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EXTREME PRESSURE LUBRICANT ADDITIVE

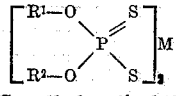
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3 Claims. (Cl. 260—429.9)

The present invention relates to additives which impart extreme pressure properties to lubricating oils and to a process for the preparation of such additives.

It has been proposed in the past to add to lubricating oils compounds containing both phosphorus and sulfur and compounds containing chlorine to impart extreme pressure properties to the oils. The applicant has discovered that a new class of compounds containing phosphorus, sulfur and chlorine may be prepared, which when added to lubricating oils impart extreme pressure properties thereto.

The present invention therefore comprises a lubricating oil composition comprising a major proportion of a lubricating oil containing a minor proportion of a compound of general formula:



wherein R^1 is a C_2–C_{24} alkyl radical, R^2 is a C_2–C_{24} alkyl radical in which one or more of the hydrogen atoms is replaced by chlorine, and M is zinc or cadmium.

The compounds specified in the above paragraph will hereafter be referred to as chlorinated metal dialkyl dithiophosphates.

The chlorinated metal dialkyl dithiophosphates of the present invention are preferably complexed with an amine when employed in lubricating oils. The feature of complexing with an amine is particularly desirable when the unsubstituted alkyl radical of the chlorinated metal dialkyl dithiophosphates contains less than about 10 carbon atoms since the amines impart greater oil solubility to the additives of the present invention when the unsubstituted alkyl group contains less than about 10 carbon atoms.

The chlorinated metal dialkyl dithiophosphates of the present invention may be prepared by reacting equimolar proportions of C_2–C_{24} aliphatic alcohol and a C_2–C_{24} chlorine-containing aliphatic alcohol with phosphorus pentasulfide and reacting the product thus obtained with an inorganic zinc or cadmium compound. Zinc compounds such as zinc oxide, zinc hydroxide and zinc carbonate, and the corresponding cadmium compounds may be employed.

The C_2–C_{24} alcohol employed in preparing the additive may be a primary, secondary or tert. alcohol such as ethyl alcohol, propyl alcohol, isopropyl alcohol, butyl alcohol, sec.-butyl alcohol and tertiary butyl alcohol, hexyl alcohol, methylisobutylcarbinol, ethylisopropylcarbinol, heptyl, isoheptyl, 2-ethyl amyl, octyl, isooctyl, 3-ethyl hexyl, 2-propyl amyl, decyl, undecyl, dodecyl, hexadecyl, stearyl and octadecyl alcohols. The alcohols may be those obtained by the so-called Oxo process.

The chlorine-containing C_2–C_{24} alcohol may contain more than one chlorine atom, the alcohol being either primary, secondary or tertiary. It is preferred however that chlorinated primary alcohols such as ethylene chlorhydrin, di- or tri-chlorethanol, 2-chloropropanol-1,2,2,3-trichlorbutanol-1 and 5-chloropentanol-1 be employed. Ethylene chlorhydrin is particularly preferred.

When employing amines to complex the chlorinated metal dialkyl dithiophosphates, it is preferred that primary amines, having 3 or more carbon atoms, be used

however secondary and tertiary amines may also be employed. It is particularly preferred that branched chain primary amines be used. Tertiary alkyl primary amines are particularly effective. Examples of such tert. alkyl primary amines are tertiary butyl amines, tertiary octyl amines and commercial mixtures of tertiary alkyl amines such as those manufactured and sold by the Rohm and Haas Company under the trade name "Primenes." "Primene 81" for example is a mixture of primary amine isomers wherein the tertiary alkyl groups contain from 12 to 15 carbon atoms. Another amine mixture designated "Primene JMT" is a mixture of isomeric amines in which the alkyl groups contain from 16 to 24 carbon atoms. In all of these tertiary alkyl type primary amines the amine is attached directly to a tertiary carbon atom.

From 0.05% by wt. to 7.5% by wt., preferably 0.1% by wt. to 5.0% by wt. of the chlorinated metal dialkyl dithiophosphate may be added to lubricating oils and when employing the amine complexes from 0.07% by wt. to 12.0% by wt., preferably 0.12% by wt. to 9.0% by wt. may be added.

