found use as fungicides and others, e.g., sodium salts, have found use as insecticides.

It is common practice to prepare dialkyl dithiophosphoric acids by reaction of aliphatic alcohols with phosphorus pentasulfide. The metal salts are then ordinarily obtained by neutralizing the acids with an oxide, hydroxide, or a carbonate of the desired metal. An alternative procedure is to neutralize the acids with an alkali metal hydroxide and then to convert the alkali metal salts to the desired polyvalent metal salt by double decomposition with an appropriate inorganic salt of the polyvalent metal.

Certain disadvantages have been encountered in the past when preparing polyvalent metal salts of dialkyl dithiophosphoric acids, particularly when neutralizing the acids with metal oxides. Utilization of the metal oxide to obtain the desired degree of acid neutralization has been very erratic both as to the proportion of metal oxide required relative to the acid being neutralized and as to the reaction time needed to effect complete neutralization. It is usually necessary to employ excess metal oxide, as for example zinc oxide, in the neutralization and this requires increased filtration time to remove the excess metal oxide. Also, particularly in the case of zinc oxide neutralization, filtration problems arise because of the

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presence of zinc pyrophosphate and slimy zinc hydro-sulfides. Furthermore, since water is formed, during the neutralization, it is necessary to apply heat, soaking and drying steps to the neutralized product. Another disadvantage of the prior art processes for preparing metal dialkyl dithiophosphates is that it is sometimes difficult to obtain materials that are satisfactory as lubricating oil additives with respect to certain specifications. One of these is that the additive must pass what is known as the copper strip corrosion test (A.S.T.M. Test D130-56), which is a measure of the corrosivity of the additive toward copper surfaces. In simple terms, this test consists in immersing a polished copper strip in a sample of lubricating oil containing the additive under test, the copper strip being contacted with the oil at a specific temperature for a specified period of time after which the copper strip is inspected for corrosion. One factor which is believed to contribute to the failure of metal dialkyl dithiophosphates to meet the copper strip corrosion test is that, in the reaction of aliphatic alcohols with P_2S_5 , not only are the desired dialkyl dithiophosphoric acids formed but often as much as 20% of deleterious materials are also formed, including unstable sulfides, hydroxythiophosphoric acids, thioesters, mercaptans, as well as undesired reaction products resulting from further reaction of the dithiophosphoric acids with P_2S_5 and the like. It is often necessary to refine the crude dialkyl dithiophosphoric acids to remove these unstable and deleterious substances in order that the metal salts prepared from the acids will be satisfactory.

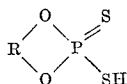
In accordance with the present invention, it has been found that metal salts of organo dithiophosphoric acids, in particular the zinc salts, can be prepared in a much more rapid and economical manner than in prior art processes by a one-step process wherein P_2S_5 is reacted with a stirred slurry of metal dust and organo hydroxy compound, e.g., an aliphatic alcohol or mixture of alcohols. While the process is particularly adaptable to the preparation of zinc salts, it is also operable with other metals including tin, antimony, cadmium, lead, chromium, nickel, sodium, molybdenum, indium, potassium, i.e., all metals above hydrogen in the electromotive series (with electrode potentials above that of hydrogen). Particle size is an important factor, with smaller metal particles (dust) favoring the reaction. Preferably the metal particles should be no coarser than about 200 mesh.

The presence of the metal has the effect of hindering further reaction of the dithiophosphoric acids with P_2S_5 , thereby impeding formation of the aforementioned undesirable products. Additionally, since no water is formed during the reaction, product hydrolysis and filtration problems are avoided.

The improvements obtained in the practice of this invention are particularly noteworthy in the preparation of the zinc salts of dialkyl dithiophosphoric acids wherein the alkyl groups have from about 1 to about 20 carbon atoms and especially wherein the alkyl groups have from about 3 to about 14 carbon atoms. The principles of the invention are likewise applicable to the preparation of the metal salts of other diorgano dithiophosphoric acids derived from organic hydroxy compounds of from 1 to 30 carbon atoms wherein the organo groups may be alkyl groups, aryl groups, cycloaliphatic groups, aralkyl groups, and mixtures of such groups derived from substituted or unsubstituted aliphatic alcohols, cycloaliphatic hydroxy compounds or phenolic compounds. Metal salts of cyclic dithiophosphoric acids can also be made according to this invention. The latter are prepared by reaction of P_2S_5

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with suitable diols such as 1,2-butylene glycol, pinacol, or neopentyl glycol, so that both of its hydroxyl groups react to form a cyclic compound as in



where R is the hydrocarbon radical of the diol.

