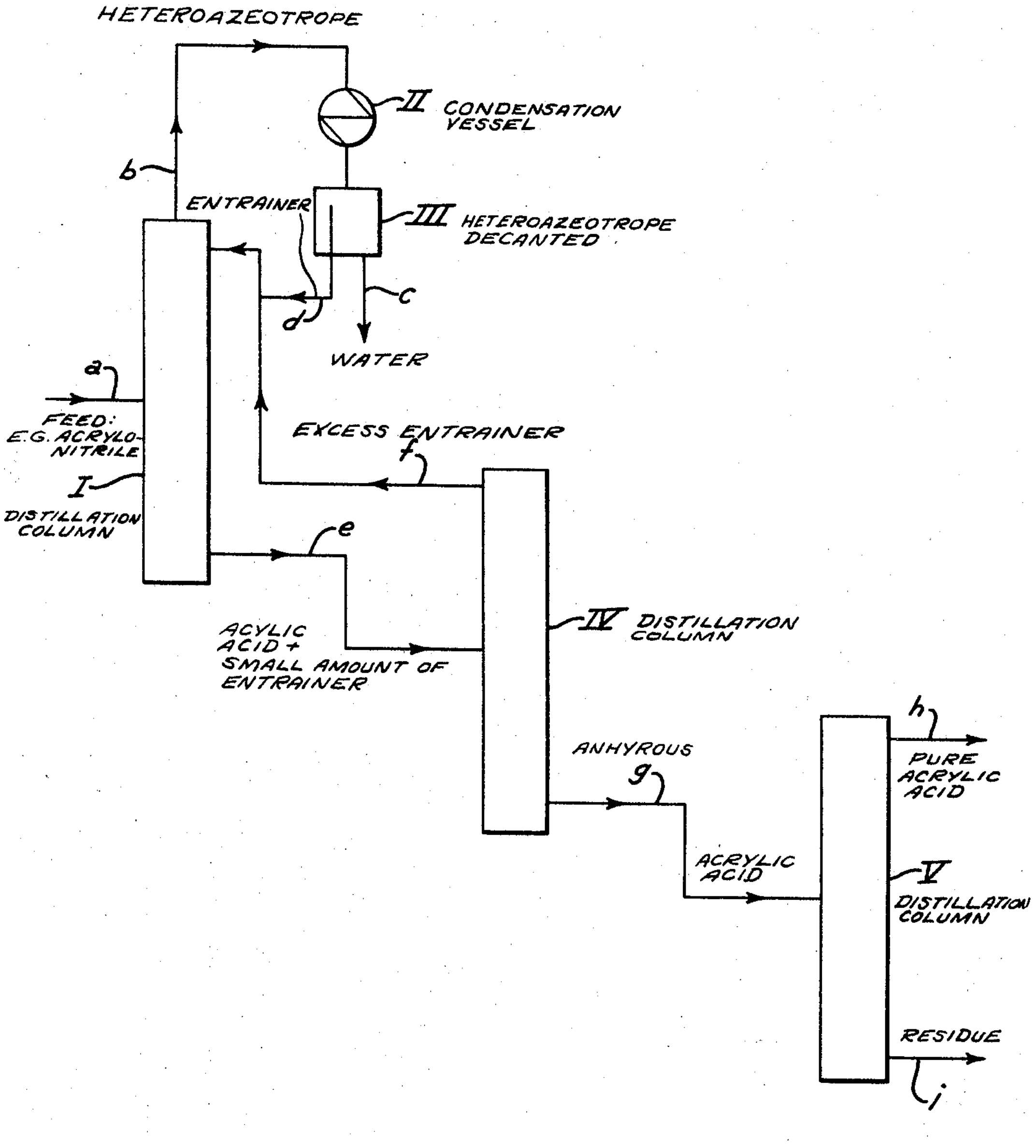
March 11, 1969 C. TCHERKAWSKY **3,432,401**

PROCESS FOR PRODUCTION OF GLACIAL ACRYLIC ACID BY
AZEOTROPIC DISTILLATION WITH A WATER ENTRAINER
Filed March 18, 1964



INVENTOR.
CLAUDE TCHERKAWSKY.
BY
Webb, Burden, Robinson & Webb,
ATTORNEYS.

