

CONTINUOUS PHOSPHORYLATION PROCESS

This invention relates to a continuous process for producing aliphatic phosphate esters by continuously reacting an alkali metal alkoxide with phosphorus oxychloride.

The production of aliphatic phosphates such as trialkyl phosphates and trialkoxyalkyl phosphates are generally done in batch processes on a relatively small scale. The production of tributyl phosphate and tri-butoxyethyl phosphate esters are described in detail in U.S. Patent 3,020,303.

The time lost between batches in batch processes make them time inefficient. Exothermic batch phosphorylation reactions can be made more time efficient by increasing available cooling capacity. This makes it possible to use higher feed rates, shorter reaction cycles and large batch sizes. Inevitable variations occur in batch size and quality. Low quality is reflected in losses of 6 to 10% which are economically undesirable and are unacceptable as they are difficult to dispose of under current environmental protection laws.

According to the present invention, there is provided a continuous process for producing aliphatic phosphates in a non-oxidizing atmosphere which comprises:

- a. continuously introducing a 20 to 30 weight percent solution of an alkali metal alkoxide

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into a reactor at a rate of 7.57 to 113.56 litres per minute (2 to 30 U.S. gallons per minute);

- b. continuously introducing phosphorus oxychloride into the reactor under ratio control;
- c. mixing the reactor contents and reacting the alkali metal alkoxide with the phosphorus oxychloride while maintaining the reaction mixture at 40°C to 60°C while continuously controlling the reaction yield;
- d. Continuously removing reaction products from the reactor; and
- e. washing the crude phosphate reaction product with water to stop the reaction and remove sodium chloride.

The present continuous process avoids the time inefficiencies of the batch phosphorylation processes. Losses are reduced to only 2-3%, typically 2 to 2.5%, compared to 6 to 10% losses in batch phosphorylation operations. Surprisingly, the overall efficiency of the present process is improved over the batch process by more than would be expected from reduced down-time by a minimum of 15%.

The alkali metal alkoxide is preferably fed to the reactor as a 28% to 30% solution in a carrier alcohol which is the alcohol from which the alkali metal alkoxide was

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produced. That is, for sodium butoxide, the carrier alcohol would be butyl alcohol and for sodium 2-butoxyethoxide the alcohol would be 2-butoxyethanol. Other alkoxides useful in practicing the process can be made

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from 2-ethylhexanol, octanol, N-dodecanol and octadecanol, and from other carbonols such as 2-ethoxyethanol, 2-propoxyethanol and 2-ethoxyethanol.

The alkoxide concentration can vary between about 5 20 to about 30 weight percent in the carrier alcohol. Higher concentrations of alkoxide in the carrier alcohol can be used but will produce high viscosity reaction mixtures which create problems in mixing and in the downstream handling of the reaction product. Lower alkoxide 10 concentrations pose no problem but when they are used, the capacity of downstream recovery equipment must be increased. Alkali metal alkoxides of sodium, potassium or lithium are employed; sodium alkoxide is preferred for economic reasons.

15 Commercial grade phosphorus oxychloride can be used in the process and nickel or glass-lined equipment should be used for storing and transporting the phosphorus oxychloride to the reactor.

The phosphorylation operation is dependent upon 20 maintaining the temperature in the reactor at about 40°C to about 60°C. The reaction is exothermic; when the reactor temperature is set for example at 50°C, the actual measured temperature can vary between 45-55°C. The reaction can be run at temperatures of 40°C and lower, but 25 at these lower temperatures the higher viscosity reaction mixtures require the use of positive displacement pumps,

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such as gear pumps, in place of conventionally used centrifugal pumps. Operating the reactor at a set point of about 50°C is convenient because at this temperature the crude product is easily pumped and side reactions are minimal.

Reactor design is not critical to the process but some mixing of the reactants is necessary. Mixing can be effected by means for example of an agitator in the reactor, mixing nozzles or static mixers.

Temperature control in a stirred tank reactor can be accomplished by continually removing a portion of the crude product from the reactor and recirculating it through coolers and back to the reactor. Analytical control of the reaction is conveniently maintained by sampling or measuring properties of this recirculating crude product stream. Changing the phosphorus oxychloride addition ratio also can affect the temperature since the reaction is exothermic. Higher reactant feed rates raise the temperature in the reactor while lower reactant feed rates help to reduce the temperature.

The normal feed rates of the reactants are arranged so that they are fed to the reactor in about a stoichiometric ratio. The crude product is monitored for the presence of an excess of either reactant and the feed rates adjusted to approach as near as possible complete reaction. Monitoring the reaction can be done

for example by automatic sampling and analytical devices,
measuring capacitance, pH or conductivity or routine analysis.

In making tributyl phosphate, a 30% solution of sodium
butoxide in butanol can be fed at a rate of 7.57 to 113.56 litres
5 per minute (2 to 20 U.S. gallons per minute) or more in a commercial
plant. When using a sodium butoxide feed rate of about 30.82
to about 41.64 litres per minute (about 8 to about 11 U.S. gallons
per minute), the phosphorus oxychloride feed is ratioed from the
alkoxide flow and typically ranges from about 204 to about 318 kg.
10 per hour (about 450 to about 700 pounds per hour) in this
operation mode. Under these conditions the process will provide
a crude phosphate ester strength of 18-26% tris(butoxyethyl)
phosphate or 19-22.5% tributyl phosphate with by-product
production of less than 6% based on washing losses. The by-products
15 are typically highly water-soluble partial esters.