The aliphatic alcohols which may be employed in preparing the salts of this invention include not only the simple alcohols, such as isopropyl, n-butyl, isobutyl, hexyl, octyl, decyl, etc., but also mixtures of such alcohols, as for example a mixture of isopropyl alcohol and methyl isobutyl carbinol, or a mixture of amyl alcohol and isobutyl alcohol, or mixed alcohols such as C₅, C₈ or C₁₃ oxo alcohols obtained by reaction of olefins with carbon monoxide and hydrogen and subsequent hydrogenation of the resultant aldehydes. Other mixed alcohols include those obtained by the hydrogenation of natural fats and oils, including mixed alcohols, such as the mixture containing chiefly lauryl alcohol that is obtained by hydrogenation of coconut oil, and the mixture of C₁₂ to C₂₀ alcohols, consisting principally of C₁₆ and C₁₈ alcohols, that is obtained from tallow by hydrogenation and/or by sodium reduction.

As stated above, the invention is also applicable to the preparation of metal salts of other organo dithiophosphoric acids such as those from cycloaliphatic alcohols, e.g. methyl cyclohexanol, ethyl cyclopentanol, cyclohexanol, methyl cycloheptanol and the like, as well as naphthenyl alcohols obtained by carboxylic reduction of naphthenic acids and their esters, e.g. by hydrogenation or sodium reduction of methyl esters of naphthenic acids. Other hydroxy compounds useful in preparing additives of the invention include phenol, cresol, amyl phenol, naphthol, tertiary octyl phenol, benzyl alcohol, phenyl butanol, heterocyclic alcohols such as furfuryl alcohol, and substituted alcohols such as ethylene chlorohydrin. Mixtures of the several types of organo hydroxy compounds may also be used, such as a mixture of cyclohexanol and isobutyl alcohol, a mixture of methylcyclohexanol and tert. octyl phenol, or the like.

Briefly stated, the process of the present invention is conducted in the following manner. A slurry is prepared consisting of the organic hydroxy compound, such as a mixture of alcohols, and a metal, such as zinc, in finely divided form. The amount of metal in the slurry should be at least 90 percent of the amount required to form the metal salts. Preferably the slurry contains a slightly greater amount of metal, say 5 to 10 weight percent excess, more than the amount theoretically required to form the metal salts. Normally the molar proportions in the case of a divalent metal will be 4 moles of hydroxy compounds, e.g. alcohols and slightly more than one mole of metal. For example, 297 lbs. of isobutyl alcohol and 70 lbs. of zinc dust may be used. The slurry of metal and organo hydroxy compound is then reacted with an amount of P₂S₅ calculated to convert the hydroxy compounds to the corresponding dithiophosphoric acids. As those acids are formed they are rapidly converted to metal salts by reaction with the metal that is present, thus preventing the dithiophosphoric acids from reacting further with P₂S₅ to form deleterious side products.

The temperature of reaction depends to some extent on the particular metal involved. In the case of tin, it is possible to conduct the reaction at room temperature, whereas in the case of zinc, some elevation in temperature is needed to impart a reasonable speed to the reaction. Also, while stepwise addition of the P₂S₅ is usually preferred for proper control of the reaction, it is also possible with some metals, such as tin, to add all of the P₂S₅ at once after the slurry has been prepared. The total reaction time is not critical and will vary with the particular system of metal and hydroxy compound that is involved. Reaction times of from 30 minutes to 16 hours or more may be

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required although more usually will involve from about 2 to about 12 hours.

