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PHOSPHORODITHIOATE INHIBITORS

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This invention relates to a new composition of matter, and in more particular sense it relates to zinc salts of phosphorodithioic acids which contain certain alkyl or isoalkyl groups tending to enhance the physical and chemical properties of these salts.

Zinc salts of phosphorodithioic acids have long been known and their utility in many applications widely acknowledged. They are useful as inhibitors of oxidation and corrosion and as such may be employed to combat such deteriorating influences on metal, asphalt, motor oils, and the like. Their principal use has been as additives for use in crankcase lubricants in which they are known to act to prevent corrosion of the relatively moving surfaces. Their use for such purpose is well established and their usefulness in this capacity has increased with the development and refinement of the internal combustion engine.

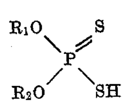
The performance of a particular lubricant in an engine is related directly to the design of a particular engine in which this performance is evaluated. A lubricant which performs well in one type of engine may perform very poorly in a different type of engine, and a very minor change in the design of a particular engine may be sufficient to pose an entirely new problem with respect to the lubrication of the new engine. The history of the development of lubricant additives therefore has been associated very closely with the development of the internal combustion engine.

Recent changes incorporated into internal combustion engines have pointed up a deficiency in the lubricant improving properties of zinc salts of phosphorodithioic acids which have been used heretofore. The somewhat higher operating temperatures of the newer engines have subjected the lubricant to correspondingly higher temperatures. Under these more severe conditions it has been observed that the zinc phosphorodithioate additive has shown a tendency to decompose so that the lubricant no longer affords protection to the moving metal surfaces from corrosion.

It is accordingly a principal object of this invention to provide novel compositions of matter.

Another object of the invention is the provision of compositions which are suitable for use in lubricants intended for use at high temperatures.

These and other objects of the invention are achieved by the zinc salts of a mixture of phosphorodithioic acids having the structure



in which R_1 and R_2 are the same or different primary aliphatic hydrocarbon radicals selected from the class consisting of lower molecular weight radicals having less than five carbon atoms and higher molecular weight radicals having at least five carbon atoms, the mole ratio of lower molecular weight radicals to higher molecular weight radicals in the zinc salt mixture being within the range of 1:1 to 3:1.

The above novel zinc salts, when used in lubricants, have been found to impart to the moving metal surfaces of the engine in which the lubricant is used a degree of protection from corrosion hitherto unrealized. Lubricants containing small proportions of the above novel zinc salts are enabled to withstand the higher operating temperatures of present-day engines to an extent not possible with previous lubricants.

The lower molecular weight primary aliphatic hydrocarbon radicals having less than 5 carbon atoms include principally isobutyl, n-butyl, and n-propyl, although ethyl and methyl likewise are suitable for use in these novel zinc salts. The higher molecular weight primary aliphatic hydrocarbon radicals having at least 5 carbon atoms include principally the primary amyl radicals, n-amyl, primary-isoamyl, 2-methyl-1-butyl and neopentyl. These primary amyl radicals are preferred because of their economy and also because of the particular utility of zinc salts which contain these primary amyl radicals as the higher molecular weight primary aliphatic hydrocarbon radicals. In any particular zinc phosphorodithioate the higher molecular weight primary aliphatic hydrocarbon radicals may be a mixture of such radicals each of which contains at least 5 carbon atoms. Thus such a mixture may consist of 40 molar percent of n-amyl and 60 molar percent of primary isooctyl radicals, it being understood of course that such a zinc phosphorodithioate composition would contain also a sufficient proportion of lower molecular weight primary aliphatic hydrocarbon radicals as to bring the ratio of lower molecular weight radicals to higher molecular weight radicals within the above-stated range of 1:1 to 3:1. A particularly preferred mixture of primary aliphatic hydrocarbon radicals having at least 5 carbon atoms is a mixture of n-amyl, primary-isoamyl and 2-methyl-1-butyl radicals. Zinc phosphorodithioates which contain this mixture of higher molecular weight aliphatic hydrocarbon radicals are especially valuable, both for reasons of economy and efficacy of use.