United States Patent Office **3,432,401**
Patented Mar. 11, 1969

3,432,401
PROCESS FOR PRODUCTION OF GLACIAL ACRYLIC ACID BY AZEOTROPIC DISTILLATION WITH A WATER ENTRAINER

Claude Tcherkawsky, Saint-Avold, Moselle, France, assignor to Societe d'Electro-Chimie, d'Electro-Metallurgie et des Acieries Electriques d'Ugine, Paris, France, a corporation of France

Filed Mar. 18, 1964, Ser. No. 352,829
Claims priority, application France, Mar. 21, 1963, 928,802
U.S. Cl. 203—15 **5 Claims**
Int. Cl. C7c *51/46;* **B01d** *3/36, 3/34*

ABSTRACT OF THE DISCLOSURE

A process for preparing glacial acrylic acid by treating a solution of from 10% to 80% acrylic acid with an entrainer that is chemically inert towards the acrylic acid and which is capable of capturing at least 3% water and which has a distillation temperature at least 5° C. different than that for the acrylic acid. The entrainer and water form a heteroazeotrope which is distilled from said acid at a temeprature not over 120° C. and thereafter glacial acrylic acid is obtained by distillation.

This invention relates to a process for production of glacial acrylic acid from dilute aqueous solutions of same by heteroazeotropic entrainment of the water contained in the aqueous solutions.

Processes for the obtention of raw acrylic acid are known, and generally they comprise treating carbon monoxide with acetylene in the presence of catalysts; treating acrylonitrile with aqueous solutions of sulphuric acid; treating ethylene cyanohydrin with aqueous solutions of sulphuric acid; or treating propylene with oxygen in the presence of a catalyst. All these processes give a raw product in the form of an aqueous solution which generally contains less than 50% by weight acrylic acid.

Heretofore, obtention of glacial acrylic acid, a product which is at least 99% acrylic acid, was delicate and difficult, and all existing processes led to insufficient outputs of the glacial acrylic acid. In some of these processes, a solution of acrylic acid is distilled under a reduced pressure, but an important portion of the acrylic acid is carried along in an overhead fraction as an aqueous solution. For example, discontinuous distillation of a 500 g. aqueous solution of 50% by weight acrylic acid gives:

A 300 g. aqueous fraction of 16% acrylic acid which must be recycled;

A 190 g. fraction of glacial acrylic acid.

The recovery of glacial acrylic acid is about 76%.

In another process, the acrylic acid is extracted from an aqueous solution by a solvent or a mixture of solvents with or without metallic salts. The resulting organic solution is afterwards distilled to obtain glacial acrylic acid. But this process produces no quantitative extraction of the acid and a substantial quantity of the acid remains in the water which effects a decreased yield of glacial acrylic acid.

Fractional crystallization does not produce glacial acrylic acid since an eutectic at 63% by weight of acrylic acid is precipitated.

My invention overcomes the foregoing disadvantages and covers a process for obtention of glacial acrylic acid from dilute aqueous solutions. Specifically, it comprises quantitatively eliminating the water contained in the raw acrylic acid by heteroazeotropic entrainment by entrainers which form heteroazeotropes with water and do not react with acrylic acid. The process is applicable to any dilute aqueous solution of acrylic acid, but has little practical interest for solutions containing less than 10% or greater than 80% by weight acrylic acid.

As used herein, the term "heteroazeotrope" means a mixture of steam and of entrainer vapor, which mixture has a constant composition for a determined boiling condition, which mixture is formed from a liquid mixture comprising acrylic acid, water and entrainer, until there is substantially complete elimination of the water, and which mixture forms a heterogeneous liquid upon condensation thereof. Azeotropic entrainment of the water may be carried out under various conditions of pressure, depending on the nature of the entrainer. With some entrainers, it is worked under higher pressure than atmospheric pressure; however, operating under vacuum or under less than atmospheric pressure gives better results. I prefer an absolute pressure inferior to 400 mm. Hg. The temperature is limited by polymerization of acrylic acid, and it is advisable not to heat beyond 120° C. and preferably to work at temperature below 80° C.

