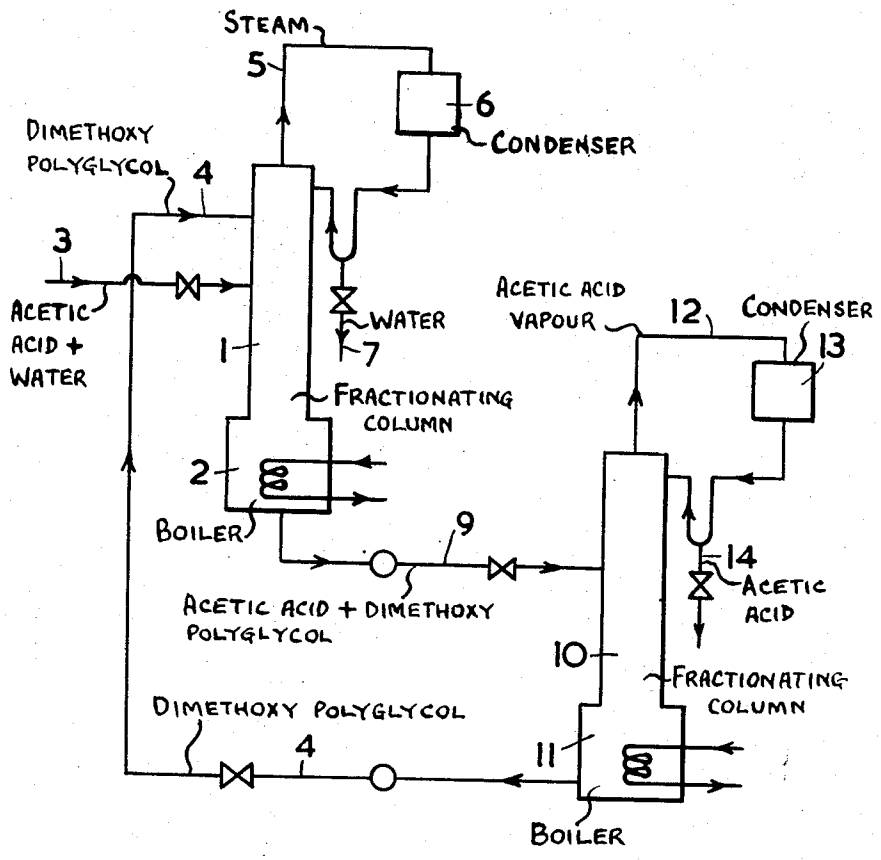
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RECOVERY OF ACETIC ACID FROM AQUEOUS ACETIC ACID SOLUTIONS BY EXTRACTIVE DISTILLATION

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RECOVERY OF ACETIC ACID FROM AQUEOUS ACETIC ACID SOLUTIONS BY EXTRACTIVE DISTILLATION

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9 Claims. (Cl. 202—39.5)

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This invention relates to the recovery of acetic acid from aqueous acetic acid solutions by extractive distillation, and is a continuation-in-part application of my application, Serial No. 177,992, now abandoned.

In the specification of application, Serial No. 122,832, now abandoned, a process is described for the production of threads of cellulose acetate by extruding a solution of the cellulose acetate through a jet into an aqueous coagulant bath containing potassium acetate and also containing free acetic acid, preferably within the range of 50 to 250 grams of acetic acid per litre of bath. Cellulose acetate solutions employed in this process are preferably the acetic acid solutions obtained by the normal acetylation process after ripening and neutralisation of the acid catalyst have been effected.

When the process described in the specification of the said application, Serial No. 122,832, is carried out continuously using an aqueous acetic acid solution of cellulose acetate together with either a potassium acetate or a potassium acetate-acetic acid coagulation bath, the concentration of acetic acid in the bath will increase under static conditions. It is therefore desirable to rectify the bath during continuous operation by withdrawing part of the bath liquor, either continuously or intermittently, recovering acetic acid from the withdrawn liquor and feeding the liquor, after any necessary further adjustment of the concentration of its constituents, to the spinning bath.

It is known to recover acetic acid from its aqueous solutions by fractional distillation, azeotropic distillation and extractive distillation. As the boiling points of water and acetic acid (100° centigrade and 118° centigrade respectively) are close together, a commercially practicable fractional distillation process requires a complex distillation column and a large expenditure of heat energy so that in general such processes are not employed commercially.

Azeotropic distillation, using azeotropic liquids such as ethyl acetate or amyl acetate, has been used commercially for the recovery of glacial acetic acid from aqueous acetic acid solutions such as are obtained for example in the manufacture of cellulose acetate. However the presence of potassium acetate in the acetic acid solution has been found to lead to difficulties, principally as follows:

(I) Water cannot be removed by extraction and rejection of the raffinate since the latter will contain valuable potassium acetate. It is therefore necessary to vaporise all the water and this results in a much greater heat requirement per unit weight of water removed.

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(II) In the case of extraction of the spinning bath liquor potassium acetate reduces the partition coefficient so that instead of complete extraction of the liquor being obtained with two parts of ethyl acetate per part of aqueous feed liquor about six parts are required.