The zinc salts of this invention comprise mixtures of different salts as well as zinc salts prepared from mixtures of different phosphorodithioic acids and zinc salts of phosphorodithioic acids prepared from mixtures of alcohols. The mixtures of different zinc salts are prepared quite obviously by the separate preparation of the individual zinc phosphorodithioates and then mixing of these two different salts. Such mixtures of salts may be illustrated by the separate preparation of zinc di-n-hexyl phosphorodithioate and zinc di-n-propyl phosphorodithioate, followed by mixing of these two different salts in such proportions as to satisfy the mole ratio of n-propyl to n-hexyl radicals as stated before. The zinc salts of mixtures of different phosphorodithioic acids is illustrated by the separate preparations of diisobutyl phosphorodithioic acid and di-n-amyl phosphorodithioic acid, followed by neutralization of an appropriate mixture of these acids with zinc oxide. The zinc salts of mixed phosphorodithioic acids is illustrated by the reaction of phosphorus pentasulfide with an appropriate mixture of n-butyl alcohol and n-octyl alcohol to prepare the corresponding phosphorodithioic acid, followed by neutralization of this mixed acid with zinc oxide.

The particular method by which the zinc salts of this invention are prepared is not critical. Any of the above illustrated methods may be used. It is necessary only that the zinc salt contain the primary aliphatic hydrocarbon radicals described earlier in the ratio stated.

It will be noted that there are two principal aspects which characterize the novel zinc salts of this invention: the first of these is the fact that the aliphatic hydrocarbon radicals are primary; the second is that these radicals include both lower molecular weight and higher molecular weight radicals. The first of these characterizing features is thought to be responsible for the peculiar thermal stability of the zinc phosphorodithioates of this invention. It appears that the attachment of a —CH_2— group to the oxygen of the phosphorodithioate is more stable than the similar attachment of a

$$-\underset{|}{C}H- \text{ or } -\overset{|}{\underset{|}{C}}- \text{ group}$$

It appears furthermore that the difference in stability is sufficient to allow the zinc phosphorodithioates of this invention to perform satisfactory as corrosion inhibitors in environments in which the zinc phosphorodithioates of the prior art have been found wanting.

The second characterizing feature of the zinc phosphorodithioates described herein is the particular distribution of lower and higher molecular weight aliphatic hydrocarbon radicals within the zinc salt composition. There are two apparently conflicting requirements which should distinguish a corrosion inhibitor: It should be oil-soluble, but it must also be inexpensive. Oil-solubility may be had by the use of higher molecular weight hydrocarbon radicals. The sources of such higher molecular weight hydrocarbon radicals, however, are relatively expensive alcohols. The cheaper lower molecular weight alcohols provide lower molecular weight hydrocarbon radicals which do not contribute sufficient oil-solubility to a zinc phosphorodithioate molecule. It is now possible, however, to provide a satisfactorily oil-soluble zinc phosphorodithioate which can be prepared economically from inexpensive alcohols.

The methods by which these zinc salts may be prepared are illustrated by the following examples.

Example 1

To a mixture of 536 grams (6 moles) of mixed primary amyl alcohols (65% n-amyl, 3% isoamyl, and 32% 2-methyl-1-butyl) and 1332 grams (18 moles) of isobutyl alcohol there was added portionwise at 60–70° C. over a period of 4.5 hours 1332 grams (6 moles) of phosphorus pentasulfide. This mixture was heated for an additional 2 hours at 60–70° C. then filtered to yield a clear, fluid filtrate. To a suspension of 358 grams (4.4 moles) of zinc oxide in 1796 grams of mineral oil there was added over a 2.5-hour period at 75–77° C., 2080 grams (8 moles) of the above filtrate. The resulting mixture was freed of water and other volatile constituents by heating at 85–95° C./120 mm. The mixture was filtered to yield a clear filtrate having the following analyses:

