

UNITED STATES PATENT OFFICE

2,610,182

HYDROCARBON THIOPHOSPHORIC ACID
SALTS OF THIALDINE AND CERTAIN
HOMOLOGUESJohn P. McDermott, Roselle, N. J., assignor to
Standard Oil Development Company, a corpo-
ration of DelawareNo Drawing. Application June 22, 1949,
Serial No. 100,741

5 Claims. (Cl. 260-243)

1

The present invention relates to an improved class of additives particularly suitable for use in lubricating oils and to the compounded mineral oils and other hydrocarbon products in which they are employed.

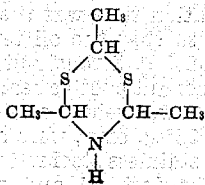
Modern developments in the design of internal combustion engines, with increasing engine speeds and compression ratios, have imposed a severe strain on the lubricants employed. In particular, the crankcase oil is raised to a high temperature and in the course of its circulation through the engine is repeatedly exposed to air under conditions highly conducive to destructive oxidation. Oxidative breakdown of the oil results in the formation of acidic products which corrode bearing surfaces and do considerable harm to the engine generally. Furthermore, the metallic corrosion products have the effect of catalyzing further oxidative breakdown of the oil.

A number of compounds, more especially those of the phenolic type, are known which exert an oxidation inhibiting effect when added to mineral lubricating oils and other hydrocarbon products. Their effect is to prevent oxidative breakdown of the oil both on storage (long potential reaction time and low temperature) and in use (short reaction time and high temperature). Although many antioxidants are known which stabilize the oil adequately on storage, the majority of them tend to break down with undesirable rapidity at high engine operating temperatures.

A principal object of the present invention is to provide a new class of lubricating oil antioxidants of good properties. Another object is to provide an antioxidant which is stable and effective at relatively high engine temperatures. Other objects and advantages will be apparent from the following description.

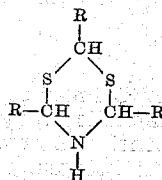
It has now been found, according to the present invention, that the salts formed by reacting thialdine or its homologs with carboxylic and thio-carboxylic acids and the thio acids of phosphorus are extremely effective antioxidants for hydrocarbon products liable to oxidation, especially mineral lubricating oils.

Thialdine, otherwise known as 5,6-dihydro-2,4,6-trimethyl-1,3,5-dithiazine, is represented by the structural formula



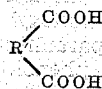
2

It is readily prepared by treating the condensation product of acetaldehyde and ammonia with hydrogen sulfide. Thialdine and the homologs of the same which are useful for the purposes of the present invention may be represented by the general formula



where R represents an alkyl group of 1 to 10 carbon atoms. However, simple thialdine in which R is methyl is preferred.

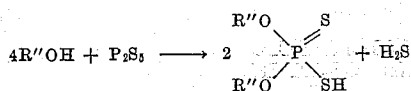
Acids which may be used in forming the thialdine salts of the present invention include mono- or dicarboxylic aliphatic acids which may be represented by the general formulas $R'COOH$ or



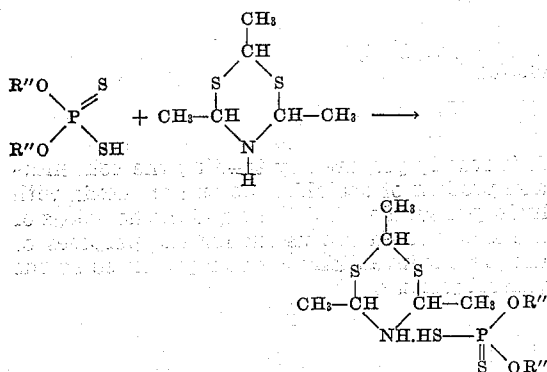
where R' represents an aliphatic or sulfurized aliphatic hydrocarbon radical having from 1 to 30 carbon atoms. The radical R' may be saturated or unsaturated, straight or branched chain, with or without cycloaliphatic substituent chains, or it may be an alkyl substituted cycloaliphatic nucleus. Examples of suitable acids are the lower mono- and dicarboxylic acids such as butyric, adipic, sebacic, and decanoic acids. Higher acids include lauric, oleic, linoleic, ricinoleic, palmitic, and stearic acids. Mixtures of acids, such as those obtained by the oxidation of paraffin wax or other high molecular weight petroleum fractions, may also be used. Sulfurized acids, in which the sulfur is in the hydrocarbon radical, are particularly desirable and may be prepared by heating the acid with elemental sulfur or with a sulfur halide. Examples are sulfurized oleic, sulfurized linoleic, and sulfurized oxidized wax acids. Thio acids of the formula $R'COSH$, or xanthic acids of the formula $R'OCSSH$, where R' has the same significance as above, may also be used. The most preferred products, however, are those prepared from the thio acids of phosphorus, such as thiophosphorous and thiophosphoric acids, both from the point of view of effectiveness and from the point of view of ease of preparation. In general, partially esterified thiophosphates or thiophosphites are used to give the mono- or di-thialdine salt. These partially esterified compounds may be prepared by reacting