When zinc salts are being prepared, the slurry is heated to a temperature in the range of about 115° to 200° F., preferably in the range of from about 130° to 160° F., in the case of aliphatic alcohols. While the reaction with zinc can proceed at lower temperatures, as for example 120° F., the reaction is usually too slow to be economic. If the temperature is permitted to exceed about 160° F. in the case of aliphatic alcohols, it tends to become too vigorous. After the zinc slurry has been heated to the desired reaction temperature, the theoretical quantity of P₂S₅ is added in small increments over a period of about 1 to 8 hours, or more usually about 2 to 3 hours. For example, about 2 to 2½ percent of the total charge can be added to the reaction mixture about every 3 minutes. Continuous addition in the proper proportions is even more desirable. If too much P₂S₅ is added at one time, the reaction tends to become too vigorous and difficult to control. During the addition of the P₂S₅ the mixture is subjected to the maximum agitation permissible without causing difficulties, such as splattering, overflow and the like. After all of the theoretical amount of P₂S₅ has been added, e.g. 1 mole of the latter per 4 moles of alcohol, some unreacted P₂S₅ will ordinarily still be present. Normally the heat of the reaction will tend to keep the reaction going spontaneously; however, it is desirable to maintain the reaction temperature at 130° to 160° F. This may be accomplished by the addition of 10 to 50 weight percent (based on the reaction mixture) of an inert solvent. The latter may have a boiling range approximating the desired reaction temperature, e.g., hexanes, heptanes. This solvent may be recovered and reused. Alternatively, and preferably, a mineral oil diluent is employed, e.g. a refined lubricating oil having a viscosity of say 100 SUS to 150 SUS at 100° F., in an amount ranging from 10 to 50 weight percent of the reaction mixture. Preferably the concentration range is about 15 to 25 weight percent of the mixture. It is often desirable to employ as the diluent a mixture of light mineral oil and one or more of the inert volatile solvents mentioned above.

Usually the reaction will be complete after about 8 hours from the time of first addition of P₂S₅. The approach of the end of the reaction will be noted by the decrease in the evolution of gas from the reaction mixture. At this point the reaction temperature is slowly raised to about 180°–190° F. until the end of the reaction has been determined by the cessation of gas evolution, which may require 1 to 4 hours. The reaction may be moderated in many instances by adding to the mixture about 1 to 10 weight percent, based on total reactants, of a metal salt of a carboxylic acid. Thus in the preparation of zinc dialkyl dithiophosphates, 1 to 10 weight percent, or more usually about 3 to 6 weight percent of a zinc salt of a C₂ to C₁₈ carboxylic acid such as zinc acetate, zinc hexoate, or zinc naphthenate may be added. A trace of a metal salt may be formed in situ by adding 0.001 to 0.1 weight percent of a mineral acid, or more usually 0.005 to 0.01 weight percent of an acid, e.g., HCl, to the reaction mixture. Moderation of the reaction can also be brought about by adding a small portion, say 5 to 10 weight percent, of zinc dialkyl dithiophosphate obtained from a previous batch.

At the end of the reaction, the mixture may still contain some dissolved H₂S and hydrogen. These are removed by sparging the mixture with an inert gas such as dry nitrogen at about 185° F. until it is essentially H₂S free. This can be determined by testing with lead acetate paper at the exit line of the reactor. Alternatively, vacuum distillation of the solvent removes dissolved gases. The product is then filtered. The filtration can be conducted at 175° to 185° F. and may or may not require the use of a filter aid such as Dicalite. Rapid filtration at lower temperatures may be obtained by not removing solvent until after filtration. The filter cake may be used to re-

place a portion of the metal charge in a subsequent reaction.

While the above-described reaction can be conducted at atmospheric pressure, there is some advantage in employing a slightly diminished pressure, as for example about 5% of an atmosphere (600 mm. of mercury). If the pressure is reduced too much, the reaction can become undesirably vigorous.

It is preferred that no water be present during the reaction because water may cause the formation of undesirable side products, such as zinc pyrophosphate or zinc hydroxyhydrosulfide. Also, the rate of filtration of the product tends to be adversely affected.

In the preparation of zinc dialkyl dithiophosphates by the process of the present invention, it will normally be found helpful to apply a finishing treat to stabilize the additive against H_2S evolution, i.e., to improve its H_2S stability. This treatment involves the addition of, in the range of 0.1 to about 5 weight percent of an alkylene oxide, such as ethylene oxide or propylene oxide, and can be conducted simply by adding the alkylene oxide to the product with stirring, using ambient temperatures. The reaction is slightly exothermic and is usually completed within from about 10 to about 40 minutes. The alkylene oxide treatment may be applied either before or after the product has been filtered.

The following examples serve to illustrate this invention.