Percent P—6.0
Percent S—13.0
Percent Zn—6.8

Example 2

A mixture of 1644 grams (6 moles) of di-isobutyl phosphorodithioic acid and 588 grams (2 moles) of a diamyl phosphorodithioic acid prepared by the reaction of phosphorus pentasulfide with a mixture (65% n-amyl, 3% isoamyl, and 32% 2-methyl-1-butyl) of amyl alcohols was prepared and added portionwise at 75–77° C. throughout a 2-hour period to a suspension of 358 grams (4.4 moles) of zinc oxide in 864 grams of mineral oil. The mixture was held at 75° C. for an additional hour, then heated to a final temperature of 85–95° C./120 mm. The residue was filtered to yield a clear filtrate having the following analyses:

Percent P—8.0
Percent S—16.8
Percent Zn—8.5

Example 3

The zinc salt of di-isobutyl phosphorodithioic acid was prepared by the reaction of isobutyl alcohol with phosphorus pentasulfide followed by neutralization of the resulting acid with zinc oxide. To 447 grams (0.36 mole) of the oil solution of this salt there was added 149 grams (0.12 mole) of a similarly prepared zinc salt of a phosphordithioic acid prepared by the reaction of phosphorus pentasulfide with the mixture of primary alcohols referred to in Example 1. This mixture was shown to have the following analysis:

Percent P—6.1

Example 4

To a mixture of 213 grams (2.4 moles) of mixed amyl alcohols (as in Example 1) and 176 grams (2.4 moles) of isobutyl alcohol there was added at 55–60° C. over a 2-hour period 264 grams (1.2 mole) of phosphorus pentasulfide. The resulting mixture was heated for an additional 1.5 hours at 60–65° C., then filtered to yield a clear liquid filtrate. The zinc salt of this acidic filtrate was prepared according to the procedure of Example 1. The resulting zinc phosphorodithioate showed the following analyses:

Percent P—5.7
Percent S—12.9
Percent Zn—6.2

Example 5

A mixture of 280 grams (1 mole) of the diamyl phosphorodithioic acid of Example 2 and 254 grams (1 mole) of the di-isobutyl phosphorodithioic acid of the same example was prepared and added portionwise over a 1.5-hour period to a suspension of 90 grams (1.1 moles) of zinc oxide in 508 grams of mineral oil at 75–77° C. This mixture was heated for an additional hour at 75° C. and then freed of water and other volatile constituents by heating to a final temperature of 85–95° C./120 mm. The residue was filtered to yield a clear filtrate having the following analyses:

Percent P—5.8
Percent S—11.9
Percent Zn—6.1

Example 6

A mixture of 447 grams (5.0 moles) of the mixed amyl alcohols of Example 1 and 370 grams (5.0 moles) of n-butyl alcohol was heated to 55° C. and then treated portionwise throughout a 1.75-hour period with 555 grams (2.5 moles) of phosphorus pentasulfide. The resulting mixture was heated for an additional hour at 60–65° C. then filtered to yield a clear filtrate. This filtrate was neutralized by the portionwise addition thereof to a suspension of an approximately equivalent amount of zinc oxide in mineral oil. The water formed by the neutralization was removed by distillation and the residue filtered to yield a clear filtrate having the following analyses:

Percent P—5.5
Percent S—12.2
Percent Zn—6.3

Example 7

A mixture of 280 grams (1 mole) of the diamyl phosphorodithioic acid of Example 2 and 257 grams (1 mole) of di-n-butyl phosphorodithioic acid was prepared and added portionwise throughout a period of 75 minutes to a suspension of 90 grams (1.1 moles) of zinc oxide in 505 grams of mineral oil at 75–77° C. The resulting mixture was heated for an additional hour at 75° C. then freed of water and other volatile constituents by heating to a final temperature of 95° C./120 mm. The residue was filtered to yield a clear filtrate having the following analyses:

