United States Patent

Horodysky

[15] **3,691,220**

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[54] **PROCESS FOR PREPARING OVERBASED ZINC PHOSPHORODITHIOATES**

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Related U.S. Application Data

[63] Continuation-in-part of Ser. No. 4,399, Jan. 20, 1970, abandoned.

[52] **U.S. Cl.** **260/429.9**
[51] **Int. Cl.** **C07f 3/06**
[58] **Field of Search** 260/429.9

[56] **References Cited**

UNITED STATES PATENTS

2,794,780	6/1957	Wystrach et al.	260/429.9 X
3,400,106	9/1968	Morita	260/429.9 X

FOREIGN PATENTS OR APPLICATIONS

823,235	11/1959	Great Britain	260/429.9
874,747	8/1961	Great Britain	260/429.9

OTHER PUBLICATIONS

Bacon et al., J. Org. Chem., Vol. 27, pp. 1,484– 1,485 (1962).

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[57] **ABSTRACT**

Overbased zinc diorganophosphorodithioates are prepared from a diorganophosphorodithioic acid and basic zinc compound in the presence of isopropyl alcohol. The reaction products obtained are used as additives for lubricating oils to impart useful properties thereto.

8 Claims, No Drawings

PROCESS FOR PREPARING OVERBASED ZINC PHOSPHORODITHIOATES

CROSS-REFERENCE TO RELATED APPLICATIONS

This application is a continuation-in-part of U.S. Pat. application Ser. No. 4,399, filed Jan. 20, 1970, now abandoned.

BACKGROUND OF THE INVENTION

1. Field of the Invention

The invention relates to a method for preparing overbased zinc diorganophosphorodithioates. More particularly, it relates to the preparation of such compounds by reacting a diorganophosphorodithioic acid with a basic zinc compound in the presence of isopropyl alcohol and no more than about 2 percent by weight of water present at the start of the reaction.

2. Summary of the Prior Art

Overbased zinc salts of phosphorus acids, such as diorganophosphorodithioic acids, are known additives for lubricants, greases and the like, and considerable effort has been devoted to their preparation. One of the most vexing problems associated with preparing these overbased salts has been the slow filtration rate of the product when made in the heretofore conventionally employed water-slurry medium. The method of the present invention overcomes this problem and provides at the same time a zinc phosphorodithioate of desirable high Zn/P ratio.

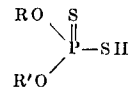
Another problem in producing overbased zinc salts of phosphorus acids has been one of obtaining a useful product in the absence of catalysts. Thus, U.S. Pat. No. 3,347,790 teaches that such salts may be prepared in the presence of catalysts such as metal carboxylates. It will become evident from the description of the present invention that high Zn/P ratios are obtained in the absence of any such catalysts.

It is known to prepare zinc salts of phosphorodithioic acids in hydrocarbon slurry media, such as in xylene, benzene or a mineral oil. U.S. Pat. No. 3,347,790 discloses the preparation of such salts in these solvents. For example, it is disclosed in this reference that Zn/P ratios of about 1.3 are obtained in overbased or "basic" phosphorodithioates when benzene is used. However, as will be disclosed hereinafter, the benzene-produced product is an extremely slow filtering one. A further reference disclosing the use of a benzene slurry medium to produce zinc phosphorodithioates is British Pat. No. 876,505.

It is also known that the yield of product in the reaction of dialkyl phosphorodithioic acid and zinc oxide is increased by carrying out the reaction in a mixture of alcohol and water. U.S. Pat. No. 3,400,106 discloses that methyl, ethyl and isopropyl alcohols are operative in this regard. However, as will appear hereinafter, this reference contains no suggestion of the unobvious advantages of the process of this invention.

SUMMARY OF THE INVENTION

In accordance with this invention, there is provided a method for producing an overbased zinc diorganophosphorodithioate having good filtering qualities which comprises the step of reacting a diorganophosphorodithioic acid of the formula



wherein R and R′ may be the same or different and are selected from the group consisting of alkyl, cycloalkyl, aryl, alkaryl and aralkyl radicals, the radicals having from about three to about 30 carbon atoms, with a basic zinc compound in the presence of isopropyl alcohol and no more than about 2 percent by weight of water present at the start of the reaction.

