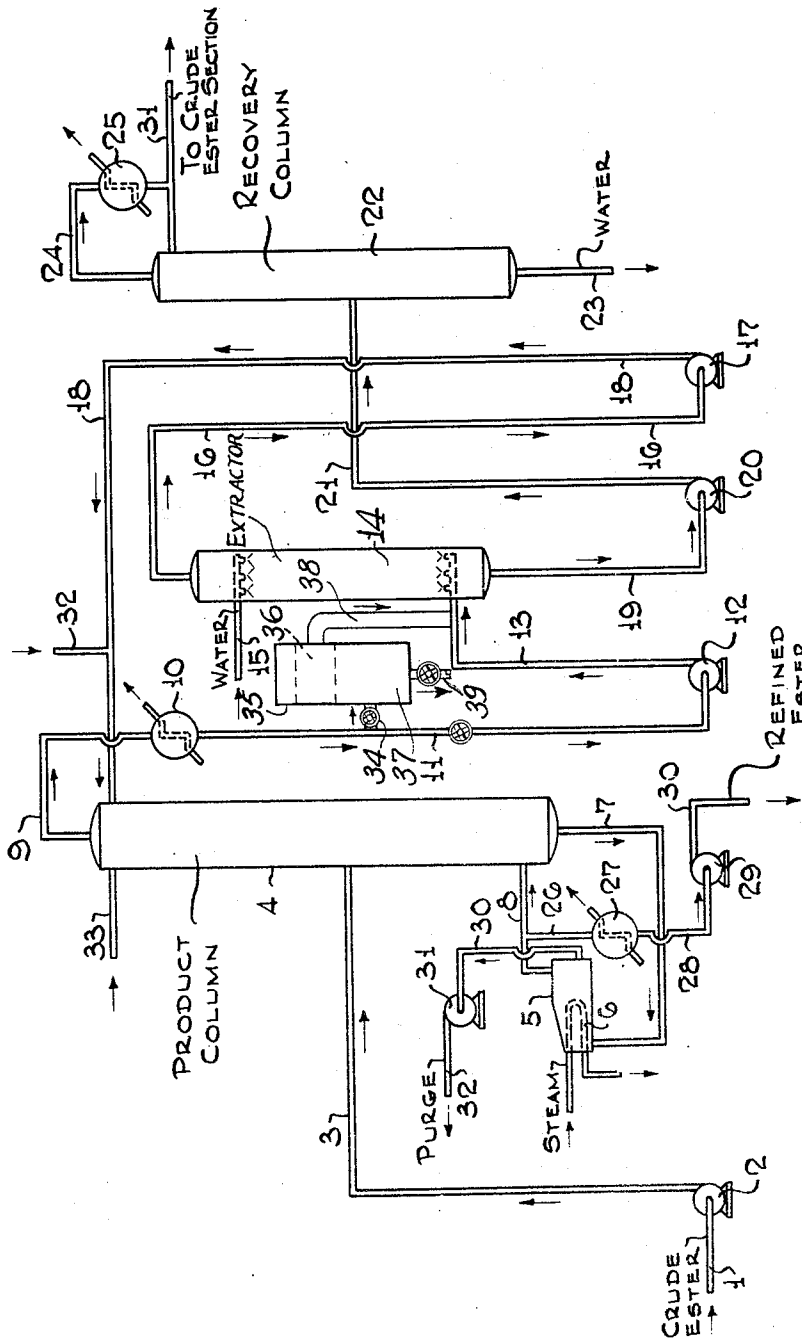


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DISTILLATION OF SECONDARY BUTYL ACETATE
FROM SECONDARY BUTYL ALCOHOL AND WATER
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DISTILLATION OF SECONDARY BUTYL ACETATE FROM SECONDARY BUTYL ALCOHOL AND WATER

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This invention relates to a method for the finishing of crude aliphatic esters, particularly by the removal of alcohols and water therefrom. More specifically, the invention is concerned with the production of a refined grade of aliphatic ester from crude aliphatic ester by a combined distillation and water-extraction process.