3

an organic hydroxy compound with a sulfide of phosphorus. Thus, a compound of the formula $R''OH$, where R'' represents an organic radical, may be treated with phosphorus pentasulfide in a molar ratio of 4:1, as shown below.



This product may then be reacted with one mol of thialdine to give an addition product or salt.



The compound $R''OH$ may be an alcohol, such as a C_2 to C_{20} aliphatic straight or branched chain or cyclic alcohol with or without substituent groups such as halogen, sulfur, amino, or nitro groups, or may be a phenol or an alkylated phenol, a hydroxy ester, hydroxy ether, etc. In general, the total number of carbon atoms in the group R'' should be from 2 to 30 and the number of aliphatic carbon atoms may be from 2 to 24. Examples of suitable compounds are isopropyl alcohol, isobutyl alcohol, 2-ethylhexanol, iso-octyl alcohol, C_8 "Oxo" alcohols, decyl alcohol, "Lorol" (C_{10} - C_{16}) alcohols, methylcyclohexyl alcohol, isopropyl cyclohexyl alcohol, mixed alcohols derived from paraffin wax or from chlorinated paraffin wax, phenol, p-cresol, 2,4,6-trisobutylphenol, p-isooctylphenol, p-tert.-octylphenol, p-tert.-octylphenol sulfide, butyl lactate, α -hydroxy butyl stearate, the various glycol ethers known as "Cellosolves," such as the monobutyl ether of ethylene glycol, etc.

The thialdine and homologous salts of the present invention may be readily formed by contacting the thialdine compound with the acid at room temperature. Since heat is evolved, the reaction is preferably conducted in the presence of an inert solvent and by contacting the reactants gradually. Suitable solvents include chloroform, carbon tetrachloride, ethylene dichloride, benzene, and the like.

The following examples illustrate the preparation and testing of various thialdine salts according to this invention, but it is to be understood that these examples do not limit the scope of the invention in any way.

Example 1.—Preparation of thialdine nonyl thiophosphate

A mixture of 115.2 grams (0.8 mol) of C_9 "Oxo" alcohol and 44.4 grams (0.2 mol) of P_2S_5 was heated at $110^\circ C$. for 45 minutes with rapid stirring in a 1-liter, 3-necked flask equipped with a stirrer, thermometer, and reflux condenser. The resultant acid was then filtered and blown with nitrogen for 10 minutes.

A solution of 95.5 grams (0.25 mol) of this product (nonyl thiophosphoric acid) in 100 cc. of $CHCl_3$ was added dropwise over a period of

4

30 minutes to a solution of 40.8 grams (0.25 mol) of thialdine in 300 cc. of $CHCl_3$, maintaining the temperature below $35^\circ C$. After stirring for an additional hour at room temperature, the product was filtered and placed on a steam bath to remove the solvent. A viscous brown liquid was obtained, which upon analysis was found to contain 5.5% phosphorus, 22.1% sulfur, and 2.4% nitrogen.

Example 2.—Preparation of thialdine methylcyclohexyl thiophosphate

Methylcyclohexyl thiophosphoric acid was prepared by the method described in Example 1, using 114 grams (1 mol) of methylcyclohexanol and 55.5 grams (0.25 mol) of P_2S_5 .

