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METHOD OF PREPARING ALKYL BORATE ESTERS

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This invention is a continuation-in-part of our previous invention Serial No. 716,532, filed February 21, 1958, now abandoned.

This invention relates as indicated to a method of preparing alkyl borate esters and has more particular reference to a method for the continuous transesterification of methyl borate by alcohols having from 2–4 carbon atoms.

Heretofore, the transesterification of methyl borate with alcohols having from 2–4 carbon atoms was done by batch processes. The methyl borate with the appropriate alcohol were placed in a stillpot surmounted by a fractionating column and the mixture placed on total reflux. After removing the methyl borate-methyl alcohol azeotrope from the reaction mixture it was then necessary to isolate the higher esters by a further distillation step.

These prior art processes resulted in poor yields, the highest previously known being on the order of 50–60% based on the alcohol.

Prior to the present invention it was the belief of those skilled in the art, that failure to achieve higher yields appeared to be due in part to the formation of mixed esters and in part to thermal decomposition of the product during the distillation step. Still further the higher alkyl borate esters were difficult to obtain in a pure state since they readily formed azeotropes with their corresponding alcohols.

The present invention is based upon the discovery that contrary to the belief of those skilled in the art, methyl borate can be transesterified without the formation of mixed esters, without the formation of azeotropes of the higher alkyl borate esters and the resulting higher alkyl borate esters can be recovered with substantially no thermal decomposition of the product. Thus, it has been discovered that methyl borate and a higher alcohol without prior reaction can be fed continuously into a fractionating column, a binary mixture having a substantially constant ratio of methanol to trimethyl borate can be removed continuously from the top of the column and at least a 90% yield of at least a 90% pure higher alkyl borate ester can be continuously removed from the bottom of the column.

It is, therefore, the principal object of the present invention to provide a continuous process for the production of alkyl borate esters wherein the alkyl group has from 2–4 carbon atoms.

A further object of the present invention is to provide a process wherein at least a 90% yield of product is obtained.

A still further object is to provide a process wherein the product is at least 90% pure.

Other objects will appear as the description proceeds.

To the accomplishment of the foregoing and related ends, the invention then comprises the features hereinafter fully described and particularly pointed out in the claims, the following description setting forth in detail certain illustrative embodiments of the invention, these being indicative, however, of but a few of the ways in which the principle of the invention may be employed.

Broadly stated, this invention comprises the method of continuously preparing alkyl borate esters which comprises continuously feeding 4 moles of trimethyl borate and from 2.8 to 3.4 moles of an absolute alcohol having from 2–4 carbon atoms into a fractionating column, continuously removing from the top of the column an azeotrope of methanol-trimethyl borate and continuously removing from the bottom of the column an at least 90% pure trialkyl borate ester of an alcohol having from 2–4 carbon atoms.

From the foregoing broadly stated paragraph it will be seen that the present process is continuous and comprises feeding the trimethyl borate and higher alcohol in a definite molecular ratio. It is immaterial to the present invention whether the trimethyl borate and higher alcohol are fed separately into the fractionating column or are admixed and then fed into the column. However, for simplicity of equipment and ease of handling, admixing of the ingredients will be found most expedient.

The important aspects of the present invention are first, the ingredients must always be in the ratio of 4 moles of trimethyl borate to from 2.8 to 3.4 moles of higher alcohol; secondly, the higher alcohol must be absolute; and thirdly, the process must be a continuous operation.

In the preferred embodiment of our invention we use 4 moles of trimethyl borate to 3 moles of absolute alcohol. By maintaining a mole ratio of this order we are able to produce a product which is at least a 99% pure trialkyl borate ester, and we are able to obtain substantantially a 100% yield. However, it will be noted that by using 4 moles of trimethyl borate and from about 2.8 to 3.4 moles of an absolute alcohol, we are able to obtain higher yields and higher purities than heretofore obtained in prior art processes.

