UNITED STATES PATENT OFFICE

2,573,658

PURIFICATION OF ESTERS OF ORTHO-PHOSPHORIC ACID

William E. Weesner, Webster Groves, Mo., assignor to Monsanto Chemical Company, St. Louis, Mo., a corporation of Delaware

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7 Claims. (Cl. 260—461)

1. This invention relates to esters of ortho-phosphoric acid; more specifically this invention relates to an improvement in the process for the purification of esters of ortho-phosphoric acid having the formula

\[
\begin{align*}
&\text{R}_1 - \overset{\text{O}}{\text{P}} - \overset{\text{O}}{\text{R}_2} \\
&\text{R}_3
\end{align*}
\]

wherein R1, R2 and R3 are selected from the group consisting of alkyl radicals having at least 6 and not more than 18 carbon atoms and alkoxyl radicals wherein the alkyl substituent contains at least 4 and not more than 18 carbon atoms.

In the preparation of the above described trialkyl phosphates or trialkoxyethyl phosphates, the formation of mono- or di-substituted acid phosphates, hereinafter referred to as partial esters of phosphoric acid, are unavoidable, yet their presence in the finished product is undesirable. These partial esters are insoluble in water and at ordinary temperatures, the alkyl metal salts of these partial esters of phosphoric acid are more soluble in the ester than in water which makes them exceedingly difficult to remove by washing. Furthermore, these partial esters of phosphoric acid which are formed during the preparation of the trialkyl phosphates or trialkoxyethyl phosphates which are the subject of this invention, are difficult to separate from the crude ester by fractionation, as at the temperatures required for such a fractionation, these partial esters tend to decompose releasing volatile products which further contaminate the finished ester and render it exceedingly difficult to maintain the low pressure necessary for such a fractionation.

It is an object of this invention to provide an improved process for the purification of esters of ortho-phosphoric acid. It is a further object of this invention to provide an improved process for the removal of the partial esters of phosphoric acid formed during the preparation of trialkyl and trialkoxyethyl phosphates. Further objects will become apparent from the description of the novel improved process of this invention and the claims.

It has now been discovered that the mono- or di-substituted esters of phosphoric acid, the so-called partial esters of phosphoric acid, found as impurities in trialkyl phosphates or trialkoxyethyl phosphates, can easily be removed from the trialkyl phosphate or trialkoxyethyl phosphate by first converting the partial ester of phosphoric acid to its alkali metal salt, and then washing with water at a temperature in excess of about 85°C. At this higher temperature the alkali metal salts of the partial esters of phosphoric acid are more soluble in water than in the ester, and hence may be washed out without difficulty.

In carrying out the novel purification process of this invention, a sufficient quantity of an alkaline alkali metal salt, that is an alkali metal salt whose aqueous solution is basic to litmus, or an alkali metal hydroxide is added to the crude ester to render the ester alkaline. The alkaline alkali metal salt or the alkali metal hydroxide may be added per se or in solution. Typical of such compounds are the phosphates, carbonates, carbonates and hydroxides of sodium, potassium and lithium. After the reaction mass has been rendered alkaline, it is then thoroughly washed with water at a temperature in excess of about 85°C, whereupon the alkali metal salts of the partial esters of phosphoric acid are removed from the reaction mass due to their greater solubility in water than in the ester at this temperature. The washing procedure may be carried out in any of several convenient manners. The reaction mass may be agitated with water at a temperature in excess of 85°C, and while maintaining this temperature, the water layer separated and decanted from the reaction mass. The washing procedure may also be conveniently carried out by introducing steam into the alkaline reaction mass, allowing the steam to condense and cool at a temperature in excess of about 85°C, and after sufficient condensation has taken place, decanting the water having dissolved therein the alkali metal salts of the partial esters of phosphoric acid.