The products are useful as additives for lubricants, as taught in U.S. Pat. No. 3,347,790.

DESCRIPTION OF SPECIFIC EMBODIMENTS

The R and R′ groups specified for the above diorganophosphorodithioic acids may be exemplified by n-propyl, iso-propyl, n-butyl, iso-butyl, amyl, hexyl, decyl, dodecyl, octadecyl, eicosyl, pentacosyl, benzyl, phenethyl, cyclohexyl, phenyl, naphthyl, tolyl, t-amylphenyl, didodecylphenyl, wax phenyl, where the wax portion contains about 24 carbon atoms, and the like. It is also contemplated that neoalkyl radicals, such as 2,2-dimethyl-1-propyl, 2,2,4-trimethyl-1-butyl, 2,2-dimethyl-1-decyl and 2,2,4-trimethyl-1-hexadecyl, may be used.

Illustrative of the acids which can be used and in which R and R′ are the same are the dipropyl, dibutyl, dihexyl, didodecyl, dioctadecyl, dicyclohexyl, dibenzyl, diphenethyl, diphenyl, ditolyl, didodecylphenyl, diwaxphenyl, di(2,2-dimethyl-1-propyl), di(2,2,4-trimethyl-1-butyl), di(2,2-dimethyl-1-decyl) and di(2,2,4-trimethyl-1-hexadecyl) phosphorodithioic acids.

Useful acids wherein R and R′ are different are illustrated by the following: n-propyl amyl, amyl decyl, hexyl dodecyl, decyl cyclohexyl, benzyl phenyl and the like phosphorodithioic acids.

For the purposes of this invention, the basic zinc compounds include zinc oxide, zinc hydroxide, zinc carbonate and the like.

As has already been mentioned, the products produced in the process of this invention are the basic zinc diorganophosphorodithioates. The term "basic zinc diorganophosphorodithioates" or equivalent expressions, is used herein to describe those zinc salts wherein the metal substituent is present in stoichiometrically greater amounts than the phosphorus acid radical. For instance, "normal" or "neutral" zinc phosphorodithioate has two equivalents (i.e., 1 mole) of zinc per two equivalents (i.e., 2 moles) of a phosphorodithioic acid, whereas a "basic zinc diorganophosphorodithioate" has more than two equivalents of zinc per two equivalents of the phosphorodithioic acid.

The amount of basic zinc compound required to give the desired overbasing is not critical. The essential factor is that there be present in the reaction mixture sufficient zinc compound for the overbasing reaction. Although it is not absolutely essential, it has been found that the reaction proceeds in a more satisfactory way if a slight excess of zinc compound over the amount required for reaction is used. This excess should be kept at a minimum level to the necessity for removing large amounts of solid from the final product. As a

general statement, the excess of zinc compound should not exceed 10–15 percent by weight.

In carrying out the method of this invention, general conditions known to be suitable for the reaction of a phosphorodithioic acid with a basic zinc compound may be used. Such conditions usually include a temperature of from about 25° C. up to the boiling point of the alcohol used, i.e., from about 25° C. to about 83° C.

The order of mixing the acid and basic zinc is not critical. The reaction can be effected simply by mixing the phosphorodithioic acid and the zinc compound prior to heating, or by any other convenient method. Preferably, however, the reaction is carried out by adding the acid to a slurry of zinc compound in the alcohol.

It has been found that minor amounts of water present in the system at the start of the reaction can be tolerated in the method of this invention. Therefore, the product and the mechanics of its handling are relatively unaffected by water which is sometimes present in solvents obtained from certain sources. The amount of such water, nonetheless, should not exceed about 2 percent by weight of the total system. Amounts of water exceeding this should be avoided since water may affect the clarity of the product and gives rise to a difficult filtration problem.