Crude aliphatic esters prepared by commercial processes, e. g. the esterification processes of U. S. 1,770,779 and U. S. 2,147,341, contain substantial quantities of water and alcohol among other impurities. It is an object of this invention to present a process whereby water and alcohol can be substantially and economically removed from the crude aliphatic ester in a finishing process resulting in the production of a refined grade of product.

Crude aliphatic esters prepared by commercial processes contain in the neighborhood of 50-85% by weight of ester, 5-35% alcohol and 2-10% water. For market purposes, it is necessary to remove water almost entirely from the product and to reduce the alcohol content to a minimum. Such is an object of my process.

In order that my invention may be clearly understood, the manner of its application to the finishing of crude secondary butyl acetate will be explained. However, my invention is not limited to the finishing of this particular ester, nor is my invention limited by any particular process by which the crude aliphatic ester has been prepared. My invention is applicable to the removal of water and alcohol from mixtures of aliphatic ester therewith, regardless of the history of the crude ester mixture.

Secondary butyl acetate has been made for a number of years by a batch esterification process using secondary butyl alcohol and acetic acid to produce a crude material containing 75-85% by weight sec-butyl acetate, 2-5% by weight water, and the remainder sec-butyl alcohol. This crude material is then further refined by a batch distillation operation to obtain a product which contains 85% by weight sec-butyl acetate and the remainder sec-butyl alcohol.

The conventional purification of secondary butyl acetate by distillation involves the following vapor-liquid equilibrium relations of the ternary system sec-butyl alcohol, sec-butyl acetate, and water.

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(1) There is formed a ternary azeotrope which boils normally at 85.7° C. and is composed as follows:

5	SBOH.....	54.6 weight per cent	} B. P. 85.7° C.
	SBAc.....	25.7 weight per cent	
	H ₂ O.....	19.7 weight per cent	

(2) Aqueous binary azeotropes as follows are formed:

10	SBOH.....	72 weight per cent	} B. P. 87.3° C.
	H ₂ O.....	28 weight per cent	
	SBAc.....	79 weight per cent	} B. P. 87.5° C.
	H ₂ O.....	21 weight per cent	

(3) As far as is known, there is no sec-butyl alcohol-sec-butyl acetate azeotrope formed. However, the system is non-ideal, and the relative volatility in the range 80 to 100 wt. % SBOH closely approaches one. Consequently, the separation of high purity SBAc from anhydrous SBOH-SBAc mixtures by simple distillation is difficult if not impossible.

If a mixture of SBAc-SBOH-H₂O containing a ratio of SBOH/H₂O greater than the same ratio in the ternary azeotrope is submitted to batch distillation in a still surmounted by a good fractionating column, the material removed overhead will be successively:

- (1) The ternary azeotrope.
- (2) A mixture of SBOH and SBAc rich in SBOH.
- (3) SBAc.

Since all the water is removed as part of the ternary azeotrope, the binary azeotropes cannot be formed.

Specifically, the batch distillation of crude acetate is carried out in the present commercial process as follows:

The crude sec-butyl acetate is charged to a still pot surmounted by a 20-plate fractionator, and fractionated at a temperature at which the overhead approaches the ternary azeotrope of acetate, alcohol and water (B. P. 85.7° C.). This operation is complicated by the occurrence of binary azeotropes of acetate-water (B. P. 87.5° C.) and alcohol-water (B. P. 87.3° C.) which distill over in the same approximate boiling range. As far as is known, there is no sec-butyl acetate-sec-butyl alcohol binary. The column is best operated so that the temperature at the top of the column lies half way between the binary azeotrope temperatures and the ternary azeotrope distillation

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temperature, the purpose of the distillation being to remove maximum water and alcohol and minimum acetate. After the azeotropes have been distilled over (called the "heads"), the overhead then distills as an 86-88% acetate distillate, the remainder being alcohol. Material of this composition (called the "heart cut"), is taken off until the acetate content begins to drop below approximately 86%. The bottoms of the column can be drawn off and combined with the "heads" and fresh crude acetate to make up the next batch to the fractionating column.

