

1

3,290,347

PREPARATION OF POLYVALENT METAL SALTS OF DIORGANO DITHIOPHOSPHORIC ACIDS

Harold N. Miller, Plainfield, N.J., assignor to Esso Research and Engineering Company, a corporation of Delaware

No Drawing. Filed Feb. 28, 1963, Ser. No. 261,816

9 Claims. (Cl. 260-429.9)

The present invention is concerned with improvements in the preparation of oil-soluble polyvalent metal salts of diorgano dithiophosphoric acids. The invention is particularly directed to the preparation of such salts for use as additives for lubricating oil compositions.

Polyvalent metal salts of diorgano dithiophosphoric acid wherein the organo groups contain in the range of from about 1 to about 30 carbon atoms are well known in the art as additives for lubricating oil compositions. Metal salts of this type, and especially the zinc salts, are particularly useful as antiwear and antioxidant additives for lubricating oils that are intended for use in the crankcases of internal combustion engines. The nickel salts have been similarly employed, as have those of cadmium and lead. In addition, other polyvalent metal salts of these acids, particularly the salts of calcium, barium, and magnesium, are applicable in automotive oils, industrial oils, marine turbine oils, hydraulic oils, and the like, functioning in many instances as detergents and dispersants, as well as antioxidants, extreme pressure agents and antiwear additives.

It is common practice to prepare dialkyl dithiophosphoric acids by reaction of aliphatic alcohols with phosphorus pentasulfide. The metal salts are then obtained by neutralizing the acids with an oxide, hydroxide, or carbonate of the desired polyvalent metal, or alternatively, with a reactive polyvalent metal salt.

Related diorgano dithiophosphoric acids may be prepared by reacting alkyl phenols, aryl-substituted alcohols, naphthenyl alcohols, cycloaliphatic alcohols and the like with P_2S_5 , and the resulting acids may be converted to their metal salts in much the same manner as with the dialkyl dithiophosphoric acids.

In the prior art, certain disadvantages have been encountered in preparing polyvalent metal diorgano dithiophosphates, particularly when neutralizing the dithiophosphoric acids with metal oxides. For example, 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. In the case of zinc oxide neutralization of dialkyl dithiophosphoric acids, for example, it has been necessary to employ from 5 to 20% excess zinc oxide and this in turn increases the time required for the final filtration step to remove the excess zinc oxide.

In accordance with the present invention, it has been found that the neutralization of diorgano dithiophosphoric acids with metal oxides, hydroxides, or carbonates, and particularly with metal oxides, can be accelerated by adding to the reaction mixture a catalytic amount, i.e., from about 1 to about 10 wt. percent, based on the weight of organo dithiophosphoric acid, of a water-soluble fatty acid or a water-soluble metal salt of a fatty acid of from 1 to 5 carbon atoms. The acid used must be a weaker acid than the dialkyl dithiophosphoric acid being neutralized. The lower fatty acids of from 1 to 5 carbon atoms include formic, acetic, propionic, butyric, pentanoic, trimethyl acetic, etc. The metal salts of those acids that may be used include those of calcium, barium, lead, cadmium, copper, zinc, aluminum and magnesium.

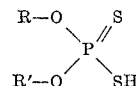
The improvements obtained in the practice of this in-

2

vention are particularly noteworthy in the preparation of zinc salts by neutralizing dialkyl dithiophosphoric acids wherein the alkyl groups have from 3 to 10 carbon atoms, using zinc oxide as the neutralizing agent. The principles of the invention are applicable also, however, to the preparation of other metal salts of such acids as well as of other diorgano dithiophosphoric acids. Salts of such metals as calcium, barium, cadmium, lead, copper, nickel, chromium, aluminum and magnesium are included. The advantages of the invention are that metal oxide, hydroxide or carbonate consumption is reduced and neutralization time is shortened, thus resulting in economies in manufacture. These economies are realized without impairing the quality of these products.

The principles of the invention are likewise applicable to other diorgano dithiophosphoric acids in addition to the dialkyl dithiophosphoric acids. The organo groups may be alkyl groups, aryl groups, cycloaliphatic groups, aralkyl groups, alkaryl groups, and mixtures of such groups, derived from substituted or unsubstituted aliphatic alcohols, cycloaliphatic hydroxy compounds, or phenolic compounds.

The diorgano dithiophosphoric acids that are useful in the process of the present invention may be characterized by the following general formula:



wherein R and R' may be the same or different organo groups having from 1 to 30 carbon atoms.

