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PREPARATION OF ZINC DIALKYL DITHIOPHOSPHATES

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This invention is concerned with an improved process for the preparation of polyvalent metal salts of dialkyl dithiophosphoric acids. The invention is particularly directed to the preparation of the zinc salts of such acids for use as wear-reducing and antioxidant additives for lubricating oil compositions.

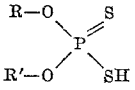
The metal salts of dialkyl dithiophosphoric acids wherein the alkyl groups contain in the range of from 1 to 20 carbon atoms, and more particularly those having from about 3 to about 10 carbon atoms, are well known in the art as additives for lubricating oil compositions. This class of metal salts is particularly useful as antiwear and antioxidant additives for lubricating oils that are suitable for use in internal combustion engines. The metal salts of the dialkyl dithiophosphoric acids are ordinarily prepared by reacting phosphorus pentasulfide with an alcohol or a mixture of alcohols containing the desired range of alkyl groups in a molar ratio of approximately 4 moles of alcohol for each mole of phosphorus pentasulfide to form the corresponding dialkyl dithiophosphoric acids. The acids are then normally neutralized, in accordance with prior art processes, with a polyvalent metal oxide or hydroxide or with a reactive polyvalent metal salt to form the metal dialkyl dithiophosphates.

In the processes of the prior art, certain disadvantages have been encountered. For example, utilization of the metal oxide or hydroxide to obtain the desired degree of acid neutralization has been very erratic, both as to the proportion of metal oxide or hydroxide required relative to the acid being neutralized and as to the batch cycle time required for neutralization. Another disadvantage is that the metal salts are often unstable as regards hydrogen sulfide evolution.

In accordance with the present invention, it has been found that the above disadvantages as well as others can be overcome if the neutralization step is conducted by adding the dialkyl dithiophosphoric acid that is to be neutralized, to a slurry of metal oxide or hydroxide in a quantity of metal salts of dialkyl dithiophosphoric acid that remains from a previous neutralization batch. The improvements are particularly noteworthy in the preparation of zinc salts by neutralizing dialkyl dithiophosphoric acids of from 3 to 10 carbon atoms per alkyl group, using zinc oxide as the neutralizing agent. The principles of the invention are also applicable, however, to the preparation of other metal salts of such acids, including such metals as calcium, barium, cadmium, lead, cooper, nickel, iron, aluminum and magnesium.

In addition to the advantages of reducing metal oxide consumption and shortening the cycle time by obtaining more rapid neutralization, the process of the present invention gives products that are more stable as regards hydrogen sulfide evolution than are the products of the processes of the prior art.

The dialkyl dithiophosphoric acids 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 alkyl

groups contaiinng from 1 to 20 and preferably from 3 to 10 carbon atoms per alkyl group.

In preparing the dialkyl dithiophosphoric acids, normally 4 moles of alcohol or alcohol mixture is reacted with 1 mole of phosphorus pentasulfide. Particularly desirable alcohol mixtures include a combination of isopropyl alcohol and methylisobutylcarbinol and a combination of primary amyl alcohol and isobutanol. It is preferred to employ in the reaction a P_2S_5 that has a phosphorus content in the range of 27.6 to 28.2 weight percent. The alcohols should be free of water. Reaction temperatures in the range of about 100 to 250° F. are employed and reaction times may vary in the range of from about 1 to 6 hours. A convenient method for controlling the end point of the reaction is to measure the specific gravity of the reaction product. The specific gravity will, of course, vary with the reaction temperature and with the excess alcohol content. The end point can also be determined by noting when the evolution of H_2S ceases. As soon as the end point has been reached, the reaction product is promptly cooled to below 100° F., preferably while being stripped with an inert gas such as nitrogen. The cooled product is then filtered.

In accordance with the present invention, the dialkyl dithiophosphoric acid prepared in the manner just described is converted to the desired metal salt by adding the dialkyl dithiophosphoric acid to a slurry of metal oxide in metal dialkyl dithiophosphate obtained in a previous preparation.

