Patented Aug. 14, 1945 2,382,775

UNITED STATES PATENT OFFICE

2,382,775

DITHIOPHOSPHORIC ACIDS AND SALTS THEREOF

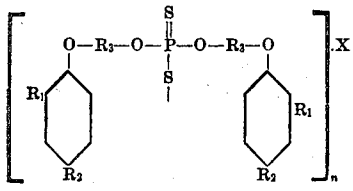
Elmer William Cook, New York, N. Y., and William David Thomas, Jr., Stamford, Conn., assignors to American Cyanamid Company, New York, N. Y., a corporation of Maine

No Drawing. Application June 16, 1942, Serial No. 447,274

4 Claims. (Cl. 260—461)

This invention relates to new chemical compounds and their preparation; more particularly to bis(dialkyl and dicycloalkyl substituted aryloxyalkyl) dithiophosphoric acids and salts thereof.

The compounds of the present invention to be described and claimed herein by us may be represented by the general formula

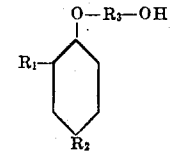


in which R_1 and R_2 are members of the group consisting of alkyl, cycloalkyl and hydrogen radicals at least one being a member of the group consisting of alkyl and cycloalkyl radicals, R_3 is an alkylene radical containing 2–4 carbon atoms inclusive, X is a member of the group consisting of hydrogen and metal salt-forming radicals, and n is the valence of X.

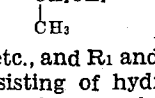
Many of the compounds of the above class have both detergent and corrosion inhibiting properties and when dissolved in hydrocarbon lubricating oils are extremely valuable in the prevention of bearing corrosion, sludge and varnish formation, ring sticking and other undesirable conditions which develop when ordinary lubricating oils are subjected to heavy duty service. Being water insoluble and polar in character they are valuable in the preparation of slushing oils. Because of their sulfur and phosphorus content they may be advantageously added to hypoid gear greases and other extreme pressure lubricants. Some of the compounds of the groups are also useful in the flotation of ores and some of their salts, particularly the lead and mercury salts, may be employed in insecticides and fungicides.

Our new compounds may be prepared by adding approximately 4 mols of an alkyl or cycloalkyl substituted phenoxyalkylol with one mol of P_2S_5 at temperatures between 90–110° C. until most of the P_2S_5 has dissolved and the evolution of H_2S has subsided. The crude product may be decanted from unreacted P_2S_5 and employed as such for certain purposes or it may be neutralized with a suitable salt-forming base as will hereinafter be described.

As will appear from the general formula given above, we may react P_2S_5 with alkyl or cycloalkyl substituted phenoxyalkylols having the general formula



in which R_3 is an alkylene radical of 2–4 carbon atoms such as —CH_2CH_2—,



—$CH_2CH_2CH_2$—, etc., and R_1 and R_2 are members of the group consisting of hydrogen, alkyl and cycloalkyl radicals of from about 1–20 carbon atoms such as methyl, ethyl, propyl, isopropyl, butyl, n-amyl, tertiary amyl, ethylhexyl, cyclopentyl, cyclohexyl, methylcyclohexyl, dimethylcyclohexyl and the ethyl, propyl, butyl and amyl mono-, di- and tri-substituted cyclohexyl radicals. Either R_1 or R_2 or both R_1 and R_2 may be alkyl or cycloalkyl radicals as indicated.

Since the compounds of the present invention have been found to be of particular value in lubricating oil as corrosion inhibitors and detergents it is preferred that they be easily soluble in ordinary hydrocarbon lubricating oils. In order that the compounds of the present invention may possess the requisite oil solubility it is therefore desirable that both R_1 and R_2 be alkyl radicals having a total number of carbon atoms equal to at least 8. More specifically, when R_1 is a propyl radical R_2 should be an alkyl radical at least as long as an amyl radical, R_1 and R_2 may both be butyl radicals, R_1 may be a hexyl radical and R_2 an ethyl radical. When R_1 is hydrogen then R_2 should be a radical of at least 8 carbon atoms such as octyl, dodecyl, tetradecyl, octadecyl or the like. Specific compounds of this group include 2,4-ditertiarybutylphenoxy ethanol, 4-octylphenoxy ethanol, 4-amyl-2-isopropylphenoxy ethanol, 4-octylphenoxy propanol, 2,4-diamylphenoxy iso-propanol, 2,4-diethylhexylphenoxy ethanol and others of a similar character.