In preparing the diorgano dithiophosphoric acid, normally about 4 moles of hydroxy compound (alcohol, alkyl phenol, etc.) or a mixture of such compounds, is reacted with 1 mole of phosphorus pentasulfide. The hydroxy compounds should be essentially free of water. Reaction temperatures are normally in the range of from about 50° to about 300° F., and reaction times may range from about 1 to about 6 hours. One convenient method for determining the end point of the reaction is to measure the specific gravity of the reaction product. This will of course vary with the reaction temperature and other factors but can be determined beforehand for any particular reaction system.

For example, mixed dialkyl dithiophosphoric acids can be prepared by reacting 35 wt. percent of primary amyl alcohols and 65 wt. percent of isobutyl alcohol with phosphorus pentasulfide, using a mole ratio of alcohol to P_2S_5 of 4 to 1. The reaction is conducted at about 170° F. for a period of from 3 to 4 hours until a specific gravity of about 1.04 to 1.05 is attained, measured at 78° F. The end point of the reaction can also be determined by noting when the evolution of H_2S has ceased. As soon as the end point has been reached, the reaction product is then cooled to a temperature below 100° F., preferably while being stripped with an inert gas such as nitrogen to remove traces of H_2S . The product is then filtered.

Among the aliphatic alcohols that may be employed in preparing diorgano dithiophosphoric acids for use in this invention are included not only the simple alcohols such as isopropyl, normal butyl, isobutyl, methyl isobutyl carbonyl, n-decyl, and so on, but also mixed alcohols such as C_5 , C_8 , or C_{13} oxo alcohols obtained by reaction of olefins with carbon monoxide and hydrogen and subsequent hydrogenation of the resultant aldehydes, and those obtained by the hydrogenation of natural fats and oils. For example, mixed alcohols in the C_8 - C_{18} range, and consisting chiefly of lauryl alcohol, can be obtained by hydrogenating coconut oil, and are sold under the trade name "Lorol." Mixed C_{12} - C_{20} alcohols, consisting principally of C_{16} and C_{18} alcohols can be ob-

3

tained from tallow by hydrogenation and/or by sodium reduction. Primary alcohols of 22 carbon atoms or more can be obtained by the hydrolysis of Ziegler-type ethylene polymers and are available commercially from Continental Oil Co. under the name of Alfol alcohols. All of these higher alcohols can be used for dialkyl dithiophosphate manufacture.

Organo dithiophosphoric acids for use in the invention may also be prepared from cycloaliphatic alcohols such as methylcyclohexanol, ethyl-cyclopentanol, cyclohexanol, methylcycloheptanol, 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 ethyl esters of naphthenic acids.

Representative aryl, alkaryl and aralkyl hydroxy compounds useful in preparing organo dithiophosphoric acids for the present invention include phenol, cresol, naphthol, amyl phenol, tert. octyl phenol, benzyl alcohol and phenyl butanol.

The diorgano phosphates of the invention include not only those derived from single hydroxy organic compounds but also mixed diorgano dithiophosphates. The latter can be prepared either by reacting each organo hydroxy compound separately with P_2S_5 and then mixing the resulting acids for the neutralization step or by reacting mixtures of the organo hydroxy compounds with P_2S_5 so that at least a portion of the product will have

4

degree of neutralization. In accordance with the present invention, essentially no excess metal oxide is required, provided as stated a catalytic quantity of a weak acid or a salt of a weak acid is present in the reaction mixture.

Specific examples of the invention are presented below.

Example 1

Mixed dialkyl dithiophosphoric acids were prepared by reacting a mixture of 35 wt. percent of primary amyl alcohols and 65 wt. percent of isobutyl alcohol with phosphorous pentasulfide in a mole ratio of alcohols to P_2S_5 of 4 to 1. The reaction was conducted at about 170° F. for 2.5 to 3 hours until a specific gravity of about 1.04 to 1.05 was attained, measured at 78° F. The reaction product was then stripped of hydrogen sulfide by means of a nitrogen stream, and the product was cooled to 90° F. and filtered.

Example 2

Two reactions were conducted simultaneously in which the mixed dialkyl dithiophosphoric acids of Example 1 were neutralized with zinc oxide. In one of the neutralizations a catalytic amount of zinc acetate was present. In each case one mole of the mixed dialkyl dithiophosphoric acids was reacted initially with 0.5 mole of zinc oxide. In the catalyzed reaction, 0.046 mole of zinc acetate was added. The progress of each reaction in comparison with the other is outlined in Table I.

