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BASIC ZINC DIALKYL DITHIOPHOSPHATES AND METHODS OF MAKING THE SAME

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The present invention relates to the stabilization of organic substances against polymerization, oxidation, and other forms of deterioration resulting from the action of atmospheric oxygen thereon. More specifically, the present invention is directed to the antioxidants, per se; to the processes of preparing them; and to the organic compositions containing the same.

It is well known in the art that the development of such undesirable oxidative effects may be deterred by the addition of small quantities of stabilizers or antioxidants to organic substances which are normally liable to oxidation and other deteriorative effects. Among the organic substances which have been so stabilized by such antioxidants have been oils, waxes, hydraulic fluids; textile softeners; paints and varnishes; petroleum products including lubricating oils, turbine oils, transformer oils, cutting oils, etc.; plastic molding powders; and the like.

More specifically, it is known that in modern internal combustion engines, including diesel engines and particularly those using high sulfur fuels, as well as aviation engines and ordinary automotive spark ignition engines, various products of combustion fuel and oil degradation, condensation, polymerization, and the like, are generally formed which cause piston ring sticking, valve sticking, and corrosion of various metal parts of the combustion zone and auxiliary parts functioning therewith. The development of lacquer and/or carbonaceous deposits on the rings and grooves and on valve stems and valve guides appears to be the most probable reason for ring and valve sticking. The production of acidic bodies by the chemical combustion of the fuel and/or by the degradation of the lubricating oil as by partial oxidation and the like appears to be responsible, at least in part, for the corrosion of the engine parts associated with the combustion chamber and lubricated by means of the same lubricant utilized in the lubrication of the piston rods, pistons, and the like. Also, the acidic oxidation products developed in the lubricating oil appear to exert a catalytic effect in the oxidation of the lubricating oil hydrocarbons.

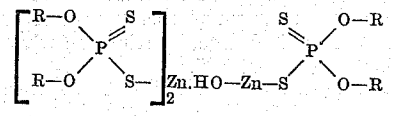
The addition of various types of metal derivatives of organic compounds to lubricating oils is known and practiced to minimize the difficulties already referred to and to improve the properties of these oils in other respects. Thus, for example, basic materials, such as basic metal compounds, have been used to provide an alkaline reserve to neutralize the developed acidic compounds.

It is also known that calcium and other polyvalent metal salts of petroleum or synthetic sulfonic acids have been used as engine oil detergent addition agents and that the corresponding basic (hydroxy) salts have been used additionally for their basicity as neutralizing agent for the acidic bodies developed in the lubricant, regardless of their source.

It is an object of the present invention to provide a new class of antioxidants for the stabilization of organic substances in general and specifically as addition agents in oils which are to be used as crankcase lubricants for internal combustion engines. These compounds exhibit to a high degree the desirable properties of inhibiting the development of corrosivity in the organic substance or oil, of improving oxidation stability of the oil, and of

promoting general cleanliness and reducing ring sticking, piston skirt varnish formation, and the like, when used in an engine.

We have found that this object and others which will become clear hereinafter may be accomplished by the use of a novel class of antioxidants falling with the chemical group of basic zinc dialkyl dithiophosphates having the following general structural formula:



wherein R is a normal or secondary alkyl radical having from 1 to 18 carbon atoms.

We have further found that the basic zinc salts of the present invention comprise a source of reserve alkalinity whereby the acid materials developed in or by the lubricating oil during actual operation is neutralized and its deleterious effects avoided.

It is, of course, to be appreciated, that, when the antioxidant is used in a specific application or for a definite purpose, such as an improvement additive in a hydrocarbon lubricating oil, it is necessary that the antioxidant be soluble in such substance to a sufficient degree to exhibit its desired antioxidant characteristics and properties. It is also to be observed that the amount used in any particular instance will vary as to the nature of the organic compound to be stabilized, the purpose for which it is to be used, etc. When used as an antioxidant in lubricating oils, amounts of from about 0.1% to about 5% by weight may be used, although, more commonly from about 0.4% by weight to about 2% by weight have been employed. When used in combination with other antioxidants or detergents, lesser amounts may be found adequate.

The radical R in the above structural formula may be any normal or secondary alkyl radical such as methyl, ethyl, propyl, isopropyl, butyl, 4-methyl-2-pentyl, hexyl, octyl, decyl, dodecyl, tridecyl, tetradecyl, octadecyl, hexadecyl, etc.

These zinc basic salt compounds are to be distinguished from the normal zinc salts which do not possess such alkaline reserve properties and these distinctions will be brought out in the following examples of preparations and evaluations of the resulting products. It should be understood, however, that although these examples and evaluations may describe in particular detail some of the more specific features of the invention, they are given primarily for purposes of illustration and the inventive concept in its broader aspects is not to be construed as limited thereto.