The amount of alcohol by weight of the total system can vary between about 10 percent and 80 percent. While the isopropyl alcohol may be used at a concentration within this wide range, the preferred amount is within the range of from about 20 percent to about 50 percent, the more preferred amount being from about 20 percent to about 40 percent.

Having described the invention in general terms, the following will specifically illustrate it. The Examples are only for the purpose of illustration and are not to be construed as limiting the inventive scope. Parts are by weight.

EXAMPLE 1

One hundred parts of isopropyl 2-ethylhexyl phosphorodithioic acid (prepared by reacting equimolar portions of isopropyl and 2-ethylhexyl alcohols with phosphorus pentasulfide) was added to a slurry of 17 parts of zinc oxide in 30 parts of isopropyl alcohol at 70°–75° C. over a period of 2 hours. Thereafter, the reaction mixture was stirred for an additional 5 hours at this temperature.

During subsequent filtration through diatomaceous earth at 45° C., the first drop of filtrate was observed after 0.2 minute. Five minutes was required to obtain 50 cc of filtrate, which was clear. The product, 92 parts, after removal of isopropyl alcohol and water of neutralization, had the following properties:

Zinc	11.8%
Phosphorus	9.3%
Sulfur	18.8%
Zn/P ratio	1.27 (1.06 = neutral)
Overbasing	20%

The following table shows additional examples and comparative examples prepared as in Example 1. The same acid as used in Example 1 was used.

TABLE I

REACTION	Comparative ex. 2	ex. 3	ex. 4	ex. 5	Examples ex. 6	ex. 7
Acid, parts	100	100	100	100	100	100
ZnO, parts	18	16	17	17	16	17
Isopropyl alcohol, parts	30	30	50	70	—	—
Methyl alcohol, parts	—	—	—	—	50	—
Ethyl alcohol, parts	—	—	—	—	—	30
Reaction Time, hrs.	2	2	2	2	2	2
Temperature, °C.	70–75	70–75	70–75	70–75	70–75	70–75
Digestion, hrs.	5	5	5.5	5.3	5	5
FILTRATION						
First Drop, min	0.1	0.1	0.1	0.1	1.5	2
50 cc, min.	5	5	3	3	15	40
Temperature, °C.	65	66	80	70	64	67
Yield, parts	94	97	97	99	99	101
Clarity	clear	clear	clear	clear	clear	
PRODUCT						
Zn, %	12.1	11.5	11.6	11.5	11.0	11.6
P, %	9.4	9.1	9.2	9.1	9.7	9.8
S, %	19.0	18.8	18.8	18.7	19.1	18.9
Zn/P	1.29	1.26	1.26	1.26	1.13	1.18
Overbasing, %	22	19	19	19	7	12

The following products prepared following the procedure of Example 1, illustrate the effect of the use of slurrying media other than isopropanol alcohol on the rate of filtration and extent of overbasing. The same acid was used as shown in Example 1.

TABLE II

REACTION	Ex. 8	Ex. 9	Ex. 10
Acid, parts	100	100	175
ZnO, parts	16	16	27.4
Benzene, parts	—	50	—
Water, parts	—	—	75
2-Ethylhexyl alcohol, parts	50	—	—
Reaction Time, hrs.	2	2	2
Temperature, °C.	70–75	70–75	50
Digestion, hrs.	5	5	5
FILTRATION			
First Drop, min.	5.5	3	Blockage
50 cc, min.	180	60	—
Temperature, °C.	85/70		80
PRODUCT			
Zn, %	10.5	10.5	10.7
P, %	9.5	10.0	10.3
S, %	18.4	19.3	17.5
Zn/P	1.11	1.05	1.04
Overbasing, %	5	0	0

The following products, made substantially as outlined in Example 1, illustrate the use of various amounts of water with isopropyl alcohol and methyl alcohol. The same acid was used.