Percent P—5.6
Percent S—11.8
Percent Zn—6.0

Example 8

A mixture of 962 grams (13 moles) of isobutyl alcohol and 624 grams (7 moles) of the amyl alcohol mixture of Example 1 was prepared and heated to 65° C. whereupon 1110 grams (5 moles) of phosphorus pentasulfide was added portionwise throughout a 3-hour period. This mixture was heated for an additional 3 hours at 69–71° C. then filtered. A 2224-gram portion of this filtrate (8.0 moles) was added portionwise throughout a 2.7-hour period to a suspension of 358 grams (4.4 moles) of zinc oxide in 622 grams of mineral oil at 75–77° C. The resulting mixture was heated for an additional hour at 75° C., then freed of water and other volatile constituents by heating to a final temperature of 78–95° C./120 mm. The residue was filtered to yield a clear filtrate having the following analyses:

Percent P—8.6
Percent S—17.9
Percent Zn—9.1

Each of the zinc salt compositions prepared as in the above examples was tested by heating at 250° F. for 8 hours. In each case the composition was perfectly clear after this test, indicating its thermal stability. Furthermore in every case there was little or no evolution of hydrogen sulfide during the test.

A 75/25 molar mixture of the zinc salts of di-isobutyl phosphorodithioic acid and di-n-hexyl phosphorodithioic acid, a 50/50 molar mixture of the zinc salts of the diamyl phosphorodithioic acid of Example 2 and di-n-butyl phosphorodithioic acid, a 50/50 molar mixture of the zinc salts of di-isobutyl phosphorodithioic acid and the diamyl phosphorodithioic acid of Example 2, and a 50/50 molar mixture of the zinc salts of di-isobutyl phosphorodithioic acid and di-n-hexyl phosphorodithioic acid all were prepared as in Example 3. Each of these salt mixtures likewise was found to possess a high degree of thermal stability as measured by the test of heating at 250° F. for 8 hours. Each of these salt mixtures was clear at the conclusion of this test, and none of them evolved hydrogen sulfide throughout the test period.

The thermal stability of the zinc salt compositions of this invention is demonstrated also by data available from a so-called "Panel Coke Test." This is a test described in a pamphlet issued in 1952 by the Pratt-Whitney Aircraft Corp. entitled "Panel Coking Test." According to the specification of this test procedure a reservoir of a sample of oil to be tested is agitated violently at room temperature so as to provide an oil mist which rises to contact a heated aluminum panel suspended above the reservoir of oil. The temperature of the aluminum panel is maintained at 570° F. and the duration of the test is 3 hours. The thermal stability of the oil sample being tested is measured by an inspection of the deposists which have accumulated on the aluminum panel. The aluminum panel is assigned a rating based upon 10.0 as an indication of the complete absence of any such deposits and 0.0 as an indication of complete coverage of the aluminum panel by such deposits.

The compositions of this invention were tested in a Midcontinent, solvent-extracted, SAE 30 oil which in each case contained also 0.67% (as sulfate ash) of a carbonated basic barium sulfonate and 0.06% (as phosphorus) of the particular zinc phosphorodithioate composition being tested. The results of these tests are shown below.

Zinc phosphorodithioate composition:	Rating
1. The zinc salt composition of Example 8	9.5
2. A zinc salt composition prepared as in Example 2 except that the molar ratio of isobutyl radicals to primary amyl radicals is 65 : 35 rather than 75 : 25	9.5
3. Zinc di-(4-methylpentyl-2) phosphorodithioate	5.5
4. The zinc salt of a 60/40 molar mixture of di-(4-methylpentyl-2) phosphorodithioic acid and diisopropyl phosphorodithioic acid	6.8
5. Zinc di-methylcyclohexyl phosphorodithioate	1.5

It will be noted that each of the zinc phosphorodithioates of numbers 3, 4, and 5 contain secondary alkyl groups and that the rating for each of these three compositions is quite inferior to the ratings which correspond to the compositions of this invention.