The thialdine salt was also prepared by the method described in Example 1, using 96.6 grams (0.3 mol) of methylcyclohexyl thiophosphoric acid and 49.0 grams (0.3 mol) of thialdine. A brown tacky solid was obtained which upon analysis was found to contain 6.0% phosphorus, 24.5% sulfur, and 2.1% nitrogen.

Example 3.—Preparation of thialdine sulfurized oleyl thiophosphate

Sulfurized oleyl thiophosphoric acid was prepared by the method described in Example 1, using 120 grams (0.4 mol) of sulfurized oleyl alcohol (prepared by heating equimolar quantities of oleyl alcohol and sulfur for one hour at $165^\circ C$.) and 22.2 grams (0.1 mol) of P_2S_5 .

The thialdine salt was prepared as described in Example 1, using 97.2 grams (0.14 mol) of sulfurized oleyl thiophosphoric acid and 22.8 grams (0.14 mol) of thialdine. A dark brown sticky solid was obtained which upon analysis was found to contain 3.3% phosphorus, 19.9% sulfur, and 1.6% nitrogen.

Example 4.—Preparation of thialdine sulfurized oleate

A mixture of 113 grams (0.4 mol) of oleic acid and 12.8 grams (0.4 mol) of sulfur was heated for $1\frac{1}{2}$ hours at $165^\circ C$.

The thialdine salt was prepared as described in Example 1, using 94.4 grams (0.3 mol) of sulfurized oleic acid and 49.0 grams (0.3 mol) of thialdine. A dark red liquid was obtained which upon analysis was found to contain 18.5% sulfur and 2.5% nitrogen.

These four products were then tested in the laboratory for their inhibiting action against the corrosion of lead in copper-lead bearings, as shown in the following examples.

Example 5

In this test the additives were blended in 0.25% by weight concentration in an extracted Mid-Continent oil of S. A. E. 20 grade and comparative tests run on these blends and on a sample of the unblended oil. The test was conducted as follows:

500 cc. of the oil was placed in a glass oxidation tube 13 inches long and 2½ inches in diameter, fitted at the bottom with a ¼ inch air inlet tube perforated to facilitate air distribution. The oxidation tube was then immersed in a heating bath so that the oil temperature was maintained at $325^\circ F$. throughout the test. Two quarter sections of automotive bearings of copper-lead alloy, of known weight and having a total surface area of 25 sq. cms., were attached to opposite sides of a stainless steel rod which was then immersed in the test oil and rotated at 600

5

R. P. M., thus providing sufficient agitation of the oil during the test. Air was then blown through the oil at the rate of 2 cu. ft. per hour. At the end of each four-hour period, the bearings were removed, washed with naphtha, and weighted to determine the amount of loss by corrosion. The bearings were then repolished (to increase the severity of the test), reweighted and then subjected to the test for additional four-hour periods in like manner. The results are given in the following table as "corrosion life," which indicates the number of hours required for the bearings to lose 100 mgs. in weight, determined by interpolation of the data obtained in the various periods.

Thialdine Salt	Corrosion Life (Hours)
None (Base oil only).....	9
Dinonyl thiophosphate (Ex. 1).....	19
Di(methylcyclohexyl)thiophosphate (Ex. 2).....	21
Di(sulfurized oleyl)thiophosphate (Ex. 3).....	21
Sulfurized oleate (Ex. 4).....	30

Example 6

To confirm the results of this laboratory test, under actual operating conditions, a further test was run, using a S. A. E. 30 extracted Coastal oil containing 1% of the thialdine methylcyclohexyl thiophosphate of Example 2 as crankcase lubricant in a Lauson engine. The operating conditions were 295° F. jacket temperature, 300° F. oil temperature, and 1800 R. P. M. at 1.5 indicated kilowatt load, and the duration of the test was 25 hours. At the end of the test the loss in weight of the copper-lead bearing was determined. A blank test was run for comparison, using the base oil alone. The results of the test are shown below.

Oil	Weight Loss per Bearing (mg.)
Base oil alone.....	99
Blend.....	20

From the preceding examples it will be evident that the thialdine salts of the present invention are effective antioxidants for lubricating oils.

As previously stated, any of the alkyl homologs of thialdine may be employed although thialdine itself is preferred. The acid radical may be that of a long chain acid such as oleic, palmitic or stearic acid, or lower mono- or dibasic acids such as butyric, adipic or sebacic acid may be used. Sulfur-containing acids are preferred in the carboxylic acid class, and these may be readily prepared, for example, by heating the acid with elemental sulfur or with a sulfur halide.