For the proper use of the product, e. g. for solvent purposes, it must be water-free. Recently, increased commercial demand for water-free acetates has resulted in greater production of acetates and, at the same time, an important market has arisen for a dry product containing 5% or less of alcohol.

My process, therefore, provides for the economical purification of a sec-butyl acetate which will meet specifications on water content and have an alcohol content as desired from 0-15% by weight starting with a crude acetate feed containing up to 35% by weight of sec-butyl acetate, 2-5% water by weight, and the remainder essentially sec-butyl alcohol. My improved process may be carried out in batch or continuous operation as will be described below.

Briefly, the crude secondary butyl acetate is fed to the central part of a rectification column, so operated that the secondary butyl alcohol and water are carried overhead with a small amount of the acetate. Although at atmospheric pressure, a ternary azeotrope of sec-butyl alcohol-sec-butyl acetate-water is formed, the crude acetate normally does not contain sufficient water to permit the required amount of alcohol to be taken overhead as the ternary azeotrope. In my process, the column is operated so that with the customary feed, the ternary azeotrope is not taken overhead, but instead, a mixture of acetate, alcohol and water which contains more alcohol than the ternary.

In order to obtain this mixture overhead I operate a fractionating tower within a definite temperature range. At atmospheric pressure the lowest fractionation temperature maintained at the head of a column when refining secondary butyl acetate is that of the boiling point of the ternary azeotrope, namely approximately 85.7° C. The highest temperature to be employed at the top of the fractionating column is approximately 95.0° C. The temperature selected within this range depends upon the quality of the feed and the quality of the desired product. Under no circumstances, however, is the fractionating tower overhead temperature permitted to fall below the boiling point of the ternary azeotrope at atmospheric pressure, nor under any circumstances is the overhead temperature allowed to exceed the boiling point of the desired ester itself. I have found the above temperature range of 85.7° C. to 95.0° C. to be particularly effective for the production of high grade secondary butyl acetate.

The total overhead from the rectification column is condensed. At this point, two possibilities exist for the treatment of the overhead even though it may separate into two phases. Either the total overhead or the acetate phase recovered by decantation of the overhead may be sent to a water extraction tower where it is contacted with water, preferably in a counter-current manner, to obtain an acetate phase sub-

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stantially free of alcohol but saturated with water, and an aqueous phase containing essentially all the alcohol and water in the overhead and some secondary butyl acetate. The secondary butyl acetate phase is returned to the rectification tower as reflux. The aqueous phase from the extraction tower is sent to a recovery column where it is fractionated to recover the alcohol and acetate. If the total overhead from the rectification tower was separated and only the acetate layer extracted with water in the extraction tower, the aqueous phase is combined with the aqueous phase from the extractor and sent to the recovery column. Secondary butyl acetate of the desired strength is obtained as a bottoms product from the rectification tower or the reboiler, preferably as a vapor stream off the reboiler, which stream is condensed and sent to storage. Generally, however, the crude acetate contains some high boiling impurities and provision must be made to purge the system of these high boilers. This is accomplished by removing the high boilers as a bottom stream from the reboiler, as will be explained later with reference to the drawing.

It will be seen from the above description of my invention that a water extraction stage, preferably a counter-current extraction stage, has been incorporated into the finishing operation of an esterification process.

The invention will be further understood from the description of an embodiment of the invention, this description being made with reference to the drawing which represents a diagrammatic elevational view of an apparatus suitable for carrying out the present process.

