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COMPLETE SPECIFICATION

Production of Trialkyl Phosphites

We, MONSANTO CHEMICAL COMPANY, a corporation organised under the laws of the State of Delaware, United States of America, of 1700, South Second Street, City of St. Louis, State of Missouri, United States of America do hereby declare the invention for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to the production of trialkyl phosphites.

It is known that trialkyl phosphites are produced by the interaction of a phosphorus trihalide, such as phosphorus trichloride, and an alkanol with concomitant production of a hydrogen halide. The latter has been shown to hydrolyse the tri-ester to acid esters, phosphorous acid and an alkyl halide. Various expedients have been proposed to remove the free hydrogen halide rapidly from the reaction mixture. One of these is to use an organic tertiary amine in at least sufficient amount to react with all the hydrogen halide as it is liberated. This gives a good yield of trialkyl phosphite but the procedure is expensive since it entails the recovery of tertiary amine for re-use in the process.

In another process (see U.S. Patent Specification No. 2,678,940) it has been proposed to add a phosphorus trihalide to at least the theoretical quantity of an alkanol, which may be diluted with an inert solvent, and simultaneously to introduce dry ammonia so that the hydrogen halide liberated is just neutralised. This materially reduces the amount of decomposition products produced but we have nevertheless found that the trialkyl phosphite produced by this process is contaminated with some dialkyl phosphite: in addition the reaction mixture contains ammonium halide and must be purified therefrom. It is believed that the use of water to dissolve the ammonium halide may result in the formation of dialkyl phosphite. If the

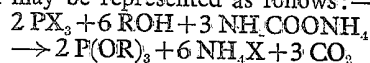
ammonium halide is separated and the organic phase distilled it is difficult to separate the di- and tri-alkyl phosphites owing to the proximity of their boiling points.

We have now found that ammonium carbamate can be used with good effect in the production of trialkyl phosphites and in the purification of reaction mixtures containing the same.

According to the present invention there is provided a process for the production of a trialkyl phosphite which comprises treating an alkanol with a phosphorus trihalide (a) in the presence of ammonium carbamate or (b) in the presence of another acid acceptor followed by purification of the reaction product in the presence of ammonium carbamate, in either case the ammonium carbamate being present in an amount which will maintain a pH of at least 7.

In one embodiment the present invention provides a process for the production of a trialkyl phosphite which comprises reacting a phosphorus trihalide and at least a stoichiometric equivalent of an alkanol under anhydrous conditions in the presence of ammonium carbamate, the pH of the reaction mixture being at least 7.

The over-all equation involved in this reaction may be represented as follows:—



in which X is a halogen atom and R is an alkyl group. Preferably the phosphorus trihalide and the alkanol are used in stoichiometric amounts and sufficient ammonium carbamate is added to maintain a pH of at least 7 throughout the course of the reaction. Preferably the amount of ammonium carbamate employed is in excess of the stoichiometric amount required to react with the phosphorus trihalide, and may be 125% to 200% of such amount. When an excess of ammonium carbamate is employed the whole amount or any part thereof may be initially charged to the