EXAMPLE 1

n-Butyl alcohol (222 grams 3.0 moles) was reacted with 166 grams (0.75 mole) of phosphorus pentasulfide on a steam bath for approximately ninety minutes. The purity of the resulting di-n-butyl dithiophosphate acid was 90%, based on its neutral equivalent of 269 (theory 242).

One mole (269 grams) of the crude acid was added slowly to 45 grams (1.1 moles) of sodium hydroxide in 400 grams of water. The temperature rose from room temperature to about 45° C. The pH was adjusted to about 9–10 by using an additional 4 grams (0.1 mole) of sodium hydroxide. Twenty-five grams of an activated carbon decolorizing agent, such as "Darco," and 20 grams of a filter aid, such as "Hyflo," were added, the solution was filtered, and 68 grams (0.50 mole) of zinc chloride in 40 grams of water was added to the filtrate. The resulting mixture was heated at 75° C. for several minutes. The product was then separated from the aqueous phase, stripped, and filtered through a coated,

steam-jacketed funnel. The yield, before the final filtration, was 233 grams.

After standing at room temperature, the filtered reaction product separated into a solid and a liquid phase. The solid phase was repeatedly washed with cold methanol, giving a white crystalline product. It was insoluble in methanol, quite soluble in hexane and very soluble in diethyl ether.

A final purification was made by dissolving the solid in hexane, filtering off the insolubles, adding methanol until incipient precipitation resulted and allowing the solvent to evaporate at room temperature. The resulting residue was composed of large, frangible, off-white crystals which melted at 145–153° C.

	Percent Zn	Percent P	Percent S
Calculated for $C_{24}H_{55}P_3O_7S_6Zn_2$	15.0	10.7	22.1
Found for $C_{24}H_{55}P_3O_7S_6Zn_2$	15.1	10.5	21.0

The solid was basic and a sample was titrated with standard acid. A mixture of one part diethyl ether and two parts ethanol was a satisfactory solvent for this titration. Based on such a titration, the equivalent weight of the material was 882 (theory 872). Titration of the solid with standard alkali gave a neutral equivalent of 283 (theory 290), which is approximately one-third of that obtained by titration with acid. These values are in very good agreement with the possible structure based on the analysis.

EXAMPLE 2

$$3(C_4H_9O)_2\overset{\overset{S}{\|}}{P}SH + 4NaOH + 2ZnCl_2 \longrightarrow \left[(C_4H_9O)_2\overset{\overset{S}{\|}}{P}S-\right]_2Zn.HOZnS\overset{\overset{S}{\|}}{P}(C_4H_9)_2 + 4NaCl + 3H_2O$$

24.2 g. (0.1 mole) di-n-butyl dithiophosphoric acid (N. E. 241.9)
9.1 g. (0.067 mole) zinc chloride
5.5 g. (0.133 mole) 97% sodium hydroxide

The sodium hydroxide was dissolved in 200 ml. of water and 50 grams of ice was added, after which the dibutyl dithiophosphoric acid was added. A solution of the zinc chloride in 50 ml. of water was then added slowly with manual stirring. A solid crystalline precipitate formed immediately. After air-drying the water-washed product, a yield of 26.0 grams (89.5%) of white, crystalline solid was obtained. It appeared to be identical with the previously-described product of Example 1 and had the following analysis: 15.1% Zn; 10.5% P; 20.8% S.

EXAMPLE 3

Three representative potassium dialkyl dithiophosphates (alkyl=isopropyl, n-hexyl, or n-decyl) were converted to the corresponding basic zinc salts by dissolving them in water, adding additional alkali, and finally adding the amount of Zn^{++} ion prescribed by the equation below:

Preparation of basic zinc dialkyl dithiophosphates

$$3(RO)_2PSSM + MOH + 2ZnCl_2 \longrightarrow [(RO)_2PSS-]_2Zn.HOZnSSP(OR)_2 + 4MCl$$

[M=K or Na]

Alkyl Group (R)	K-salt, g.	H_2O, ml.	1.0 M NaOH, ml.	2.0 M $ZnCl_2$, ml.	Yield	
					g.	Percent
Isopropyl	15.2	200	20.0	20.0	13.5	86.0
n-Hexyl	10.1	300	10.0	10.0	10.0	96.1
n-Decyl	13.5	100	10.0	10.0	11.5	83.9

The basic isopropyl salt was a white crystalline solid, whereas the n-hexyl and n-decyl derivatives were yellow viscous liquids and were worked up via solution in hexane followed by drying over sodium sulfate and evaporation in air-stream. Analyses of these products are presented in the following table.