In general, the slurry will comprise about 10 parts by weight of metal oxide or hydroxide in from about 5 to 25 parts, or more, preferably from about 10 to 20 parts by weight of the metal dialkyl dithiophosphate. Where successive batches are of about the same size, a "heel" representing from about 10 to 30 percent of a reaction batch can be left in the reaction vessel to serve as the medium in which to slurry the metal oxide or hydroxide for the succeeding batch.

The dialkyl dithiophosphoric acid is added to the slurry in such proportion that no more than a slight excess of metal oxide or hydroxide is provided over the amount theoretically required to convert the acids to the salts; e.g. in the proportion of say 100 combining parts of the acid to 100–110 combining parts of the metal oxide or hydroxide.

The following examples illustrate the operation of this invention.

EXAMPLE 1

Mixed dialkyl dithiophosphoric acids are prepared by reacting 35 wt. percent of primary amyl alcohols and 65 wt. percent of isobutyl alcohol with P_2S_5 having in the range of from about 27.6 to 28.2% phosphorus, preferably about 28.0 wt. percent of phosphorus. A mole ratio of alcohol to P_2S_5 of 4:1 is employed. The reaction is conducted at about 170° F. for a period of about 3 to 4 hours until a specific gravity of about 1.04 to 1.05 is attained, measured at 78° F. The reaction product is then stripped of hydrogen sulfide by use of a nitrogen stream, the product being cooled to about 90 to 100° F. The product is then filtered.

EXAMPLE 2

The mixed dialkyl dithiophosphoric acids prepared as in Example 1 are converted to the zinc salts in the following manner.

To about 800 gallons of the zinc salts prepared from the mixed dialkyl dithiophosphoric acids of Example 1, representing a "heel" of such zinc salts amounting to about 25 to 30 percent of a previously prepared batch of the zinc salts, there is stirred in about 2,520 pounds of zinc oxide to make a slurry. Then, over a period of about 20

minutes, 1,690 gallons of mixed dialkyl dithiophosphoric acids prepared as in Example 1 is added. In these proportions, the zinc oxide present is about 104 percent of the theoretical amount for neutralization. The temperature rises spontaneously to 187° F. and the desired pH of 5.8 is reached within 30 minutes. The reaction mixture is then held at 165–175° F. for a two-hour soaking period, after which time the product is stripped with inert gas to remove any H_2S that may be present. About 25 to 30 percent of the product is retained as the dispersing medium for a zinc oxide slurry to prepare a successive similar batch of the zinc salts. The product analyzes 11.30 weight percent zinc, 10.43 weight percent phosphorus, and 19.96 weight percent sulfur. The Zn/P ratio is 1.04 and the Zn/S ratio is 0.57.

As compared with the prior art process of preparing zinc dialkyl dithiophosphates, i.e. wherein zinc oxides were added to the dialkyl dithiophosphoric acids to produce the zinc salts, the process of the present invention employing the slurry method has a major advantage in that it provides a quicker end point of neutralization as measured by the pH value and thus reduces the process cycle time. This is shown by the following examples. In order to insure that there will be essentially no evolution of H_2S from the product, it has been determined that a minimum pH value in the range of 5.65 to 5.8 should be reached in the neutralization step.

EXAMPLE 3

This example demonstrates the advantage of the slurry operation of the present invention as compared with the prior art method of adding zinc oxide to dialkyl dithiophosphoric acids.

(a) 300 grams of mixed dialkyl dithiophosphoric acids prepared as in Example 1 was heated to 160° F. Then 52.5 grams of zinc oxide was added in small portions to maintain the temperature at 155–165° F., this step taking 50 minutes. During this step, there was copious evolution of H_2S. After the zinc oxide addition had been completed, the mixture was maintained ("soaked") at 160° F. and periodic measurements of the pH were made. After 1 hour of "soaking," the pH was 4.9; and after 2 hours, it was 5.0. The target pH of 5.8 minimum was never reached.