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- reactor and the remainder added as the reaction proceeds so as to maintain a pH of at least 7. The invention is not limited to the use of an excess of preformed ammonium carbamate but
- 5 may involve production thereof in situ at a pH of at least 7. Thus, ammonium carbamate in an amount less than the stoichiometric equivalent of the phosphorus trihalide may be charged initially, and, as the reaction
- 10 proceeds and carbon dioxide is evolved, anhydrous ammonia may be added so as to react with the carbon dioxide to form additional ammonium carbamate to maintain the reaction system at a pH of 7 or above. However,
- 15 the amount of anhydrous ammonia should not substantially exceed that which theoretically combines with the carbon dioxide evolved to provide ammonium carbamate.
- The alkanol may be employed in the stoichiometric amount or in excess with respect to the phosphorus trihalide and may be diluted with an inert organic solvent. Examples of inert organic solvents which may be employed are diethyl ether, petroleum
- 20 ether, methyl chloride, dichloromethane, ethyl chloride, methyl ethyl ether, butane, pentane, hexane and heptane. The phosphorus halide may also be added in solution. It is preferred that the temperature be maintained between
- 25 -40° and $+30^{\circ}$ C.
- After the reaction between the phosphorus trihalide, the alkanol and the ammonium carbamate has been completed, the reaction mixture contains solid ammonium halide together
- 30 with any excess of ammonium carbamate. The solid materials may be removed by filtration and washed with an organic solvent for the trialkyl phosphite. However, it is preferred to add at least sufficient water to dissolve the
- 35 solid materials and to agitate the resulting mixture. The presence of excess ammonium carbamate in solution appears to stabilise the trialkyl phosphite against hydrolysis whilst impurities pass into the aqueous phase. The
- 40 use of an excess of ammonium carbamate is thus of advantage in working up the reaction product. Aqueous ammonium carbamate may likewise be used to wash the combined filtrate and organic solvent washings referred to
- 45 above.
- It has further been found that the presence of ammonium carbamate is advantageous in working up the product when an acid acceptor other than ammonium carbamate has been
- 50 used to remove the hydrogen halide liberated by the reaction between the phosphorus trihalide and the alkanol. This is particularly the case when anhydrous ammonia is used since the product concomitantly produced is an ammonium halide and the product may be
- 55 worked up in the manner described above, aqueous ammonium carbamate solution being used instead of water to dissolve the solid ammonium halide phase or for washing the
- combined filtrate and organic solvent washings.
- 65 Accordingly the invention also provides a process for the production of a trialkyl phosphite which comprises reacting a phosphorus trihalide and at least the stoichiometric equivalent of an alkanol, adding anhydrous ammonia thereto as acid acceptor to maintain the reaction mixture substantially neutral and washing the resulting reaction mixture with
- 70 an aqueous solution containing sufficient ammonium carbamate to maintain a pH of at least 7.
- Such process may be carried out by the gradual addition of a phosphorus trihalide, more especially phosphorus trichloride, to an alkanol present in an amount at least stoichiometrically equivalent to the phosphorus trihalide. Dry ammonia is introduced in such amounts that the hydrogen halide liberated is just neutralised substantially as it is formed.
- 75 An organic solvent, which may be any of those previously named, may be present. The crude reaction mass so obtained is a heterogeneous mixture of the desired trialkyl phosphite, some dialkyl phosphite, ammonium halide, an organic solvent, if used, and usually some other impurities. Upon intimate mixing with an aqueous solution of ammonium carbamate an aqueous layer and an organic layer are formed. The organic layer in most instances consists of the organic solvent and the trialkyl phosphite. This organic layer, after separation from the aqueous layer, and fractional distillation provides substantially
- 80 pure trialkyl phosphite. The amount of trialkyl phosphite recovered is substantially quantitative based upon the amount present in the crude reaction mass.
- The trialkyl phosphite may be washed in a plurality of countercurrent stages with an aqueous solution of ammonium carbamate or by countercurrent flow. The concentration of ammonium carbamate may vary widely, but sufficient should be present to destroy any acid esters and there should be sufficient
- 85 water to dissolve the water-soluble by-products. The aqueous solution of ammonium carbamate should be used in such concentration and amount as to maintain a pH of at least 7, preferably 7 to 10, throughout the
- 90 washing operation. The temperature at which the washing operation is conducted may vary widely; temperatures between 0° and 30° C. are preferably employed.
- Whilst the process of this invention is applicable to the preparation of trialkyl phosphites from a wide variety of straight and branched chain alkanols, it is especially useful for the preparation of trialkyl phosphites from methanol, ethanol and isopropanol.
- 95 While any pH of at least 7 may be employed in the process of preparation and/or purification according to this invention, it is preferred that a pH of 7 to 10 be employed. The pH
- 100
- 105
- 110
- 115
- 120
- 125

is that of an aqueous solution of a representative sample of the reacting mass or of the aqueous washing solution.

