

## UNITED STATES PATENT OFFICE

2,226,552

ALICYCLIC PHOSPHITE COMPOUNDS AND  
METHOD OF MANUFACTURING SAMERobert E. Conary and Harry V. Ashburn, Beacon,  
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York, N. Y., a corporation of DelawareNo Drawing. Application March 16, 1939,  
Serial No. 262,199

6 Claims. (Cl. 260-461)

This invention relates to novel alicyclic phosphite compounds and to their method of preparation.

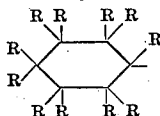
Heretofore, certain aryl and alkyl phosphites have been prepared, such as triphenyl phosphite, tricresyl phosphite, tributyl phosphite, etc. These materials have been suggested as additives for lubricating oil to impart certain advantageous properties thereto, particularly to inhibit bearing corrosion when employed in a motor oil adapted for crank case lubrication.

We have now discovered that a novel group of alicyclic organic compounds can be prepared in accordance with the method of this invention, these compounds constituting superior additives for lubricating oil having unexpected and additional properties over those previously known. The compounded oil and the method of lubricating the bearings and cylinders of internal combustion engines with mineral lubricating oil containing these compounds, are described and claimed in the co-pending application of Harry V. Ashburn, Robert E. Conary and Paul S. Stutsman filed concurrently herewith.

The alicyclic organic phosphite compounds of this invention are represented by the formula

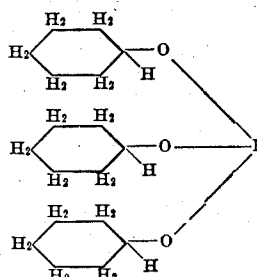


in which A is an alicyclic organic radical of the type



in which R represents hydrogen or the same or different alkyl, aryl or aralkyl radicals, and in which R<sub>1</sub> and R<sub>2</sub> above represent hydrogen or the same or different alicyclic radicals of the type enumerated for A above. By alicyclic phosphite compounds, it is understood that this means the phosphite esters of that group of cyclic compounds derived from the corresponding acyclic compounds, such as the cycloparaffins of the formula C<sub>6</sub>H<sub>12</sub>, in which the alicyclic radical is substituted for one or more of the hydrogens of phosphorous acid giving the corresponding mono-, di- or tri-phosphite.

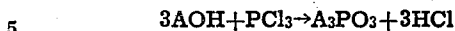
As representative of compounds of this invention, there is mentioned tri-cyclohexyl-phosphite having the structural formula



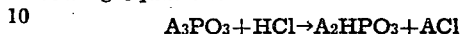
which may be written (C<sub>6</sub>H<sub>11</sub>)<sub>3</sub>PO<sub>3</sub>, in which three cyclohexyl radicals are substituted for the three hydrogen atoms of phosphorous acid. Similar di- and mono-cyclohexyl phosphite compounds are also included, such as di-cyclohexyl mono-hydrogen phosphite and mono-cyclohexyl di-hydrogen phosphite. Similarly, the mono-, di- or tri-alkyl substituted cyclohexyl phosphite compounds are included, such as those containing the corresponding substituted radicals of methyl-cyclohexane, 1,1-dimethyl-cyclohexane, 1,2-dimethyl-cyclohexane, 1,3-dimethyl-cyclohexane, 1,4-dimethyl-cyclohexane, ethyl-cyclohexane, 1,2-methyl-ethyl-cyclohexane, normal propyl-cyclohexane, 1,3,5-trimethyl-cyclohexane, 1,3,4-trimethyl-cyclohexane, 1,3,5-dimethyl-ethyl-cyclohexane, 1,4-methyl-isopropyl-cyclohexane, and the like. Likewise, similar phosphite compounds containing the aryl or aralkyl substituted cyclohexyl radical or radicals are contemplated, including those in which one or more of the hydrogens of a substituted cyclohexyl radical or radicals is substituted by phenyl, tolyl, xylol and the like.

These compounds are prepared by reacting a phosphorus trihalide, such as phosphorus trichloride, phosphorus tribromide, etc., with the corresponding alicyclic alcohol, frequently termed a ring-alcohol of a hydro-aromatic hydrocarbon. The reaction is carried out in the presence of a suitable low boiling organic solvent and a material which is effective to take up HCl or other hydrogen halide as formed in the reaction. The chlorine of the phosphorus trichloride splits off hydrogen of the OH group of the alcohol, forming

hydrochloric acid, the valence of the oxygen being satisfied by attaching to the phosphorus atom. This is represented by the equation:



In the presence of free HCl, the resulting normal ester tends to decompose into the acid ester and alicyclic organic chloride, as shown by the following equation:



But by carrying out the reaction in the presence of a material which reacts readily with HCl to form a stable hydrochloride addition product or a chloride and thereby remove the HCl from the scene of reaction, it can be made to go to substantial completion with the formation of the normal ester. Three mols of the alicyclic alcohol are used with one mol of phosphorus trichloride in the presence of at least three mols or more of an HCl sequestering reagent to form the corresponding tri-substituted phosphite.