(b) Then, 80 grams, representing a 22 weight percent "heel" from another batch of zinc dialkyl dithiophosphate which had been satisfactorily prepared from 300 grams of the dialkyl dithiophosphoric acids of Example 1 and 53 grams of zinc oxide, was mixed with 52 grams of zinc oxide to form a slurry. This mixture was heated to 160° F. and to it was added, all at one time, 300 grams of mixed dialkyl dithiophosphoric acids prepared as in Example 1. The reaction temperature was held at 160–165° F. and a pH of 5.9 was reached in 35 minutes. There was no evolution of H_2S during the neutralization.

Other important advantages of the present invention are that zinc oxide consumption is reduced and little or no excess zinc oxide over the theoretical amount is required to reach the proper end point. The process of the present invention also eliminates the critical relationship that exists between the zinc oxide addition rate and the neutralization temperature when the prior art process is employed wherein zinc oxide is added to the dialkyl dithiophosphoric acids. Thus, in the present invention, neutralization temperatures as high as 210° F. could be used, although there is normally no need to go that high, and temperatures of 150 to 190° F. are normally employed.

The reaction of zinc oxide with the dialkyl dithiophosphoric acids is exothermic, and the reaction temperature must be left reasonably low when employing the prior art procedure of adding the metal oxide to the acids; otherwise zinc oxide consumption is increased and greater difficulty is encountered in obtaining the desired pH end point of neutralization. This is demonstrated by the following example.

EXAMPLE 4

Separate runs were made in which 300 grams of dialkyl dithiophosphoric acids prepared as in Example 1, and 60 grams of light mineral oil were initially charged to a reactor. Then 47.5 grams of zinc oxide (98% of theoretical quantity for neutralization) was charged to the reactor at such a rate as to control the temperature within a preselected limit. Thereafter additional 5 gram increments of zinc oxide were added in each instance until the desired pH of 5.8 was reached. An initial reaction temperature of 60° F. and maximum temperatures of 130°, 160° and 190° F. were selected. The quantitiees of zinc oxide and the reaction times required to attain the desired pH in each instance are given in Table I.

Table I

Temperatures, ° F.		Zinc Oxide Consumption		Neutralization Time to 5.8 pH, Hours
Initial	Peak	Grams	Percent Theory	
60	130	57.5	120	3.3
60	160	67.5	140	6.9
60	190	72.5	150	7.2

In contrast to the temperature sensitivity of the prior are process, the slurry process of the present invention is essentially non-temperature-sensitive as shown by Example 5.

EXAMPLE 5

The preparation of Example 3(*b*) was essentially repeated except that a reaction temperature of 200° F. was employed. No H_2S evolution was noted, and a pH value of 5.75 was attained in 1.5 hours.

If the metal dialkyl 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 70 wt. percent of salt. This makes for convenience in blending operations.

The additives of the invention 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, glycol esters such as C_{13} 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.

The lubricating oil compositions will normally contain in the range of from about 0.1 to about 3 wt. percent of the metal dialkyl 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.

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 the zinc salts of mixed dialkyl dithiophosphoric acids derived from a mixture of primary amyl alcohol and isobutyl alcohol by treatment

with P_2S_5, which comprises the steps of preparing a slurry of zinc oxide in a previously prepared quantity of the said zinc salts, in the proportion of 10 parts of zinc oxide and from 5 to 25 parts by weight of the said zinc salt, adding said mixed dialkyl dithiophosphoric acids to the said slurry and effecting the reaction of said acids with said zinc oxide at a temperature in the range of 150° to 210° F.

2. A process for preparing a zinc salt of a dialkyl dithiophosphoric acid having alkyl groups in the range of from 3 to 10 carbon atoms, which comprises the steps of preparing a slurry of zinc oxide in a previously prepared

quantity of the said zinc salt, in the proportion of 10 parts of zinc oxide and from 5 to 25 parts by weight of the said zinc salt, adding to the slurry the said dialkyl dithiophosphoric acid in a quantity calculated to react with the zinc oxide, and completing the reaction.

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