5 The following examples illustrate the nature of this invention and the manner in which it may be performed. All parts are by weight. In all cases the amount of ammonium carbamate used is at least sufficient to maintain a pH of at least 7 during the reaction and
10 for purification.

EXAMPLE I

To a reaction vessel equipped with a stirrer, thermometer and a condenser is charged 58 parts of methyl alcohol, 140 parts
15 of ammonium carbamate and 468 parts of dichloromethane. During 4.5 hours there is added, with agitation, a mixture of 68.7 parts of phosphorus trichloride and 134 parts of dichloromethane, while maintaining the temperature at substantially -5° C. When all
20 the phosphorus trichloride has been added the mass is agitated at room temperature and subsequently admixed with 300 parts of water and the mixture agitated at room temperature for 15 minutes. The organic layer is separated
25 (analysis indicated that the organic layer contained 96.5% of the theoretical of trivalent phosphorus), dried over anhydrous sodium sulphate, and distilled at atmospheric pressure to remove dichloromethane. Upon dis-
30 stilling the residue a yield of 86.45% of pure trimethyl phosphite is obtained.

EXAMPLE II

To a reaction vessel equipped with a stirrer thermometer and a condenser is charged 82.8
35 parts of ethyl alcohol, 85.8 parts of ammonium carbamate and 334 parts of dichloromethane. There is added during 1.1 hours a mixture of 68.8 parts of phosphorus trichloride and 134 parts of dichloromethane, whilst agitating
40 and maintaining the temperature at -5° to 0° C. Upon completion of the addition the mass is agitated at room temperature for 1.2 hours. It is washed with 270 parts of
45 water to remove the water-soluble substances. The organic layer is separated (analysis indicated that it contained 99.2% of the theoretical of trivalent phosphorus) and distilled at atmospheric pressure to remove the dichloro-
50 methane. Upon subjecting the residue to distillation under reduced pressure a yield in excess of 93% of pure triethyl phosphite is obtained.

EXAMPLE III

55 To a reaction vessel equipped with a stirrer, thermometer and a condenser is charged 108 parts of isopropyl alcohol, 78 parts of ammonium carbamate, and 334 parts of dichloro-
60 methane. There is added during 4 hours a mixture of 68.8 parts of phosphorus trichloride and 67 parts of dichloromethane, whilst agitating and maintaining the temperature at -2° to $+4^{\circ}$ C. Upon completion of the addition the mass is agitated at room

temperature for 3 hours. It is washed with 250 parts of water to remove the ammonium chloride and excess of ammonium carbamate. The organic layer is separated, dried over anhydrous sodium sulphate, and distilled at atmospheric pressure to remove the dichloro-
70 methane. Upon distilling the residue under reduced pressure a yield of 92.5% of pure tri-isopropyl phosphite is obtained.

Similarly high yields of the corresponding trialkyl phosphite are obtained employing in place of the alcohols of Examples I, II and III such alcohols as *n*-hexanol-*n*-heptanol,
75 2-ethylhexanol, decanol and dodecanol.

In the preparation of trialkyl phosphites from higher molecular weight alkanols, such as those having six to twelve carbon atoms, it is an advantage to employ a small proportion of a trialkylamine in the reaction mixture.
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EXAMPLE IV

To a reaction vessel equipped with a stirrer, thermometer and a condenser is charged 217 parts of *n*-heptyl alcohol, 85.8 parts of ammonium carbamate, 15 parts of triethylamine, and 400 parts of dichloro-
90 methane. There is added during 3 hours a mixture of 68.8 parts of phosphorus trichloride and 134 parts of dichloromethane, whilst agitating and maintaining the temperature at 0° C. Upon completion of the addition the mass is agitated at room temperature for 3 hours. It is washed with 310
95 parts of water to remove the water-soluble materials present. The organic layer is separated, dried over anhydrous sodium sulphate, and distilled to remove the dichloromethane. The residue (162.3 parts) is admixed with 30 parts of *n*-heptyl alcohol and refluxed for 3 hours. It is then distilled under reduced pressure. The product collects at $112-114^{\circ}$ C. at 0.08 mm. and is pure tri-*n*-heptyl phosphite (yield 52% of theory based on the phosphorus trichloride charged).
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EXAMPLE V