TABLE I

Time Elapsed, Hr.:Min.	Non-Catalyzed Reaction		Catalyzed Reaction	
	pH Reading	Remarks	pH Reading	Remarks
Start.....		Zn O addn. Begun, initial temp. 80° F.		Zn O addn. Begun, initial temp. 80° F.
0:25.....		Zn O addn. Completed, max. temp. 146° F.		Zn O addn. Completed, max. temp. 156° F. (Note A).
0:30.....	4.85	Very Hazy (solid Zn O).....	5.85	Slightly Hazy (Target pH=5.80).
1:00.....	5.55	Extremely Hazy.....	5.94	Slightly Hazy (essentially all Zn O reacted).
1:27.....		Began heating reaction mixture.....		Began heating reaction mixture.
1:35.....		Temp. 160° F.		Temp. 160° F.
2:05.....	5.79	Still very hazy (Note B).....	6.10	Slightly Hazy.
2:30.....	5.68		5.87	Slightly Hazy—haze due to H ₂ O.
3:15.....	5.65	Hazy-clear.....	5.88	Clear.
4:15.....	5.71	Hazy-clear.....	5.91	Do.
4:30.....		Added 4.1 g. Zn O (5% excess).....		Added 0.8 g. Zn O (0.1% excess).
4:32.....	6.14	Very Hazy (Zn O).....	5.99	Very Clear.
6:15.....		Heat off—filtered.....		Heat off—filtered.

NOTE A: Reaction was much faster, product much lighter in color, and rate of heat evolution greater than in non-catalyzed reaction.

NOTE B: Could not see through toluene, isopropanol, water solution of reaction product (1 gram in 25-35 ml).

molecules in which two different organo groups will be present. For example, mixed diorgano dithiophosphates may be prepared from p-tert. amyl phenol and C_8 oxo alcohols; from a mixture of mixed amyl alcohols and technical lauryl alcohol (e.g. Lorol); from isopropyl alcohol and C_{13} oxo alcohols; from isobutyl alcohol and mixed primary amyl alcohols; from methylcyclohexanol and tert. octyl phenol; or from a mixture of isopropyl alcohol, methylisobutyl carbinol and C_5 oxo alcohols.

To convert the organo dithiophosphoric acids to their metal salts, a metal oxide, hydroxide or carbonate such as ZnO, BaO, $Ba(OH)_2 \cdot 5H_2O$, $CaCO_3$, $Ca(OH)_2$, $PbCO_3$, etc. is added to the dithiophosphoric acids until it is determined that the proper neutralization has been effected, as for example by measuring the pH of the product. Then a diluent oil may be added to produce a concentrate of the metal salts which may be later blended in the proper concentration in a finished lubricating oil composition. After the diluent oil has been added the salts may be stabilized by heating for a period of time, and then the concentrate may be filtered and dried by stripping with an inert gas.

Ideally, the amount of metal oxide or its equivalent that is needed to obtain proper neutralization of the diorgano dithiophosphoric acids approximates a stoichiometric quantity. However, in actual practice in the past it has been necessary to employ an excess. For example, in the case of zinc salt preparation 5 or more weight percent excess zinc oxide has been needed to obtain the desired

It will be seen from the notations in Table I that the reaction is catalyzed by the use of the zinc acetate, that is, the reaction has been brought to completion more quickly. Furthermore, no excess zinc oxide was needed to bring the catalyzed reaction to completion, whereas 5% excess zinc oxide was employed in the non-catalyzed reaction and the product was still hazy before filtering. The addition of the 1% excess zinc oxide in the catalyzed reaction was not necessary to the process, since the target pH of 5.8 had already been reached; it was added merely to note what effect it would have, if any, on the catalyzed reaction as compared to the non-catalyzed reaction.

Example 3

The wear-prevention properties of each of the zinc salts prepared in Example 2 were compared in the well-known Shell 4-Ball Wear Test. For this test, 0.9 wt. percent of each of the products was dissolved in separate portions of a solvent neutral mineral oil having 100 SUS viscosity at 100° F. The test was conducted as follows. The test lubricant is placed in the cup of the machine and heated to 100° C. The test cup contains three steel balls which are fixed in position by a screw cap. A fourth steel ball, held in a chuck, is pressed against the lower three balls with a force of 20 kg. and is rotated at 1200 r.p.m. for a period of ½ hour. At the end of the test, the amount of wear is determined by measuring the diameter of the wear scar on each of these balls and averaging the results. The results obtained in the wear test are shown in Table II.

5
TABLE II

Test oil:	Wear scar diameter, mm.
Base oil -----	0.60
Base oil +0.9% non-catalyzed product -----	0.27
Base oil +0.9% catalyzed product -----	0.27

It will be seen from the above data that the material prepared in the catalyzed reaction was equivalent to the non-catalyzed product in its wear-reducing properties.