The invention is illustrated further by the following specific example: A solution of 75.1 wt. percent trimethyl borate in absolute ethyl alcohol was prepared. This corresponds to 4 moles of trimethyl borate to 3 moles of absolute ethanol as indicated in the following equation:

$$4(CH_3O)_3B + 3CH_3CH_2OH \rightarrow 3[(CH_3O)_3B \cdot CH_3OH] + (CH_3CH_2O)_3B$$

This prepared solution was added at an intermediate point in the fractionating column. The trimethyl borate methanol azeotrope was distilled through the column and the triethyl borate formed was collected in a constant level pot.

The column consisted of a 35 plate, 28 mm. Oldershaw bubble plate column. The reboiler was equipped with a bottoms level controller and was heated electrically. The distillation head was of the tipping bucket type controlled by a timer and solenoid. The feed addition rate and product withdrawal rate were controlled by flowmeters. The run was started by refluxing pure triethyl borate in the reboiler and adding the feed mixture at room temperature when the reflux approached the feed tray. The material balance started after the system was on stream for about 45 minutes and had approached equilibrium conditions.

Substantially 100% of the theoretical methanol-methyl borate azeotrope was produced and the triethyl borate was at least 99% pure, contained 7.42% boron (theoretical 7.41%), and the yield was substantially 100%.

Identical procedures were utilized for the preparation of isopropyl, n-propyl, n-butyl and t-butyl borates with substantially identical results. Additionally, procedures were utilized for the preparation of the trialkyl borate esters wherein the lower and upper range of the absolute alcohol was used in the process. In every instance a product was obtained which was at least 90% pure with at least a 90% yield.

Other modes of applying the principle of the invention may be employed provided the features stated in any of the following claims or the equivalent of such be employed.

We, therefore, particularly point out and claim as our invention:

1. The method of continuously producing at least a 90% yield of alkyl borate esters which comprises continuously feeding 4 moles of trimethyl borate and from 2.8 to 3.4 moles of an absolute alcohol having from 2–4 carbon atoms into a fractionating column, continuously removing from the top of the column an azeotrope of methanol-trimethyl borate and continuously removing from the bottom of the column an at least 90% pure trialkyl borate ester of an alcohol selected from the group consisting of ethyl, isopropyl, n-propyl and t-butyl.

2. The method of claim 1 wherein the trimethyl borate and absolute alcohol are admixed prior to feeding into the fractionating column.

3. The method of continuously producing a substantially 100% yield of alkyl borate esters which comprises continuously feeding 4 moles of trimethyl borate and 3 moles of an absolute alcohol having from 2–4 carbon atoms into a fractionating column, continuously removing from the top of the column an azeotrope of methanol-trimethyl borate and continuously removing from the bottom of the column an at least 99% pure trialkyl borate ester of an alcohol selected from the group consisting of ethyl, isopropyl, n-propyl and t-butyl.

4. The method of continuously producing at least a 90% yield of triethyl borate which comprises continuously feeding 4 moles of trimethyl borate and from 2.8 to 3.4 moles of absolute ethyl alcohol into a fractionating column, continuously removing from the top of the column an azeotrope of methanol-trimethyl borate and continuously removing from the bottom of the column at least 90% pure triethyl borate.

5. The method of continuously producing at least a 90% yield of triisopropyl borate which comprises continuously feeding 4 moles of trimethyl borate and from 2.8 to 3.4 moles of absolute isopropyl alcohol into a fractionating column, continuously removing from the top of the column an azeotrope of methanol-trimethyl borate and continuously removing from the bottom of the column at least 90% pure triisopropyl borate.

6. The method of continuously producing at least a 90% yield of tri-n-propyl borate which comprises continuously feeding 4 moles of trimethyl borate and from 2.8 to 3.4 moles of absolute n-propyl alcohol into a fractionating column, continuously removing from the top of the column an azeotrope of methanol-trimethylborate and continuously removing from the bottom of the column at least 90% pure tri-n-propyl borate.

7. The method of continuously producing at least a 90% yield of tri-t-butyl borate which comprises continuously feeding 4 moles of trimethyl borate and from 2.8 to 3.4 moles of absolute t-butyl alcohol into a fractionating column, continuously removing from the top of the column an azeotrope of methanol-trimethyl borate, and continuously removing from the bottom of the column at least 90% pure tri-t-butyl borate.

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