Zinc Dialkyl Dithiophosphate		Analysis					
		Calculated			Found		
R	Empir. Formula	Percent Zn	Percent P	Percent S	Percent Zn	Percent P	Percent S
i-Propyl	$C_{18}H_{43}P_3O_7S_6Zn_2$	16.6	11.8	24.4	18.2	11.6	22.7
n-Hexyl	$C_{30}H_{67}P_3O_7S_6Zn_2$	12.5	8.9	18.5	12.2	9.0	18.6
n-Decyl	$C_{60}H_{127}P_3O_7S_6Zn_2$	9.5	6.8	13.9	8.7	7.0	14.0

An acid titration of the solid material derived from the preparation of basic zinc dibutyl dithiophosphate (a 1.2131 gram sample in 30 ml. ether and 60 ml. ethanol) required 13.75 ml. of 0.100 N HCl, the endpoint occurring at pH 4.5. Using these values, it can be calculated that the strong acid neutralizing ability of the above basic zinc dibutyl dithiophosphate corresponds to that of a conventional basic petroleum sulfonate having a neutralization number of about −63.

Representative antioxidant compositions, some comprising the normal salt of zinc di-n-butyl dithiophosphate and others comprising the basic salt of this invention were used in comparative tests to inhibit the oxidation of a white mineral oil. The test was carried out as follows: 300-gram portions of the mineral oil were weighed out and to each was added approximately 0.1 gram of the representative salt. The mixtures were placed in cylindrical glass vessels 40 cm. diameter x 400 cm. height with a fritted-glass air-inlet tube at the bottom and an exit-gas tube at the top. The vessels were then placed in a thermostated bath, controlled at 155° C. and pure nitrogen bubbled through the solution at 200 cc. per minute for 1 hour, during which time the solutions reached the bath temperature.

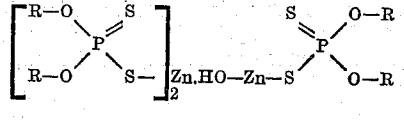
The gas stream was then switched to air at 200 cc. per minute and the time noted. The outlet gas stream was then passed through a paramagnetic type oxygen analyzer, where its oxygen content was measured and recorded as a function of time. The time at which the solution began to absorb oxygen was noted by the rapid drop in the oxygen content of the outlet gas stream. This time can be determined very accurately and is recorded in the table as the "induction period," being the number of minutes elapsed between the switch from nitrogen to air, and the rapid drop in the oxygen content of the outlet gas stream.

Additive	Induction Period	Oil Appearance
None (blank)	less than 60 mins.	dark.
Normal salt	715 mins.	dark.
Basic salt	975 mins.	light.

Although we have described but a few specific examples of our invention, we consider the case not to be limited thereby nor to the specific substances mentioned therein, but to include various other equivalent compounds of similar constitution as set forth in the claims appended hereto. It is understood that any suitable changes or variations may be made without departing from the spirit or scope of the inventive concept.

We claim:

1. A basic zinc dithiophosphate having the formula



wherein R is a member of the group consisting of normal and secondary alkyl radicals containing from 1 to 18 carbon atoms.

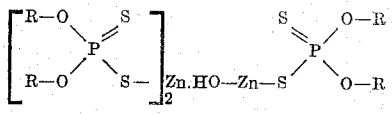
2. A basic zinc dithiophosphate as defined in claim 1 in which R is butyl.

3. A basic zinc dithiophosphate as defined in claim 1 in which R is isopropyl.

4. A basic zinc dithiophosphate as defined in claim 1 in which R is hexyl.

5. A basic zinc dithiophosphate as defined in claim 1 in which R is decyl.

6. A hydrocarbon mineral lubricating oil composition comprising a relatively large proportion of a hydrocarbon mineral lubricating oil having dissolved therein a relatively small amount from about 0.1% to about 5% by weight, sufficient to inhibit deterioration of the oil by oxidation, of a basic zinc dithiophosphate having the formula



wherein R is a member of the group consisting of normal and secondary alkyl radicals containing from 3 to 18 carbon atoms.

7. A hydrocarbon mineral lubricating oil composition comprising a basic zinc dithiophosphate as defined in claim 6 in which R is butyl.

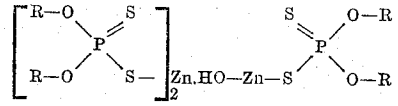
8. A hydrocarbon mineral lubricating oil composition

comprising a basic zinc dithiophosphate as defined in claim 6 in which R is isopropyl.

9. A hydrocarbon mineral lubricating oil composition comprising a basic zinc dithiophosphate as defined in claim 6 in which R is hexyl.

10. A hydrocarbon mineral lubricating oil composition comprising a basic zinc dithiophosphate as defined in claim 6 in which R is decyl.

11. A method of preparing a basic zinc dithiophosphate having the formula



wherein R is a member of the group consisting of normal and secondary alkyl radicals containing from 1 to 18 carbon atoms which comprises reacting a dialkyl dithiophosphoric acid in which the alkyl groups contain from 1 to 18 carbon atoms with a stoichiometric excess of a zinc salt in the presence of a stoichiometric excess of an alkali metal hydroxide whereby the reaction proceeds under alkaline conditions at all times to form the basic zinc dithiophosphate.

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