Example 1

A slurry was prepared by mixing 818 g. of n-hexanol with 144 g. of zinc dust (325 mesh). This slurry was heated to 155° F. and then over a period of about 2½ to 3 hrs. 445 g. of P_2S_5 was added at the rate of about 10 g. every 4 minutes. During the addition of the P_2S_5 , the mixture was stirred at a rate of about 400 r.p.m. At the end of the period of P_2S_5 addition, the temperature of the mixture was raised to 185° F. and held at that temperature for about 8 hrs. while the mixture was continuously stirred at about 700 r.p.m. The mixture was held at a temperature of 180° F. and filtered, using Dicalite filter aid. The filter residue was mostly zinc dust and weighed 24.5 g. The filtered material was a water-white, slightly viscous, clear liquid weighing 1290 g. and having a specific gravity of 1.145 at 77° F. The product was found on analysis to contain 9.9% zinc, 9.48% phosphorus and 18.5% sulfur (theoretical 9.9% zinc, 9.4% phosphorus and 19.4% sulfur). The product was free of H_2S and showed no tendency to evolve H_2S . Its copper strip rating was 1 (by A.S.T.M. Test D130-56).

Example 2

A slurry was prepared by mixing 271 g. of isobutanol, 443 g. of oxo hexanols, 144 g. of zinc dust (325 mesh), and 325 g. of hexane. This slurry was heated to 130° F. and then, over a period of 3 hrs., 445 g. of P_2S_5 was added at the rate of about 10 g. every 4 minutes. Vigorous stirring was maintained. The temperature was raised to 150° F. during a period of an hour. Vigorous gas evolution continued for another half hour. The hexane was then removed by distillation at 160° F. and the reaction mixture was heated at 185° F. for 4 hours. The mixture was then filtered at 185° F. without using any filter aid. The filter residue weighed 23.6 g. and the colorless filtrate weighed 1190 g. The product analyzed for 10.52% zinc, 10.72% phosphorus, and 20.58% sulfur (theoretical 10.65% zinc, 10.20% phosphorus and 21.0% sulfur). The product was free of H_2S and did not evolve H_2S . It gave a copper strip rating of 1.

Example 3

A slurry was prepared by mixing 121 g. of powdered manganese of about 300 mesh with 600 g. of normal hexanol, 186 g. of isobutanol and 210 g. of a refined mineral lubricating oil (150 SUS viscosity at 100° F.). The mixture was heated to about 120° F., and then over

a period of five hours 445 g. of P_2S_5 was added gradually, the slurry being stirred continuously. The temperature was then raised to 175° F. and heating and stirring were continued for an additional five hours with the temperature being gradually raised to a final value of about 195° F. The product was then filtered, giving a concentrate of 85 weight percent of the manganese salt in mineral lubricating oil. The concentrate had a purple color. It was found on analysis to contain 10.65 weight percent manganese, 9.15 weight percent phosphorus, and 16.7 weight percent sulfur.

Example 4

A slurry was prepared by mixing 104.4 g. of powdered tin, 108.4 g. of isobutanol, and 175.2 g. of C_6 oxo alcohols. To this slurry was added, with stirring, 178 g. of P_2S_5 . The mixture was stirred at room temperature for 24 hours. Vigorous bubbling was noted in the reaction mixture, and it attained an orange color. The reaction product was filtered and then was sparged with nitrogen to free it of H_2S .

Example 5

A slurry was prepared by stirring 113 g. of 99.9 percent pure molybdenum dust of less than 250 mesh into 506 g. of normal hexanol and 126 g. of mineral lubricating oil (150 SUS viscosity at 100° F.). The mixture was heated to 120° F. with stirring and then while stirring was continued 252 g. of P_2S_5 was added gradually over a period of six hours. At the end of this time, the temperature was raised to 175° F. and stirring was continued for an additional five hours. During the entire reaction period, a total of 49 liters of gas was evolved, measured at NTP. The reaction product was filtered, leaving on the filter a small amount of grey residue with a trace of yellow, and yielding as the filtrate, an additive concentrate having a slightly reddish brown color.