TABLE III

REACTION	Ex. 11	Ex. 12	Ex. 13	Ex. 14
Acid, parts	100	100	100	100
ZnO, parts	17	15	17	17
Isopropyl alcohol, parts	50	50	30	19.2
Methyl alcohol, parts	—	—	—	—
Water, parts	1[1]	5[2]	35[3]	25[4]
Reaction Time,	2	2	2	0.1

hrs.				
Temperature, °C.	70–75	70–75	70–75	50
Digestion, hrs.	4	5	3	1
FILTRATION				
First Drop, min.	0.1	2	4	10
50 cc, min.	4	12	24(5cc)	200
Temperature, °C.	70	77	72	50
Clarity	clear	clear	clear	clear
PRODUCT				
Zn, %	11.3	11.0	11	10.7
P, %	9.2	9.6	9.4	9.4
S, %	18.9	18.6	17.8	18.2
Zn/P	1.23	1.15	1.17	1.14
Overbasing, %	17	10	10	10

(1) about 0.6% by weight of water
(2) about 2.9% by weight of water
(3) about 19.2% by weight of water
(4) about 15.5% by weight of water

It is evident from an inspection of Tables I–III that the process utilizing isopropanol substantially free of water gives a product having excellent filtering qualities. This is shown in Examples 1–5 of Table I. Water added in very small amounts has no appreciable effect on filtering. For instance, Example II (Table III) shows that 50 cc of product is obtained in 4 minutes when only 0.6 percent by weight of water is added. However, larger amounts of water do affect the filtering rate, as is shown, in one case, by Example 12 (Table III). This example illustrates a marked increase in the time required to obtain 50 cc of product as compared to any of Examples 1 (page 7), 2–5 (Table I) or 11 (Table III).

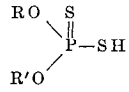
In addition, the tables teach the effect on the process of using even higher amounts of water with the isopropyl alcohol of this invention, or of employing the methyl alcohol-water system as taught in Example 1 (column 7) of U.S. Pat. No. 3,400,106. As may be seen from Example 13 (Table III), which was run in accordance with the process of this invention except that about 19.2 percent water by weight was used, after 24 minutes of observation only 5 cc of product had filtered. Example 14 of Table III is patterned after the U.S. Pat. No. 3,400,106 Example 1, and it shows that when a methyl alcohol-water system is used such that the water constitutes about 15.5 percent by weight of the whole reaction system, the product obtained requires more than 200 minutes to yield 50 cc in the filtrate.

With regard to the use of methanol or ethanol alone, Examples 6 and 7 of Table I show that the filtration time for the product made using either of them is excessively long, amounting to 15 minutes and 40 minutes, respectively, to obtain the usual 50 cc of material.

Although the present invention has been described with preferred embodiments, it is to be understood that modifications and variations may be resorted to, without departing from the spirit and scope of this invention, as those skilled in the art will readily understand. Such variations and modifications are considered to be within the purview and scope of the appended claims.

I claim:

1. A process for the production of overbased zinc diorganophosphorodithioates having good filtering qualities which comprises the step of reacting (1) a diorganophosphorodithioic acid of the formula



wherein R and R′ are individually selected from the group consisting of alkyl, cycloalkyl, aryl, alkaryl and aralkyl radicals, the radicals having from three to about 30 carbon atoms, with (2) a basic zinc compound in the presence of isopropyl alcohol and no more than about 2 percent by weight of water.

2. The process of claim 1 wherein R and R′ are selected from the group consisting of isopropyl and 2-ethylhexyl.

3. The process of claim 1 wherein one of R and R′ is isopropyl and the other is 2-ethylhexyl.

4. The process of claim 1 wherein the basic zinc compound is zinc oxide.

5. The process of claim 1 wherein the diorganophosphorodithioic acid is added to a slurry of the basic zinc compound in the isopropanol.

6. The process of claim 1 wherein the isopropyl alcohol comprises from about 10 percent to about 80 percent by weight of the system.

7. The process of claim 1 wherein one of R and R′ is isopropyl and the other is 2-ethylhexyl and the basic zinc compound is zinc oxide.

8. The process of claim 1 wherein the reaction is run at from about 25° C. to about 83° C.

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