The reaction is conducted in a non-oxidizing
atmosphere for example in methane. To avoid the dangers
of methane explosions, it is preferred to use inert
gases such as for example nitrogen or carbon dioxide.

20 The present process will be described with refer-
ence to the Figure and the manufacture of tributyl
phosphate. Sodium butoxide is removed from vessel T1 by
pump P1 and fed through line L1 to the cooler H1 where
the temperature of the butoxide, if it is hot, is cooled
25 to at least 50°C. The sodium butoxide leaves the cooler

through line L8 and enters the agitated reactor R1. Phosphorus oxychloride is removed from storage vessel T2 and enters the reactor R1 through L2. Crude reaction product is removed from the reactor R1 by the pump P2
5 and circulated through line L3 through cooling device H2 and H3 after which cooled crude product is returned through line L6 to the reactor. A small side stream is removed from line L3 through line L5 which contains analytical devices A1 and an in-line spare analytical
10 device A2. Part of the crude product is continuously removed from line L3 through L4 into a quenching decanter D1 to which water is added to remove sodium chloride and stop the reaction.

The invention is illustrated by the following
15 Examples. The equipment configuration in the Examples is as shown in the block diagram and the operation is as described below. In the following Examples nitrogen was used as the non-oxidizing atmosphere. The first three Examples produced tri-butoxyethyl phosphate and Examples
20 4 to 6 produced tributyl phosphate.

Example 1

The plant was started up using a sodium 2-butoxyethoxide 30% solution in a 2-butoxyethanol at a flow rate of 18.93 litres per minute (5.0 U.S. gallons per minute) and a phosphorus
25 oxychloride flow rate of 150.14 kg. per hour (331 pounds per hour). The temperature of the incoming sodium alkoxide solution and the

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recycled crude product solution were adjusted to maintain the reaction temperature at 45°C. At steady state conditions and substantially cooler reaction, the crude product contained 31% by weight tris-butoxyethyl phosphate.

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Example 2

Example 1 was repeated except that the sodium 2-butoxyethoxide 2-butoxyethanol solution flow rate was maintained at 30.82 litres per minute (8.0 U.S. gallons per minute) and the phosphorus oxychloride flow rate at 218 kg per hour (481 pounds per hour). The crude product contained 26.0% by weight tris-butoxyethyl phosphate.

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Example 3

The process of Example 1 was repeated except that the sodium 2-butoxyethoxide solution in 2-butoxyethanol flow rate was maintained at 82.90 litres per minute (21.9 U.S. gallons per minute), and the phosphorus oxychloride addition rate was maintained at 281 kg per hour (620 pounds per hour). The tributoxyethyl phosphate in the crude product going to the quencher was 22.3% by weight percent.

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Example 4

The plant as described in the figure and examples above was started up using 30% sodium butoxide solution in butanol at a flow rate of 18.93 litres per minute (5.0 U.S. gallons per minute) and a phosphorus oxychloride flow rate of 137 kg per hour (303 pounds per hour). The temperature of the incoming alkoxide and the

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crude product recycle were such that the reactor temperature was maintained at 45°C. Under steady state conditions the process produced 17.5% by weight tributyl phosphate in the crude reaction mixture going to the quencher decanter.

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Example 5

Example 4 was repeated with a sodium butoxide flow rate of 75.71 litres per minute (20.0 U.S. gallons per minute) and a phosphorus oxychloride flow rate of 426 kg per hour (939 pounds per hour). The reaction temperature was maintained at 46°C.

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The crude product going to the quencher decanter contained 19.3% by weight tributyl phosphate.

Example 6

The process of Example 4 was repeated but using a sodium butoxide flow rate of 49.21 litres per minute (13.0 U.S. gallons per minute) and a phosphorus oxychloride flow rate of 271 kg per hour (597 pounds per hour). The reactor temperature was maintained at 49°C. The crude product flowing to the quencher decanter contained 17.4% by weight tributyl phosphate.

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CLAIMS

1. A continuous process for producing aliphatic phosphates in a non-oxidizing atmosphere which comprises:

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- a. continuously introducing a 20 to 30 weight percent solution of an alkali metal alkoxide into a reactor at a rate of 7.57 to 113.56 litres per minute (2 to 30 U.S. gallons per minute);
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- b. continuously introducing phosphorus oxychloride into the reactor under ratio control;
- c. mixing the reactor contents and reacting the alkali metal alkoxide with the phosphorus oxychloride while maintaining the reaction mixture at 40°C to 60°C and continuously controlling the reaction yield;
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- d. continuously removing reaction products from the reactor; and
- e. washing the crude phosphate reaction product with water to stop the reaction and remove sodium choride.

2. A process according to claim 1, in which the reaction mixture temperature is 45°C to 55°C.

3. A process according to claim 1 or 2, in which the alkali metal alkoxide is at a temperature of 50°C or less when added to the reactor.

4. A process according to claim 1, 2 or 3, in which the alkali metal alkoxide is fed to the reactor as a 28 to 30% solution by weight in the alcohol from which the alkali metal alkoxide was prepared.



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5. A process according to any of claims 1 to 4,
in which the nonoxidising atmosphere is nitrogen or
carbon dioxide.

5 6. A process according to any of claims 1 to 5,
in which the alkoxide is sodium alkoxide.

7. A continuous process for producing aliphatic
phosphates substantially as herein described with
reference to and as illustrated in any of the Examples.

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