Typical, but not exhaustive, of the phosphates that may be purified in the above described manner are those symmetrical trialkyl or trialkoxyethyl phosphates wherein the substituents are straight or branched hexyl, heptyl, octyl, nonyl, decyl, dodecyl, tridecyl, tetradecyl, octadecyl, butoxyethyl, hexoxyethyl, octoxyethyl, deoxyethyl, tetradecoxyethyl and octadecoxyethyl radicals. Unsymmetrical esters of phosphoric acid that may be purified according to the novel process of this invention may contain 2 or more dissimilar radicals of which the aforementioned radicals are illustrative.

The novel process of this invention has also been found to be of some utility in the purifica-
tion of mixed alkyl aryl phosphates. Its utility in the preparation of such esters is not, however, as pronounced or outstanding as in the preparation of trialkyl and trialkoxyethyl phosphates. The following examples illustrate the novel improved process of this invention:

Example I

273.0 g. of 2-ethylhexyl alcohol was placed in a glass reactor and 40 g. of POCl₃ added with stirring at 6 to 10° C. over a period of one hour. The mass was stirred and heated to 23° C. for a two hour period, after which time vacuum was applied and the heating continued until 80° C., and 22 mm. Hg pressure was obtained. The mass was held at this temperature and pressure for 15 hours. 50 ml. of water was then added and the mixture was made alkaline with 2.2 g. of sodium carbonate. Excess alcohol was then removed by heating the mass gradually to 142° C. under 30 mm. Hg pressure. Water was then added to the material left in the reactor, and the mass was steamed at 100 to 105° C. until 300 ml. of distillate had been collected. The layer was still alkaline after steaming and the mass was settled at 90 to 95° C. and the water layer drained off. Five additional water washes were made at 90 to 95° C. to complete the removal of partial esters. The layer was then dried under vacuum at about 100° C. The tri(2-ethylhexyl) phosphate thus obtained had the following properties:

Acidity as H₃PO₄ ——— per cent. 0.015
Sp. gr. 25/25° C. ———— 0.9195
Color ——— Nearly water white

Example II

Crude tri(n-hexyl) phosphate was prepared in the manner described in Example I utilizing 1,235.4 g. of n-hexyl alcohol and 307.0 g. of POCl₃. The partial esters were removed by first forming the sodium salts using sodium carbonate and then washing with water at 85 to 90° C. The ester was then dried under vacuum and the thus refined material exhibited the following properties:

Acidity as H₃PO₄ ———— per cent. 0.002
Sp. gr. 25/25° C. ———— 0.937
N₀² ———— 1.4040

Example III

Crude tri(n-octyl) phosphate was prepared as described in Example I utilizing 1,188.2 g. of n-octyl alcohol and 293.0 g. of POCl₃. The n-octyl acid phosphates in the crude ester were removed by first forming their alkali metal salts by adding sufficient sodium carbonate to render the entire reaction medium alkaline, and then washing with water at about 100° C. The washed ester was then dried under vacuum and the thus refined material had the following properties:

Acidity as H₃PO₄ ———— per cent. 0.02
Sp. gr. 25/25° C. ———— 0.915
N₀² ———— 1.4403

Example IV

The crude tri(n-decyl) phosphate was prepared in the manner described in Example I utilizing 533.0 g. of n-decanol and 84.4 g. of POCl₃. The partial esters formed in the preparation were removed by treating the reaction mass with alkali with an alkali alkali metal salt, sodium carbonate, and then washing with water at about 95° C. The washed ester was then dried under vacuum. Tri(n-decyl) phosphate was thus obtained in an 86% yield based on POCl₃ and exhibited the following properties:

Acidity as H₃PO₄ ———— per cent. 0.04
Sp. gr. 25/25° C. ———— 0.901
N₀² ———— 1.4452

Example V

Crude tri(methylhexyl) phosphate was prepared in the manner described in Example I utilizing 76.7 g. of POCl₃ and 230 g. of 6-methyl-1-heptanol. The partial esters formed in the preparation were removed by treating the reaction mass until alkaline with potassium carbonate, and then washing with water at about 100° C. The washed ester was dried under vacuum thereby obtaining in excellent yield and purity tri(methylhexyl) phosphate.