Example 4

Mixed dialkyl dithiophosphoric acids are prepared by reacting a mixture of 30 wt. percent of isopropyl alcohol and 70 wt. percent of methyl isobutyl carbinol with P_2S_5 for 2 hours at 185–195° F. using a ratio of 4 moles of mixed alcohols to 1 mole of P_2S_5 . The product is cooled to about 100° F. and filtered. After 4 wt. percent of acetic acid is added to the mixed dialkyl dithiophosphoric acids they are neutralized with zinc oxide at about 180° F. Only a slight excess of zinc oxide over the theoretical is required, as contrasted with about 15 wt. percent excess in the absence of the acetic acid.

Example 5

A mixture of 500 grams of dodecyl phenol and 106 grams of P_2S_5 is heated with stirring at 295–300° F. until essentially all of the P_2S_5 has disappeared and H_2S evolution has ceased, requiring about 2.5 to 3 hours of reaction time. The product obtained, when cooled, is a solid.

A solution is prepared by adding 200 grams of the di(dodecyl phenyl)dithiophosphoric acid thus obtained to a mixture of 600 grams of light mineral oil and 200 grams of benzene, with warming and stirring. Then 10 grams of propionic acid is added, followed by 26 grams of BaO. The mixture is then heated gradually to about 250° F., water of reaction and benzene being thus distilled overhead. It is found that the reaction is more rapid and less BaO is required for neutralization than when the propionic acid is not employed in the reaction mixture.

The product upon cooling may be filtered, employing additional benzene as a diluent if desired to aid in filtration, and removing benzene from the filtrate by distillation. The concentrate may be blended in a lubricating oil composition to furnish, for example, 0.1 to 5 wt. percent of the barium salt in the finished lubricant.

It is to be understood that the examples herein presented are for the purpose of illustrating the invention and that the invention is not to be limited thereto. The scope of the invention is to be determined by the appended claims.

What is claimed is:

1. In the preparation of a polyvalent metal salt of a diorgano dithiophosphoric acid wherein the organo groups contain from 1 to 30 carbon atoms and wherein the diorgano dithiophosphoric acid is neutralized with a com-

pound selected from the group consisting of the oxides, hydroxides and carbonates of calcium, barium, cadmium, lead, zinc, copper, nickel, chromium, aluminum and magnesium, the improvement, whereby the time required for neutralization is reduced and the need for an excess of neutralizing compound is eliminated, which comprises conducting the neutralization in the presence of 1 to 10 wt. percent, based on the weight of diorgano dithiophosphoric acid, of a material selected from the class consisting of water-soluble carboxylic acids of from 1 to 5 carbon atoms and the water-soluble metal salts of said carboxylic acids, said carboxylic acid salt in each instance being of the same metal as the metal of said compound.

2. Improvement as defined by claim 1 wherein said diorgano dithiophosphoric acid is derived from an aliphatic alcohol.

3. Improvement as defined by claim 1 wherein said diorgano dithiophosphoric acid is derived from a phenolic compound.

4. Improvement as defined by claim 1 wherein said organo dithiophosphoric acid contains mixed organo radicals.

5. In a process for preparing the zinc salt of a dialkyl dithiophosphoric acid derived from an aliphatic alcohol of 1 to 30 carbon atoms by treatment with P_2S_5 wherein said dialkyl dithiophosphoric acid is neutralized by reaction with zinc oxide at a temperature in the range of 50 to 300° F., the improvement which comprises conducting said neutralization in the presence of from 1 to 10 wt. percent, based on the weight of said dialkyl dithiophosphoric acid, of a catalytic material selected from the class consisting of water-soluble carboxylic acids of from 1 to 5 carbon atoms and water-soluble zinc salts of said salt carboxylic acids, whereby the time required for neutralization is reduced and the need for an excess of zinc oxide for neutralization is eliminated.

6. Process as defined by claim 5 wherein said catalytic material is zinc acetate.

7. Process as defined by claim 5 wherein said dialkyl dithiophosphoric acid is derived from the reaction of a mixture of primary amyl alcohol and isobutyl alcohol.

8. Process as defined by claim 5 wherein said dialkyl dithiophosphoric acid is derived from a mixture of methyl isobutyl carbinol and isopropyl alcohol.

9. Process as defined by claim 5 wherein said catalytic material is acetic acid.

References Cited by the Examiner

UNITED STATES PATENTS

2,790,767	4/1957	Giammaria	260—987 X
3,008,900	11/1961	May et al.	260—429.9
3,102,096	8/1963	Nygaard et al.	260—429.9

55 TOBIAS E. LEVOW, *Primary Examiner*.

E. C. BARTLETT, H. M. S. SNEED,
Assistant Examiners.