It is preferable that the entrainer have a little solubility in water, form a heteroazeotrope rich in water, be substantially chemically inert towards said acrylic acid, and be easily separated from acrylic acid by distillation. An excessive solubility of the entrainer in water would lead to losses of the entrainer through water elimination, and the latter then has to be redistilled. To make the entrainer efficient, the quantity of water captured by it must be at least 3%, and preferably 7% by weight. Finally, the difference between the distillation temperatures of the entrainer and of the acrylic acid must be between 5° C. and 100° C., and preferably between 15° C. and 40° C.

Examples of the entrainers are: benzene, toluene, esters of acrylic and methacrylic acids, acrylonitrile, monochlorobenzene, carbon tetrachloride, orthodichlorobenzene, etc.

This distillation of the heteroazeotrope may be carried out by a continuous or a discontinuous process, but it is preferable to operate continuously to avoid prolonged super heatings which can alter the product. The ulterior separation of the small quantity of entrainer remaining in the glacial acrylic acid is carried out, if desired, by further distillation; but this operation is not necessary.

The accompanying drawing shows one example of continuous industrial installation for practicing my process. Referring to the drawing, a dilute aqueous solution of acrylonitrile is introduced through pipe *a* into a distillation column I from which the heteroazeotrope exits through conduit *b* and is condensed in a vessel II and then decanted in apparatus III. The water is eliminated through pipe *c* and the entrainer is returned to the column I through conduit *d*.

The acrylic acid, practically anhydrous but containing a small amount of the entrainer, leaves column I through pipe *e* and is introduced into a column IV where the acrylic acid is separated from excess entrainer. The separated entrainer is recycled to column I by conduit *f*.

The anhydrous acrylic acid exits from column IV through pipe *g* and is introduced into a column V where the pure acrylic acid is removed through pipe *h* and residues are obtained through line *i*.

The following, non-limitative examples illustrate may process. The mentioned percentages must be understood in percent by weight.

EXAMPLE I

500 g. of an aqueous solution of a 50% acrylic acid and 100 g. of benzene as an entrainer were introduced into a one-liter flask surmounted by a Fenske ring-column to which is connected a condenser. 0.5 g. of hydroquinone

and 1 g. of copper turnings as polymerization inhibitors were added to the flask.

Distillation was effected under an absolute pressure of 200 mm. Hg and a benzene-water heteroazeotrope passed at 37° C. The benzene was sent back into the flask as a reflux, and 249 g. of water containing 0.1% acrylic acid were recovered. After substantially complete elimination of the water, distillation temperature rose and 103 g. of a benzene solution containing 4% acrylic acid were recovered. This acrylic acid was not lost as the benzene solution was reutilized in further operations.

Then the vacuum was extended to an absolute pressure of 100 mm. Hg at a temperature of 87° C., and the distillation was completed. 240 g. of 99.8% glacial acrylic acid (percentage determined by measuring acidity) and containing less than 0.01% benzene (determined by vapor chromatography) were obtained.

The amount of acrylic acid obtained as glacial acid was 95.8% of the total amount of acrylic acid utilized.

EXAMPLE II

The operation was carried out in the same apparatus as hereabove, but the benzene was replaced by toluene.

The entire distillation was effected under a pressure of 100 mm. Hg at increasing temperatures and at 38° C. a water-toluene heteroazeotrope was obtained. After separation of this heteroazeotrope into two phases, the toluene was sent back as reflux into the flask. When formation of the heteroazeotrope stopped, the temperature rose to 53° C. and a dilute solution of acrylic acid in toluene was obtained. After elimination of the toluene, the temperature rose to 87° C. and then the glacial acrylic acid desired was recovered.