Referring to the drawing, crude secondary butyl acetate enters line 1 and is pumped by pump 2 through line 3 into the middle of the rectification tower 4. The tower 4 is operated at temperatures between approximately 85.7° C. and 95.0° C. and at atmospheric pressure. In tower 4 the crude acetate mixture is distilled, heat being supplied by means of reboiler 5. Steam is circulated through coil 6 in reboiler 5 supplying heat to the tower bottoms removed from the tower through line 7 and returned to the tower through line 8. Taken overhead from tower 4 through line 9 is a mixture of alcohol, acetate and water, the mixture containing more alcohol and acetate than the ternary azeotrope. The overhead is condensed in condenser 10. The total condensed overhead from line 11 is picked up by pump 12 and transmitted via line 13 into the bottom of extraction tower 14. In tower 14 the overhead is countercurrently washed with water entering through line 15. From extraction tower 14 an acetate phase substantially free of alcohol but saturated with water is taken overhead through line 16 to pump 17 which pumps it via line 18 into the top of rectification tower 4 as reflux. The aqueous phase containing essentially all the alcohol and water and some sec-butyl acetate (less than 1 wt. %) is taken as bottoms from extraction tower 14 through line 19 to pump 20 which pumps it through line 21 into recovery column 22. In the recovery column the water is substantially completely removed via line 23 and alcohol and acetate vapors are taken overhead in line 24 and condensed in condenser 25. The condensate in line 31 may be returned to the crude acetate feed entering the system through line 1. The refined acetate, from which water has been substantially completely removed, and whose alcohol content has been cut to the

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desired maximum, is removed as bottoms from tower 4 through line 7 to reboiler 5. Refined product is taken as a vapor stream off the reboiler through lines 8 and 26, condensed in condenser 27 and led through line 28 to pump 29 which pumps the product through line 30 to storage. High boilers are removed from the acetate product by withdrawing them as a stream off the reboiler by means of line 30, led to pump 31 and removed from the process via line 32.

If desired only the ester phase of the overhead need be submitted to water extraction. In this event the total condensed overhead is lead via line 34 to decanter 35 in which the distillate separates into two phases, namely, an upper ester phase 36 which is removed via line 38 and sent to the extraction tower and a lower aqueous phase which is removed via line 39.

The process just described may be modified somewhat by operating the rectification column in such a manner as to take overhead the ternary azeotrope of acetate-alcohol-water. The ternary azeotrope can then be extracted with water to obtain a raffinate essentially free of alcohol. The water washed acetate would contain about 95% SBAC, 2.5% SBOH, and 2.5% H₂O if optimum extracting conditions were used. Therefore, if further alcohol were to be removed enough water would have to be added to meet the demand of the overhead composition. The reflux to the rectification column would then consist of the raffinate and sufficiently extraneous water to permit the alcohol to be taken overhead as the ternary azeotrope. Extraneous water may be added through line 32, along any point in line 18, or to the column directly, e. g. through line 33.

In a typical example directed to the purification of secondary butyl acetate, I have found it possible to obtain a high quality acetate product by proceeding in the following manner:

120 lbs. of distillate are taken overhead from the fractionating column. This distillate consists of 100 lbs. of the ternary mixture and 20 lbs. of the mixture containing 85% alcohol and 15% acetate by weight. The following then is the composition of the distillate.

SBAC	SBOH	H ₂ O
54.6	25.7	19.7— <small>from the ternary.</small>
3.0	17.0	----- <small>from the alcohol-acetate mixture.</small>
57.6	42.7	19.7

= 120 total parts of distillate.

The overall composition, therefore, of the distillate is 48 weight per cent acetate, 35.6 weight per cent alcohol, 16.4 weight per cent water. In order to obtain this distillate, crude acetate is fed to the column and the heat input to the column bottoms is increased until the distillate of this composition is obtained. This can be accomplished by maintaining a constant bottoms temperature at atmospheric pressure and varying the reflux ratio or by maintaining a constant reflux ratio and varying the heat input to the bottoms. The ratio of alcohol to acetate in the overhead will be a function of the number of plates and the reflux ratio of the column. The column can be operated so that any desired amount of alcohol-acetate mixture can be taken overhead in addition to a given amount of the ternary mixture.