(III) The presence of potassium acetate in the spinning bath liquor increases the relative volatility of water with respect to acetic acid so that distillation gives a weaker acid than would be obtained if the salt were "neutral" or not present. Whereas a distillate containing 20 per cent acetic acid would be obtained in the absence of the salt, evaporation of the spinning bath liquor gives a 10 to 11 per cent acetic acid distillate.

It has also been proposed to separate acetic acid from its aqueous solutions by an extractive distillation process, for example in United States patent specification No. 2,350,256.

It is the object of the present invention to recover acetic acid from aqueous solutions of acetic acid particularly from the dilute aqueous acetic acid distillate obtained from solutions which also contain potassium acetate.

According to the present invention, a process for the recovery of acetic acid from aqueous solutions of acetic acid comprises adding a dimethoxy polyglycol chosen from the group consisting of

(*a*) Dimethoxytetraethylene glycol

$$(O(CH_2.CH_2.O.CH_2.CH_2.OCH_3)_2)$$

(*b*) Dimethoxy triethylene glycol

$$(CH_3.O.CH_2.CH_2.OCH_2.CH_2.OCH_2.CH_2.OCH_3)$$

and

(*c*) dimethoxy diethylene glycol

$$(CH_3.O.CH_2.CH_2.O.CH_2.CH_2.OCH_3)$$

to the solution, fractionally distilling from the mixture substantially all the water present and then recovering acetic acid, preferably by fractional distillation from the water-free or substantially water-free mixture of acetic acid and the dimethoxy polyglycol. The molecular ratio of the dimethoxy polyglycol to the water present in the aqueous acetic acid solution is preferably within the range of from 1 to 5:1.

The process according to the present invention employs the principle of extractive distillation in which an extraction solvent is added to the aqueous acetic acid solution to increase the volatility of the water with respect to the acid so

that the water can be removed more readily and more completely than in the case of simple fractional distillation. Such an extraction solvent must be miscible in all proportions with and chemically inert to both water and acetic acid and must not form an azeotrope with either; it must also have a boiling point sufficiently higher than that of acetic acid to permit separation of the acid and the solvent by fractional distillation. Thus dimethoxy tetraethylene glycol boils at 276° centigrade, dimethoxy triethylene glycol at 220° centigrade and dimethoxy diethylene glycol at 161° centigrade. The dimethoxy polyglycols as defined are suitable extraction solvents which not only have the properties outlined above but also give a pronounced increase in the volatility of water with respect to the acid. As examples of the increase in volatility of water obtained by using dimethoxy tetraethylene glycol, in a mixture of 70 mols of dimethoxy tetraethylene glycol, 15 mols of acetic acid and 15 mols of water, the volatility of the water with respect to the acid is increased by a factor of 6 over the value obtained in the absence of the dimethoxy tetraethylene glycol; with a mixture of 50 mols of dimethoxy tetraethylene glycol, 25 mols of acetic acid and 25 mols of water, the relative volatility is increased 5-fold above the normal value for equimolecular mixtures of water and acetic acid. Similar increases in relative volatility are obtained with dimethoxy triethylene glycol and dimethoxy diethylene glycol.

The process according to the invention is particularly applicable to the recovery of acetic acid from dilute aqueous solutions of acetic acid containing for example up to about 15 per cent of acetic acid where the usual azeotropic distillation processes are uneconomical. As described above, distillation of the potassium acetate spinning bath liquors used in carrying out the process of application, Serial No. 122,832 yields distillates containing 10 to 11 per cent of acetic acid and such solutions are particularly suitable for rectification by the present invention.

The process for separating acetic acid and water using a dimethoxy glycol in accordance with this invention may be carried out in a continuously operated apparatus as illustrated in the accompanying drawing. The apparatus shown in the drawing comprises a distillation column 1 heated by a boiler 2 which may conveniently be heated by steam under pressure. A mixture of acetic acid and water, preferably in the vapour state, is fed into the column 1 at an intermediate point by way of a pipe 3 and the dimethoxy polyglycol is simultaneously fed in near the top of the column 1 by way of a pipe 4. The proportion of the dimethoxy polyglycol to the acid-water mixture is adjusted to give the required increase in the normal volatility of the water as indicated above. Heat is applied to the boiler 2, a suitable temperature for dimethoxy tetraethylene glycol being approximately 260° centigrade and steam driven off in the column 1 passes by way of a pipe 5 to a condenser 6 from which it may be withdrawn as desired by a waste pipe 7. At the same time a mixture of acetic acid and the dimethoxy polyglycol collects in the boiler 2 and this mixture is passed by way of a pipe 9 to a second distillation column 10 heated by a boiler 11. A suitable temperature for the boiler 11 when using dimethoxy tetraethylene glycol is approximately

280° centigrade. In column 10 acetic acid is distilled off and the acid vapour passes by way of a pipe 12 to a condenser 13 from which the separated acetic acid may be withdrawn for re-use by a pipe 14. The dimethoxy polyglycol passes into the boiler 11 from the column 10 and thence into the feed pipe 4 so that it may be fed back to the column 1 for re-use. The presence of a small amount of acetic acid in the dimethoxy polyglycol which passes from the boiler 11 to the column 1 is not detrimental. An additional advantage of this continuously operated process is that the dimethoxy polyglycol is not distilled at any stage. In order to reduce the temperature in the boiler 11, the column 10 is preferably operated under reduced pressure.