Example 6

Part A.—A slurry was prepared by adding to 1000 g. of mixed C_4/C_5 aliphatic alcohols (65/35 molar ratio of isobutanol to mixed primary amyl alcohols), 188 g. of refined mineral lubricating oil (150 SUS viscosity at 100° F.), 216 g. of zinc dust and 94 g. of a previously prepared zinc dialkyl dithiophosphate, derived from the same mixture of alcohols. To this slurry, which was first heated to 120° F., there was added with stirring over a period of 6 hours 667 g. of P_2S_5 . Stirring was continued for an additional 3 hours after which the temperature was raised to 165° F. and the product was maintained at the latter temperature until gas evolution had ceased, which required about 1 hour of heating. The product was filtered at 160° F. through paper in the presence of 2 weight percent of diatomaceous earth filter aid and then blown free of hydrogen sulfide by means of a stream of nitrogen. The rate of filtration was found to be 120 gallons per square foot per hour.

Part B.—The product of Part A was treated with 1.1 weight percent of ethylene oxide at room temperature. The heat of reaction raised the temperature of the mixture to 105° F. The reaction was completed in about 15 minutes. The resulting material had a pH of 5.8 as compared with 4.2 for the product of Part A. The analysis of the product, which consisted of 89 percent of additive and 11 percent of diluent oil, showed a content of 10.44 weight percent of zinc, 9.75 percent of phosphorus, and 19.61 percent of sulfur.

Part C.—A comparative product was prepared by reacting 4 moles of the mixture of C_4 and C_5 alcohols used in Part A with 1 mole of P_2S_5 at 170° F. for 3 hours, after which the mixture was cooled to 65° F. and filtered. A 400 g. portion of the dialkyl dithiophosphoric acids thus obtained was reacted with 75 g. of zinc oxide at 160° F., the zinc oxide being added gradually over a period of 2 hours. At the end of the first 10 minutes of zinc oxide addition, 100 ml. of a refined mineral lubricating oil

(150 SUS viscosity at 100° F.) were added as a diluent. At the end of the 2 hour period of zinc oxide addition, the heating was continued at 160° F. for an additional hour. After the addition of 2 weight percent of diatomaceous earth filter aid the product was filtered. The rate of filtration was found to be 3 gallons per square foot per hour.

Example 7

Compositions were prepared using as the base oil a refined mineral lubricating oil having an SAE-30 viscosity rating. To separate portions of the base oil were added 0.5 to 0.7 weight percent of the products of Parts A, B and C of Example 6. Each of these compositions was tested in the well-known Four-Ball Wear Test. The test conditions were: a force of 10 kilograms; rotational speed, 1800 r.p.m.; temperature, 300° F.; and test duration, 30 minutes. The results obtained in the wear test are shown in Table I. It will be noted that the zinc dialkyl dithiophosphate prepared by the methods of the present invention were superior in wear reducing properties as compared to the additive prepared by conventional methods.

TABLE I

Example 6 Additive in Base Oil	Avg. Wear Scar Diameter, mm.
0.5 Wt. Percent Part A	0.245
0.6 Wt. Percent Part B	0.222
0.7 Wt. Percent Part C	0.379

Example 8

Blends were prepared using as the base oil a refined SAE-30 mineral lubricating oil. To separate portions were added small quantities of the products of Examples 1, 2, and 3 and of Part A of Example 6. Each of these blends and the base oil were subjected to the Falex Wear Test, using as the test conditions a 500 pound load and a test duration of 30 minutes. The results obtained are given in Table II.

TABLE II
Falex Wear Tests

Product Used	Wt. Percent Concentration	Pin Weight Loss, mg.
Example 1.....	0.6	0.7
Example 2.....	0.6	0.8
Example 3.....	0.07	3.3
Base Oil.....		6.0

If the metal organo dithiophosphate is to be employed as a lubricating oil additive, it is convenient to dissolve the material in a lubricating oil fraction to provide a concentrate containing say from about 30 to 85 wt. percent of salt. This makes for convenience in blending operations.

When the additives of the invention are employed as lubricating oil additives they can be added to any conventional type of lubricating oil including animal and vegetable oils as well as mineral oils. The mineral lubricating oils may be of any preferred type including those derived from paraffinic, naphthenic, asphaltic, or mixed base mineral crude oils by suitable refining methods. Synthetic hydrocarbon lubricating oils may also be employed. Other synthetic oils include those of the ester type such as di-2-ethylhexyl sebacate, carbonate esters, phosphate esters, glycol esters such as C₁₃ oxo acid diesters of tetraethylene glycol, and complex esters as for example the complex ester formed by the reaction of 1 mole of sebacic acid with 2 moles of tetraethylene glycol and 2 moles of 2-ethylhexanoic acid, as well as polysilicones, halogenated hydrocarbons, etc.