In order to produce a di-substituted alicyclic phosphite, the same molecular proportions of phosphorus trichloride and the alcohol are used so as to replace the three chlorine atoms of the phosphorus trichloride and form the corresponding alicyclic phosphite, but in this case two mols of the HCl sequestering reagent are used so that one mol of HCl is left to react with the tri-alicyclic-phosphite to split off one alicyclic radical from the molecule, forming the di-alicyclic monohydrogen phosphite and the corresponding alicyclic chloride. These can then be separated by distillation to recover the acid ester.

The above reactions are carried out generally at low temperatures, such as from about 0° F. to about 50° F. In the case of the normal ester and the mono-hydrogen ester, the phosphorus trichloride is preferably added dropwise to the cooled mixture of alicyclic alcohol, solvent and HCl sequestering agent. After completion of the addition of the phosphorus trichloride, the mixture is preferably refluxed for a period of time at the boiling point of the solvent used. It is then cooled, washed with water to remove any free acid, and then dried in the presence of a suitable desiccant such as anhydrous sodium or calcium sulfate. The dried mixture is then distilled under vacuum to remove the solvent and any remaining HCl sequestering agent and unreacted alcohol as well as any alicyclic chloride which may be present. The residue is then distilled under high vacuum to recover the desired ester as a distillate.

Any low boiling aliphatic or aromatic hydrocarbon or chlorinated hydrocarbon solvent can be employed, although preferably one is selected which boils below about 212° F. Examples of suitable solvents are pentane, hexane, heptane, carbon tetrachloride, benzene, and the like. If the reaction is carried out under pressure, liquefied normally gaseous hydrocarbons of the character of propane, butane, and the like may be used, and the temperature of the reacting mass can be controlled by evaporative cooling upon controlled release of pressure to vaporize and liberate a portion of the solvent.

Any suitable HCl sequestering reagent which is nonreactive with the other ingredients of the mix and which can be readily separated from the reaction product, can be employed. Examples of these reagents are pyridine and its homologs, various amines, particularly the tertiary amines such as trimethyl amine, triethyl amine, and the

like. Also, various alkali and alkaline earth carbonates may be employed, such as calcium carbonate.

By way of example, the preparation of tri-cyclohexyl-phosphite is described herein, although it is understood that this is given for the purpose of illustration and the invention is not limited thereto. In this case one mol of phosphorus trichloride was added dropwise to a cooled agitated mixture of three mols of dry cyclohexanol about 3.3 mols of dry pyridine and an approximately equal weight of dry benzene, while the temperature was maintained between 23° F.-50° F. After complete addition of the phosphorus trichloride, the mixture was allowed to warm up to room temperature, then heated to boiling and refluxed for two hours. After cooling to room temperature, the mixture was washed with cold water until the wash water gave no acid test to litmus. The mixture was then dried over anhydrous calcium sulfate; and the dried mixture distilled under vacuum to remove remaining pyridine, benzene and cyclohexanol. The resulting product by constituent analysis and particularly phosphorus content was found to consist primarily of tri-cyclohexyl phosphite, containing roughly 80-90% of tri-cyclohexyl phosphite and about 20-10% of di-cyclohexyl monohydrogen phosphite.

Distillation under vacuum was continued and the desired product passed over at about 315-347° F. under an absolute pressure of 10-15 mm. mercury. This material was an oily liquid soluble in mineral lubricating oil and insoluble in water.

Wherever the expression "phosphorus trichloride" appears in the specification and claims, it is to be understood that other phosphorus trihalides are included under the doctrine of equivalents; likewise, wherever the expression "HCl sequestering reagent" appears in the description and claims, it is to be understood that this includes a reagent which is active to react with other hydrogen halides produced in the reaction by the use of other phosphorus trihalides than the chloride.

Obviously many modifications and variations of the invention as hereinbefore set forth may be made without departing from the spirit and scope thereof, and only such limitations should be imposed as are indicated in the appended claims.

We claim:

1. The method of preparing an alicyclic phosphite material consisting primarily of the tri-alicyclic ester of phosphorus acid, in which the alicyclic radical is selected from the group consisting of cyclohexyl and alkyl, aryl and aralkyl substituted cyclohexyl, which comprises reacting three mols of an alicyclic alcohol selected from the group consisting of cyclohexanol and alkyl, aryl and aralkyl substituted cyclohexanol, with one mol of phosphorus tri-chloride in the presence of at least three mols of an HCl sequestering reagent.

2. As a new composition of matter, an alicyclic phosphite material consisting primarily of the tri-alicyclic ester of phosphorus acid, in which the alicyclic radical is selected from the group consisting of cyclohexyl and alkyl, aryl and aralkyl substituted cyclohexyl.

3. The composition as defined in claim 2, in which the alicyclic phosphite material consists primarily of tri-cyclohexyl phosphite.

4. The composition as defined in claim 2, in which the alicyclic phosphite material consists primarily of a tri-methylcyclohexyl phosphite.

5 5. The method of manufacturing tri-cyclohexyl-phosphite, which comprises reacting three mols of cyclohexanol with one mol of phosphorus trichloride in the presence of at least three mols of an HCl sequestering reagent.

6. The method of manufacturing tri-cyclohexyl-phosphite, which comprises adding one mol of phosphorus trichloride to a cooled and agitated

mixture of three mols of cyclohexanol and at least three mols of an HCl sequestering reagent in the presence of a low boiling organic solvent, refluxing the mixture, and then recovering the resultant tricyclohexyl phosphite by vacuum distillation.

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