Metal salts of the bis(alkyl or aryl substituted phenoxy alkyl) dithiophosphoric acids may be prepared by simple neutralization of the acid with a suitable salt-forming base or by double-decomposition. A wide variety of salt-forming radicals include those of Ni, Al, Pb, Hg, Cd, Sn, Zn, Mg, Na, K, NH_4, Ca, Sr, Ba and others which may be introduced by neutralization of the acid

with a corresponding oxide, hydroxide or carbonate and in some cases sulfide. Some of these salts may be more easily prepared by double-decomposition of the Na salt of the dithiophosphoric acid with a desired metal salt, for example $ZnCl_2$ etc.

The preparation of our new compounds will now be described in greater detail by means of the following example in which the preparation of bis(2,4-diamylphenoxyethyl) dithiophosphoric acid and the Ba salt thereof is described. It will be understood that our invention is not limited to the preparation of this particular compound since it is given primarily for purposes of illustration and our invention is to be construed only by the scope of the appended claims.

Example

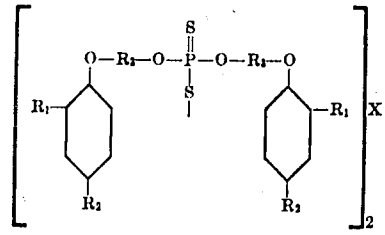
100 parts by weight of 2,4-diamylphenoxy ethanol was stirred and heated for 3.5 hours at 95–105° C. with 22 parts by weight of finely ground P_2S_5. At the end of this time practically all of the P_2S_5 had dissolved and the evolution of the H_2S subsided. The product, crude bis(2,4-diamylphenoxyethyl) dithiophosphoric acid, a light brown liquid, was recovered by decantation from the small amount of unreacted P_2S_5.

The barium salt of the above product was prepared by dissolving 90 parts by weight thereof in 30 parts by weight of toluene and 20 parts by weight of ethanol. 12 parts by weight of finely powdered barium oxide was added and the mixture was warmed at 40–50° C. for 30 minutes at the end of which time the dithiophosphoric acid was neutralized. After filtration of traces of inorganic barium salts the solvent was evaporated, the last of the solvent being removed under reduced pressure. Barium bis(2,4-diamylphenoxyethyl) dithiophosphate remained as a yellow liquid that was practically insoluble in water but easily soluble in hydrocarbon lubricating oils.

Since other alkyl and cycloalkyl substituted phenoxyalkylols may be reacted with P_2S_5 in the same way using similar proportions of materials and reaction conditions further description of the preparation of these products is not thought necessary.

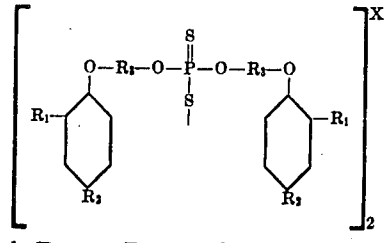
We claim:

1. Chemical compounds having the formula



in which R_1 and R_2 are alkyl radicals having a combined number of carbon atoms of at least 8, R_3 is an alkylene radical containing 2 to 4 carbon atoms inclusive, and X is a metal selected from the group consisting of calcium, barium, strontium, magnesium, zinc, mercury, cadmium and tin.

2. Chemical compounds having the general formula



in which R_1 and R_2 are alkyl radicals having a combined number of carbon atoms of at least 8, R_3 is an alkylene radical containing 2–4 carbon atoms inclusive, and X is an alkaline earth metal.

3. Barium bis(2,4-diamyl phenoxyethyl) dithiophosphoric acid.

4. Barium bis(2,4-dibutyl phenoxyethyl) dithiophosphoric acid.

ELMER WILLIAM COOK.
WILLIAM DAVID THOMAS, JR.