A further demonstration of the superiority of the compositions of this invention is available from the results of tests performed in a Buda Diesel Engine. These tests were run at an engine speed of 1815–1820 r.p.m., a water jacket temperature of 175–180° F., oil temperature of 145–150° F., under a load of 3000 watts and using a fuel containing a minimum of 1% sulfur. In each case the lubricant tested was a Midcontinent, solvent-extracted, SAE 30 oil containing 0.67% (as sulfate ash) of a carbonated basic barium sulfonate and 0.06% (as phosphorus) of the zinc phosphorodithioate composition being tested. The results of the test were determined after 100 hours and again after 150 hours of operation under the above conditions. The piston was inspected for over-all cleanliness and a rating based on a scale of 0 was completely dirty and 100 as completely clean assigned to the test lubricant. A further rating was also determined based upon the degree to which the top ring groove of the piston was filled with deposits. This latter rating appears as a percent figure so that it obviously ranges from 0 to 100 percent. The results of these tests are as follows:

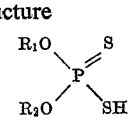
Zinc Phosphorodithioate Composition	Overall Piston Cleanliness	Percent Filling Top Ring Groove
1. Zinc salt of a 60/40 molar mixture of di-(4-methylpentyl-2) phosphorodithioic acid and diisopropyl phosphorodithioic acid:		
100 hours	83	16
150 hours	78	16
2. The zinc salt composition of Example 3:		
100 hours	96	0
150 hours	95	1

It is apparent from the above data that the compositions of this invention possess a much higher order of thermal stability than that shown by the zinc phosphorodithioate compositions known heretofore.

Other modes of applying the principle of the invention may be employed, change being made as regards the details described, provided the features stated in any of the following claims or the equivalent of such be employed.

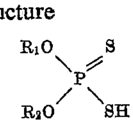
We therefore particularly point out and distinctly claim as our invention:

1. The zinc salts of a mixture of phosphorodithioic acids having the structure



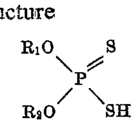
in which R_1 and R_2 are selected from the class consisting of lower molecular weight primary aliphatic hydrocarbon radicals having less than five carbon atoms and higher molecular weight primary aliphatic hydrocarbon radicals having at least five carbon atoms, the mole ratio of lower molecular weight radicals to higher molecular weight radicals in the zinc salt mixture being within the range of 1:1 to 3:1.

2. The zinc salts of a mixture of phosphorodithioic acids having the structure



in which R_1 and R_2 are selected from the class consisting of primary butyl radicals and primary amyl radicals, the mole ratio of butyl radicals to amyl radicals in the zinc salt mixture being within the range of 1:1 to 3:1.

3. The zinc salts of a mixture of phosphorodithioic acids having the structure



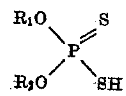
in which R_1 and R_2 are selected from the class consisting of isobutyl and a mixture of amyl radicals said mixture containing 65% n-amyl, 3% isoamyl, and 32% 2-methyl-1-butyl radicals, the mole ratio of isobutyl radicals to amyl radicals in the zinc salt mixture being within the range of 1:1 to 3:1.

4. The zinc salts of claim 1 characterized further in that the said zinc salts comprise a mixture of different salts prepared by the separate preparation of individual zinc phosphorodithioates and subsequent mixing of these salts.

5. The zinc salts of claim 1 characterized further in that the said zinc salts are prepared by reaction of zinc oxide with a mixture of different phosphorodithioic acids.

6. The zinc salts of claim 1 characterized further in that the said zinc salts are prepared by reaction of zinc oxide with phosphorodithioic acids prepared by the reaction of phosphorus pentasulfide with mixtures of alcohols.

7. The zinc salts of a mixture of phosphorodithioic acids having the structure



in which R_1 and R_2 are selected from the class consisting of isobutyl radicals and a mixture of amyl radicals said mixture containing 65% n-amyl, 3% isoamyl, and 32% 2-methyl-1-butyl radicals, the mole ratio of isobutyl radicals to amyl radicals in the zinc salt mixture being within the range of 1:1 to 3:1, said zinc salts prepared by the reaction of zinc oxide with a mixture of phosphorodithioic acids prepared by the reaction of phosphorus pentasulfide with a mixture of alcohols.

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