A crude trimethyl phosphite obtained by reacting phosphorus trichloride and methanol in the stoichiometric amounts necessary to provide trimethyl phosphite in the presence of dichloromethane while maintaining the system substantially neutral by the addition of ammonia and consisting essentially of:—
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	Parts by Weight	
Trimethyl phosphite	14	
Dimethyl phosphite	4.7	
Ammonium chloride	30	
Dichloromethane	234	120

was intimately mixed with an aqueous solution containing 25 parts of ammonium carbamate and 130 parts of water at room temperature. After 15 minutes of mixing substantially 90% of the dimethyl phosphite was destroyed,
125 whilst after 30 minutes all was destroyed and the decomposition products were present

in the aqueous layer. The organic layer consisted of dichloromethane and trimethyl phosphite. Upon fractionally distilling the organic layer substantially 14 parts of pure trimethyl phosphite was obtained.

- 5 Similarly by washing the crude trialkyl phosphite obtained by reacting, in stoichiometric proportions, a phosphorus halide and ethanol, propanol or isopropanol in the presence of an inert organic solvent, the reaction mixture being maintained substantially neutral by the addition of anhydrous ammonia, with an aqueous solution containing sufficient ammonium carbamate to maintain a pH of at least 7, the corresponding trialkyl phosphite is recovered in a substantially quantitative amount of that present in the crude reaction mass.

WHAT WE CLAIM IS:—

- 20 1. A process for the production of a trialkyl phosphite which comprises treating an alkanol with a phosphorus trihalide (a) in the presence of ammonium carbamate or (b) in the presence of another acid acceptor followed by purification of the reaction product in the presence of ammonium carbamate, in either case the ammonium carbamate being present in an amount which will maintain a pH of at least 7.
- 30 2. A process for the production of a trialkyl phosphite which comprises reacting a phosphorus trihalide and at least a stoichiometric equivalent of an alkanol under anhydrous conditions in the presence of ammonium carbamate, the pH of the reaction mixture being at least 7.
- 35 3. A process according to Claim 2 in which the temperature of the reaction mixture is between -40° and $+30^{\circ}$ C.
- 40 4. A process according to either of Claims 2 or 3 in which the reaction is carried out in the presence of an inert, organic solvent.
5. A process according to any of Claims 2 to 4 in which the ammonium carbamate is in excess of the stoichiometric amount required to react with the phosphorus trihalide.

6. A process according to Claim 5 in which the amount of ammonium carbamate is 125—200% of the stoichiometric amount.

7. A process according to any of Claims 2 to 6 in which water is added to the crude reaction product, the resulting mixture agitated and the aqueous phase thus separated.

8. A process for the production of a trialkyl phosphite which comprises reacting a phosphorus trihalide and at least the stoichiometric equivalent of an alkanol, adding anhydrous ammonia thereto as acid acceptor to maintain the reaction mixture substantially neutral and washing the resulting reaction mixture with an aqueous solution containing sufficient ammonium carbamate to maintain a pH of at least 7.

9. A process according to Claim 8 in which the reaction is carried out in the presence of an inert inorganic solvent.

10. A process according to either of Claims 8 or 9 in which the reaction mixture is washed with the ammonium carbamate until any dialkyl phosphite present has been substantially wholly decomposed.

11. A process according to any of Claims 8 to 10 in which the aqueous solution contains sufficient ammonium carbamate to maintain the pH between 7 and 10.

12. A process according to any of Claims 8 to 11 in which the washing is carried out at 0 to 30° C.

13. A process according to any of the preceding claims in which the alkanol is methanol, ethanol or a propanol.

14. A process according to any of the preceding claims in which the phosphorus trihalide is phosphorus trichloride.

15. A trialkyl phosphite whenever produced by the process according to any of the preceding claims.

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