The lubricating oil compositions may contain from 0.03 to 5 wt. percent or more, generally in the range of from about 0.1 to about 3 wt. percent of the metal organo dithiophosphate. The concentration will vary in accordance with the particular metal salt used, the particular base stock employed and the function of the additive; i.e., whether it is to be simply an antioxidant or whether it

is also to serve as a wear reducing or extreme pressure agent. The lubricating oil composition may of course contain other additives including viscosity index improvers, pour-point depressants, extreme pressure agents, antioxidants, antifoamants, and detergents. The additives may also be employed in a concentration of 0.02 to 2 wt. percent in petroleum middle distillate fuels, including jet fuels, diesel fuels, and heating oils, as corrosion inhibitors and wear reducing agents.

It will be understood that the scope of this invention is not to be limited to the particular examples herein presented but is to be determined by the claims appended hereto.

What is claimed is:

1. A process for preparing a metal salt of an organo dithiophosphoric acid which comprises the steps of preparing a slurry of at least one organic hydroxy compound having in the range of from about 1 to 30 carbon atoms with at least one metal in powdered form, said metal being selected from the metals above hydrogen in the electromotive series, the quantity of metal in said slurry being at least 90 percent of the amount of metal theoretically required to convert the organo hydroxy compound to a metal diorganodithiophosphate, and thereafter reacting said slurry with an amount of P₂S₅ sufficient to convert said hydroxy compound to a dithiophosphoric acid, no water being present during the aforesaid preparation.

2. Process as defined by claim 1 wherein said metal powder is at least as fine as 200 mesh.

3. Process as defined by claim 1 wherein said reaction is conducted by gradual addition of the P₂S₅ to the slurry of metal and organic hydroxy compound over a period of time.

4. Process as defined by claim 1 wherein said reaction is conducted in the presence of an inert solvent in the amount of from 10 to 50 weight percent based on the reaction mixture.

5. Process as defined by claim 1 wherein said organo hydroxy compound comprises at least one aliphatic alcohol having in the range of from 1 to 20 carbon atoms.

6. Process as defined by claim 1 wherein said metal is zinc.

7. Process as defined by claim 1 wherein said metal is tin.

8. Process as defined by claim 1 wherein said metal is molybdenum.

9. Process for preparing a zinc salt of a dialkyl dithiophosphoric acid which comprises the steps of preparing a slurry of zinc powder and at least one aliphatic alcohol of from 1 to 20 carbon atoms, heating said slurry to a temperature in the range of 115° to 200° F., adding to said slurry over a period of from 1 to 6 hours a quantity of P₂S₅ in the proportion of 1 mole of P₂S₅ for 4 moles of alcohol and thereafter continuing the reaction at a temperature in the range of 130° to 160° F. until all of the P₂S₅ has reacted, the quantity of zinc in said slurry being at least 90 weight percent of the amount of zinc theoretically required to convert the dialkyl dithiophosphoric acids to their zinc salts, no water being present during the aforesaid preparation.

10. Process as defined by claim 9 wherein the amount of zinc present is in the range of from about 5 to 10 weight percent in excess of the amount theoretically required to convert the dialkyl dithiophosphoric acids to their zinc salts.

11. Process as defined by claim 9 wherein said reaction is conducted in the presence of a mineral lubricating oil in the amount of from 10 to 50 weight percent based on the reaction mixture.

12. Process as defined by claim 9 wherein subsequent to the addition of P₂S₅ the reaction temperature is increased to 180° to 190° F. until the reaction has been completed as evidenced by the cessation of gas evolution.

(References on following page)

References Cited

UNITED STATES PATENTS

2,540,084	2/1951	Asseff -----	260—429
2,838,555	6/1958	Goldsmith -----	260—429.9
3,102,096	8/1963	Nygaard et al. -----	252—32.7
3,234,250	2/1966	Schneider et al. -----	260—429.9
3,290,347	12/1966	Miller -----	260—429.9

OTHER REFERENCES

Brewster, Organic Chemistry, Prentice-Hall Inc., New York, New York, (1948) pp. 184 and 186.

5 TOBIAS E. LEVOW, *Primary Examiner*.

A. P. DEMERS, *Assistant Examiner*.