My process differs from the usual azeotropic distillation process in the following respects:

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1. Normally, the feed contains one impurity which is to be removed, but here there are two, viz., water and alcohol, which are removed simultaneously.

2. Usually, an entrainer is added to the rectification zone to increase the volatility of the impurity so that it will be taken overhead, but in my process the desired product, i. e. the ester itself, is the entrainer.

A review of the process described discloses that alcohol and water have been removed from the crude acetate by a process which, in effect, causes the concentration of acetate in the rectification column. The countercurrent water extraction of the rectifier overhead produces a reflux acetate phase which is substantially free of alcohol. By this procedure, the overhead can be extracted to an extent governed by the amount of alcohol desired in the final acetate product.

As previously stated, my process can be carried out in batch or continuous operation. If batch operation is employed, the fractionator is operated until the alcohol content of the overhead drops off considerably, indicating that it has been substantially removed from the tower feed. The bottoms are drawn off and a new batch charged to the fractionator. When operating in a continuous manner, the process consists of continually charging crude ester to the rectification column at a constant rate, removing an overhead and a bottoms product, condensing the overhead, extracting alcohol from the overhead by countercurrent washing with water and providing a predominately ester phase as reflux for the rectification column. The predominately alcohol-water extract is continuously removed from the extractor and sent to a recovery column where water is removed as bottoms and discarded, and the predominately alcohol overhead containing small amounts of ester, is condensed and returned if desired as recycle feed to the crude ester producing unit.

My process is of general application in the finishing of aliphatic esters and it will be readily apparent to one skilled in the art that the propyl and isopropyl, the butyl and isobutyl, the amyl and isoamyl esters of aliphatic acids may be finished by a method entirely analogous to the process described for my secondary butyl acetate purification. If the process is applied to the finishing of the above esters of hydroxy aliphatic acids and dicarboxylic acids, the finishing should be preferably carried out under vacuum.

Having thus described my invention, what I desire to claim as new and to protect by Letters Patent is:

1. A process for the purification and recovery of secondary butyl acetate from a mixture thereof with minor proportions of secondary butyl alcohol and water, said mixture containing insufficient water to form a ternary azeotrope with all the alcohol and acetate, which comprises distilling the mixture in a fractionation zone at a temperature between the boiling point of the ternary azeotrope and the boiling point of the acetate so as to remove from the fractionation zone a distillate comprising the ternary azeotrope plus additional amounts of secondary butyl acetate and substantially all the secondary butyl alcohol extracting the distillate with water to form a raffinate consisting substantially of secondary butyl acetate and substantially free of secondary butyl alcohol and an extract containing substantially all of the secondary butyl alcohol from the distillate, refluxing the raffinate

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to a top part of the fractionation zone and removing as bottoms from the fractionation zone secondary butyl acetate substantially free of water and secondary butyl alcohol.

2. A process for the purification and recovery 5 of secondary butyl acetate from a mixture thereof with minor proportions of secondary butyl alcohol and water, said mixture containing insufficient water to form a ternary azeotrope with all the alcohol and acetate, which comprises dis- 10 stilling the mixture in a fractionation zone at atmospheric pressure at a temperature between 85.7° C. and 95.0° C., removing from the frac- tionation zone a distillate comprising the ternary azeotrope plus additional amounts of secondary 15 butyl acetate and substantially all the secondary butyl alcohol, extracting the distillate with water to form a raffinate consisting substantially of secondary butyl acetate and substantially free of secondary butyl alcohol, and an extract con- 20 taining substantially all the secondary butyl alcohol from the distillate, refluxing the raffinate to a top part of the fractionation zone, and removing as bottoms from the fractionation zone

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secondary butyl acetate substantially free of water and secondary butyl alcohol.

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