For the rectification of spinning bath liquors containing potassium acetate as well as acetic acid, an evaporator is connected to the feed pipe 3 and the vapours recovered from the evaporator, which contain 10 to 11 per cent of acetic acid, are passed into the column 1 by way of pipe 3, as shown while potassium acetate is recovered from the evaporator.

When using a continuously operated apparatus of the type shown in the drawings with dimethoxy triethylene glycol the boiler 2 may conveniently be maintained at 150° centigrade with the boiler 11 at 220° centigrade and atmospheric pressure or at 168° centigrade and an absolute pressure of 150 mm. of mercury; with dimethoxy diethylene glycol corresponding temperatures are 110° centigrade for boiler 2 and 161° centigrade (at atmospheric pressure) for boiler 11.

What I claim is:

1. A process for the recovery of acetic acid from aqueous solutions of acetic acid which comprises adding a dimethoxy polyglycol chosen from the class consisting of dimethoxy tetraethylene glycol, dimethoxy triethylene glycol and dimethoxy, diethylene glycol to the solution, fractionally distilling from the mixture substantially all the water present and then recovering acetic acid from the residual mixture of acetic acid and dimethoxy polyglycol.

2. A process for the recovery of acetic acid from aqueous solutions of acetic acid which comprises adding a dimethoxy polyglycol chosen from the class consisting of dimethoxy tetraethylene glycol, dimethoxy triethylene glycol and dimethoxy diethylene glycol to the solution, fractionally distilling from the mixture substantially all the water present and then fractionally distilling acetic acid from the residual mixture of acetic acid and dimethoxy polyglycol.

3. A process for the recovery of acetic acid from aqueous solutions of acetic acid which comprises adding a dimethoxy polyglycol chosen from the class consisting of dimethoxy tetraethylene glycol, dimethoxy triethylene glycol and dimethoxy diethylene glycol to the solution in an amount such that molecular ratio of the dimethoxy polyglycol to the water present in the solution is from 1 to 5:1, fractionally distilling from the mixture substantially all the water present and then fractionally distilling acetic acid from the residual mixture of acetic acid and dimethoxy polyglycol.

4. A continuous process for the recovery of acetic acid from aqueous solutions of acetic acid which comprises feeding the aqueous acid solution and a dimethoxy polyglycol chosen from the class consisting of dimethoxy tetraethylene glycol, dimethoxy triethylene glycol and dimethoxy

diethylene glycol into a fractionating column, fractionally distilling substantially all the water from the mixture formed within the column, withdrawing the residual mixture of acetic acid and dimethoxy polyglycol from the fractionating column and passing it to a second fractionating column, fractionally distilling off acetic acid from the acetic acid-dimethoxy polyglycol mixture in the second fractionating column and returning the residual dimethoxy polyglycol to the first fractionating column.

5. A continuous process as claimed in claim 4 wherein the rates of feed of the aqueous acetic acid solution and of the dimethoxy polyglycol are so adjusted that the molecular ratio of the dimethoxy polyglycol to the water in the fractionating column is within the range of 1 to 5:1.

6. A continuous process as claimed in claim 4 wherein the second fractionating column is operated under reduced pressure.

7. A process for the recovery of acetic acid from aqueous solutions of acetic acid which comprises adding dimethoxy tetraethylene glycol to the solution, fractionally distilling from the mixture substantially all the water present and then recovering acetic acid from the residual mixture of acetic acid and dimethoxytetraethylene glycol.

8. A process for the recovery of acetic acid from aqueous solutions of acetic acid which comprises adding dimethoxy triethylene glycol to the solution, fractionally distilling from the mixture substantially all the water present and then recovering acetic acid from the residual mixture of acetic acid and dimethoxy triethylene glycol.

9. A process for the recovery of acetic acid from aqueous solutions of acetic acid which comprises adding dimethoxy diethylene glycol to the solution, fractionally distilling from the mixture substantially all the water present and then recovering acetic acid from the residual mixture of acetic acid and dimethoxy diethylene glycol.

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References Cited in the file of this patent

UNITED STATES PATENTS

Number	Name	Date
1,624,811	Suida	Apr. 12, 1927
2,123,348	Wentworth	July 12, 1938
2,339,160	Dunn et al.	Jan. 11, 1944
2,350,256	Shiras	May 30, 1944
2,357,344	Norris et al.	Sept. 5, 1944
2,430,086	Staff	Nov. 4, 1947
2,559,519	Smith et al.	July 3, 1951
2,575,243	Carlson et al.	Nov. 13, 1951

FOREIGN PATENTS

Number	Country	Date
560,169	Great Britain	Mar. 23, 1944
563,164	Great Britain	Aug. 1, 1944