The three fractions obtained were respectively formed of:

249 g. water containing 0.1% acrylic acid,
109 g. toluene containing 9% acrylic acid,
236 g. of 99.7% glacial acrylic acid which contained less than 0.03% toluene.

The amount of acrylic acid obtained as glacial acrylic acid reached 94% of the total amount utilized.

EXAMPLE III

Into a semi-industrial installation for discontinuous distillation were charged 2000 kg. of a mixture containing:

	Percent
Acrylic acid	45
Water	45
Entrainer, acrylonitrile	10

2 kg. of hydroquinone and 5 kg. of copper turnings as polymerization inhibitors were added.

Distillation was effected under an absolute pressure of 200 mm. Hg and an acrylonitrile-water heteroazeotrope passed at 35° C. After condensation and decanting, two phases were obtained: one, composed essentially of acrylonitrile, was sent back as reflux into the distillation column; and, the other, aqueous, was drawn off.

960 kg. of the recovered aqueous solution contained 7.3% acrylonitrile and 0.08% acrylic acid. This solution can be distilled again to recover the acrylonitrile contained therein, or can be used to produce acrylic acid by hydrolysis of the acrylonitrile.

When there was no water left, the temperature rose to 40.5° C., and then 132 kg. of acrylonitrile containing 4% acrylic acid were recovered.

Then the vacuum was extended to an absolute pressure of 100 mm. Hg and 885 kg. of 99.8% glacial acrylic acid containing 0.02% acrylonitrile were obtained.

The amount of acrylic acid obtained as glacial acid was 98% of the total amount utilized.

While I have shown and described preferred embodiments of my invention, it may be otherwise embodied within the scope of the appended claims.

I claim:

1. A process for the production of at least 98% glacial acrylic acid from an aqueous solution containing 10% to 80% acrylic acid comprising:

(A) adding to said solution an entrainer that is chemically inert towards the acrylic acid to form a heteroazeotrope of the entrainer and water that has a distillation temperature at least 5° C. different from the distillation temperature of acrylic acid; and,

(B) heating said acrylic acid and heteroazeotrope to a temperature not greater than 120° C. to separate by distillation the heteroazeotrope from said acid.

2. The process of claim **1** characterized by said entrainer being selected from the group consisting of benzene, toluene, esters of acrylic and methacrylic acids, acrylonitrile, monochlorobenzene, carbon tetrachloride and orthodichlorobenzene.

3. The process of claim **1** characterized by carrying out said distillation of said heteroazeotrope under an absolute pressure less than substantially about 400 mm. Hg.

4. A process for the production of at least 98% glacial acrylic acid from an aqueous solution containing 10% to 80% acrylic acid comprising:

(A) adding to said solution an entrainer that is chemically inert towards said acrylic acid to form a heteroazeotrope of the entrainer and water that has a distillation temperature at least 5° C. different from the distillation temperature of acrylic acid;

(B) heating said acrylic acid and heteroazeotrope to a temperature not greater than 120° C. to separate by distillation the heteroazeotrope from said acid; and,

(C) continuing said heating to substantially eliminate any remaining entrainer from said acid to form at least 98% glacial acrylic acid.

5. The process of claim **4** characterized by said entrainer being selected from the group consisting of benzene, toluene, esters of acrylic and methacrylic acids, acrylonitrile, monochlorobenzene, carbon tetrachloride and orthodichlorobenzene.

References Cited

UNITED STATES PATENTS

1,668,380	5/1928	Ricard	203—15
1,915,002	6/1933	Ricard et al.	203—15
2,033,978	3/1936	Dreyfus	203—16
3,337,740	8/1967	Gray et al.	203—69

FOREIGN PATENTS

1,169,740	9/1958	France.

OTHER REFERENCES

Weissberger, Distillation, Technique of Organic Chemistry, vol. IV, 1st edition, New York, Interscience, 1951, p. 363.

WILBUR L. BASCOMB, *Primary Examiner.*

U.S. Cl. X.R.

203—8, 60, 67, 69, 71, 78, 80, 94; 260—526