The additives may be blended in the oil in amounts of from about 0.02 to 5% by weight, 0.5 to 2% being the preferred range. For load-bearing purposes quantities of 2 to 15% may be used. For handling and storage, concentrates containing 15 to 50% or more may be prepared. These may be added to base stocks to give blends of the desired concentration.

In addition to the additives of this invention there may also be added to the oil other conven-

6

tional additives including detergent type additives, such as metal soaps, metal petroleum sulfonates, metal phenates, metal alcoholates, metal alkyl phenol sulfides, and the like. Examples of such additional additives are barium tert.-octyl phenol sulfide, calcium tert.-amyl phenol sulfide, cadmium or nickel oleates, calcium phenyl stearate, aluminum naphthenate, and zinc methylcyclohexyl thiophosphate.

The lubricating oil base stocks used may be straight mineral lubricating oils or distillates derived from any suitable or desired crudes, or, if desired, blended oils may be employed. The oils may have been subjected to any conventional refining treatment such as acid, alkali and/or clay treatment, or solvent extraction. Synthetic oils such as those prepared by the polymerization of olefins or by the Fischer-Tropsch synthesis may alternatively be employed, alone, mixed, or in combination with mineral oils.

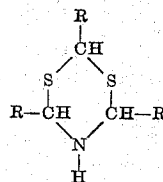
Further types of additives which may be present if desired include dyes, pour point depressants, heat thickened fatty oils, sulfurized fatty oils, organo-metallic compounds, sludge dispersers, thickeners, viscosity index improvers, oiliness agents, volatilized fats, waxes or oils, and colloidal solids such as graphite or zinc oxide, etc. Solvents and assisting agents such as esters, ketones, alcohols, aldehydes, and halogenated or nitrated hydrocarbons may also be employed where necessary or desirable.

Particularly suitable assisting agents are the C₈ and higher alcohols (preferably C₈ to C₁₂) such as lauryl and stearyl alcohols, and the "Oxo" alcohols of corresponding chain length.

In addition to being employed in lubricants, the additives of the present invention may also be employed in other hydrocarbon products susceptible to oxidative breakdown. Among these may be mentioned motor fuels, mineral oil base hydraulic fluids, torque converter fluids, cutting oils, flushing oils, turbine oils, transformer oils, industrial oils and process oils, natural and synthetic hydrocarbon rubbers, and the like. They may also be used in gear lubricants, greases, and in other products containing hydrocarbon oils as ingredients.

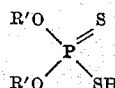
What is claimed is:

1. As a new composition of matter, the salt of a compound of the general formula



wherein R is a C₁ to C₁₀ alkyl radical, and a thiophosphoric acid in which at least one of the hydrogen atoms is replaced by a hydrocarbon radical containing in the range of 2 to 30 carbon atoms.

2. A composition as in claim 1 in which said thiophosphoric acid has the formula



wherein R' represents a monovalent aliphatic hydrocarbon radical having in the range of 2 to 20 carbon atoms.

7

3. A composition as in claim 2 in which all of said R radicals are methyl radicals.

4. A composition as in claim 3 wherein said R radicals are methylcyclohexyl radicals.

5. A composition as in claim 3 wherein said R radicals are nonyl radicals.

JOHN P. McDERMOTT.

REFERENCES CITED

The following references are of record in the file of this patent:

UNITED STATES PATENTS

Number	Name	Date
2,050,204	Ter Horst	Aug. 4, 1936
2,054,903	Hagedorn	Sept. 22, 1936

8

Number	Name	Date
2,109,158	Teppema	Feb. 22, 1938
2,220,156	Jacobson	Nov. 5, 1940
2,273,664	Searle	Feb. 17, 1942
2,283,186	Coghill	May 19, 1942
2,353,170	Lincoln et al.	July 11, 1944

FOREIGN PATENTS

Number	Country	Date
224,925	Great Britain	Nov. 24, 1924
396,177	Great Britain	Aug. 3, 1933

OTHER REFERENCES

McClure: Chem. and Eng. News, vol. 22 (1944), p. 420.