The lubricating oils to which the additives of the present invention may be added may be mineral oils or synthetic oils. The mineral oils may be naphthenic, paraffinic or mixed base oils. The synthetic oils may be polymer oils, ester oils such as esters of dicarboxylic acids and esters of phosphorus acids.

Other additives such as antioxidants, detergent and viscosity improving additives may be added to lubricant compositions containing the chlorinated metal dialkyl dithiophosphates of the present invention.

The following examples illustrate both the process for the preparation of chlorinated zinc dialkyl dithiophosphates according to the present invention and their effectiveness in lubricating oil compositions.

Example I

Zinc chloroethyloctyl dithiophosphate was prepared by mixing 32 gm. of ethylene chlorhydrin with 52 gm. of isomeric C_8 Oxo alcohols in 100 ml. of toluene. The mixture was stirred and refluxed with 44 gm. of phosphorus pentasulfide for 2 hours. 20 gm. of zinc oxide were then added with stirring at 100° C. The product was filtered and stripped under vacuum.

Example II

The zinc chloroethyloctyl dithiophosphate prepared in Example I was complexed with Primene JMT in equimolar proportions and the complex added to a mineral oil to give a zinc content of .1 wt. percent in the oil. The oil was then tested for extreme pressure properties in the four ball machine test, which is described in the Institute of Petroleum Journal, vol. 32, No. 268, April, 1946. Four other oils were similarly tested. One was the base oil without any additive and the other three the base oil containing three different commercially available zinc dialkyl dithiophosphates; the latter compounds being added in sufficient quantities to give .1 wt. percent zinc in the oils. The following results were obtained.

Lubricant	Critical Load, kg.	Weld Load, kg.
Base lubricant (mineral oil SAE 30 Grade)	<50	180
Base lubricant+zinc C_4-C_5 dialkyl dithiophosphate	90	216
Base lubricant+zinc C_3-C_6 dialkyl dithiophosphate	90	250
Base lubricant+zinc C_8 dialkyl dithiophosphate	98	288
Base lubricant+additive prepared in Example II	117	304

It will be seen from the above data, that both the critical load and weld load of the base oil were considerably improved by the addition of the additive according

to the present invention, and that the additive gave better results than commercially available zinc dialkyldithiophosphates.

Example III

Zinc chloroethyl ceto-stearyl dithiophosphate was prepared by mixing 40.3 gm. of ethylene chlorhydrin with 128 gm. of ceto-stearyl alcohol in 500 ml. of benzene. The mixture was stirred and refluxed with 55.5 gm. of phosphorus pentasulfide for 2 hours; 11 gm. of zinc oxide were then added with stirring at 100° C. The product was filtered and stripped under vacuum.

Example IV

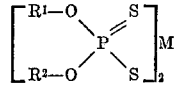
The zinc chloroethyl ceto-stearyl dithiophosphate was added to a mineral oil in three differing proportions. The base oil and the three oils containing the additive were tested in the four ball machine test referred to in Example II. The following results were obtained.

Lubricant	Critical Load, kg.	Weld Load, kg.
Base lubricant (mineral oil SAE 30 Grade)	50	180
Base Oil+0.5 wt. percent additive	100	208
Base Oil+1.0 wt. percent additive	100	232
Base Oil+2.5 wt. percent additive	135	256

It will be seen from the above data that both the critical load and weld load of the base oil were appreciably improved by the addition of the additive.

What is claimed is:

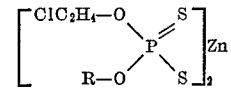
1. A complex of a tertiary alkyl primary amine containing 3 to 24 carbon atoms and a compound having the general formula:



where R^1 is a C_2–C_{24} alkyl radical, R^2 is a C_2–C_{24} alkyl radical in which at least one of the hydrogen atoms is replaced by a chlorine atom and M is selected from the group consisting of zinc and cadmium.

2. A complex consisting of substantially equimolar proportions of zinc chloroethyloctyl dithiophosphate and a mixture of isomeric tertiary alkyl primary amines, wherein said alkyl groups contain 16 to 24 carbon atoms.

3. An oil-soluble complex having extreme pressure properties when added to a mineral oil, which consists essentially of the product obtained by reacting mixed tertiary alkyl primary amines having alkyl groups of 16–24 carbon atoms with a substantially equimolar proportion of a mixture of compounds of the formula:



wherein R represents mixed alkyl radicals of isomeric Oxo C_8 alcohols.

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