Example VI

Crude tri(but-a-butoxyethyl) phosphate was prepared in the manner described in Example I using 144 g. of ethylene glycol monobutyl ether and 154.4 g. of POCl₃. The partial esters were removed by rendering the crude ester alkaline by the addition of sodium hydroxide followed by washing with water at a temperature in the range of about 85° to 90° C. The washed ester was then dried under vacuum thereby obtaining substantially pure tri(butyloxyethyl) phosphate.

What is claimed is:

1. In the process for the purification of esters of ortho-phosphoric acid having the formula

   ![](https://via.placeholder.com/150)

   wherein R₁, R₂ and R₃ represent a radical selected from the group consisting of alkyl radicals having at least 6 and not more than 18 carbon atoms and alkoxyalkyl radicals wherein the alkyl substituent contains at least 4 and not more than 18 carbon atoms, the steps comprising adding to the crude ester a compound selected from the group consisting of the alkali metal salts and alkali metal hydroxides so as to render said crude ester alkaline and then washing with water at a temperature in excess of about 85° C.

2. In the process for the purification of esters of ortho-phosphoric acid having the formula

   ![](https://via.placeholder.com/150)

   wherein R₁, R₂ and R₃ represent an alkyl radical having at least 6 and not more than 18 carbon atoms, the steps comprising adding to the crude ester a compound selected from the group consisting of the alkali metal salts and alkali metal hydroxides so as to render said crude ester alkaline and then washing with water at a temperature in excess of about 85° C.

3. In the process for the purification of a triolyl phosphate the steps comprising adding to the crude triolyl phosphate a compound selected from the group consisting of the alkali metal salts and alkali metal hydroxides so as to render said crude triolyl phosphate alkaline and then washing with water at a temperature in excess of about 85° C.

4. In the process for the purification of tri-(2-ethylhexyl) phosphate the steps comprising...
adding to the crude tri(2-ethylhexyl) phosphate a compound selected from the group consisting of the alkaline alkali metal salts and alkali metal hydroxides so as to render said crude tri(2-ethylhexyl) phosphate alkaline and then washing with water at a temperature in excess of about 85°C.

5. In the process for the purification of tri-(6-methylheptyl) phosphate the steps comprising adding to the crude tri(6-methylheptyl) phosphate a compound selected from the group consisting of the alkaline alkali metal salts and alkali metal hydroxides so as to render said crude tri(6-methylheptyl) phosphate alkaline and then washing with water at a temperature in excess of about 85°C.

6. In the process for the purification of esters of ortho-phosphoric acid having the formula

\[
\begin{align*}
\text{O} & \quad \text{O} \\
\text{R}_1 & \quad \text{R}_2 \\
\text{R}_3 & \quad \text{R}_4
\end{align*}
\]

wherein R₁, R₂ and R₄ represent an alkoxyethyl radical wherein the alkyl substituent contains at least 4 and not more than 18 carbon atoms, the steps comprising adding to the crude ester a compound selected from the group consisting of the alkaline alkali metal salts and alkali metal hydroxides so as to render said crude ester alkaline and then washing with water at a temperature in excess of about 85°C.

7. In the process for the purification of tri-(beta-butoxyethyl) phosphate the steps comprising adding to the crude tri(beta-butoxyethyl) phosphate a compound selected from the group consisting of the alkaline alkali metal salts and alkali metal hydroxides so as to render said crude tri(beta-butoxyethyl) phosphate alkaline and then washing with water at a temperature in excess of about 85°C.

WILLIAM F. WEESENER.

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

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Certificate of Correction

Patent No. 2,573,658

WILLIAM W. WEESNER

October 30, 1951

It is hereby certified that error appears in the printed specification of the above numbered patent requiring correction as follows:

Column 4, line 24, for "and 154.4" read "and 153.4;"

and that the said Letters Patent should be read as corrected above, so that the same may conform to the record of the case in the Patent Office.

Signed and sealed this 19th day of February, A. D. 1952.

[SEAL]

THOMAS F. MURPHY,
Assistant Commissioner of Patents.