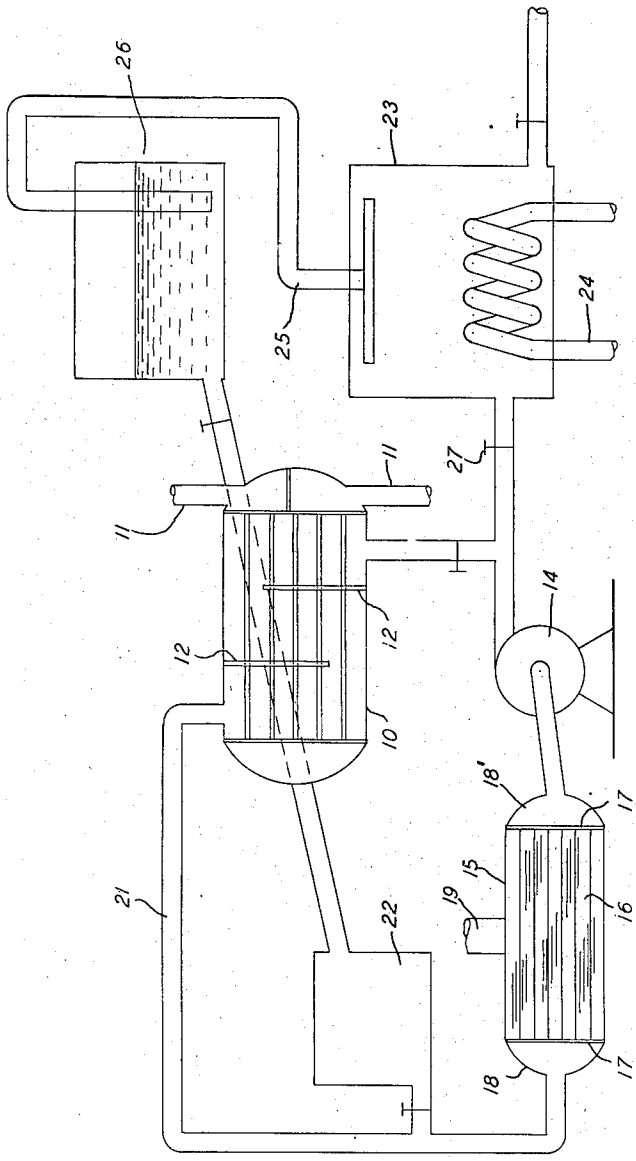
April 18, 1933. E. W. REID ET AL 1,904,013

METHOD OF PRODUCTION OF ETHANOL AMINES

Filed Aug. 18, 1927



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Patented Apr. 18, 1933 1,904,013

UNITED STATES PATENT OFFICE

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METHOD OF PRODUCTION OF ETHANOL AMINES

Application filed August 18, 1927. Serial No. 213,890.

Our invention relates to a method for the production of ethanol amines and particularly to a method in which the reaction is controlled to yield definite percentages of the several amines.

The ethanol amines may be produced by the action of ethylene oxide and ammonia, the following reactions being possible:

$$C_2H_4O + NH_3 = C_2H_5ONH_2$$
$$2C_2H_4O + NH_3 = (C_2H_5O)_2NH$$
$$3C_2H_4O + NH_3 = (C_2H_5O)_3N$$

These products have the following physical properties:

	Boiling point	Density 20°
Monoethanol amine	171° C. at 757 mm.	1.022
Diethanol amine	270° C. at 748 mm.	1.0966
Triethanol amine	278° C. at 150 mm.	1.1242

The reaction will proceed with anhydrous ammonia and anhydrous ethylene oxide but with almost explosive violence. It is preferable, therefore, to carry out the reaction in aqueous solution in order that the conditions may be controlled.

The tendency of the reaction is to produce the triethanol amine. We prefer to carry out the reaction in such a manner as to result in a product composed of approximately 25% diethanol amine and 75% triethanol amine. This mixture has been found to be more useful in the arts than a unitary product. It is useful for causing the deeper penetration of dyes on cotton, silk or cellulose fibers and also for securing a deeper penetration of creosote oil in preserving wood. Other uses for this mixture will be evident to those skilled in the art, such as the manufacture of rubber accelerators, preparation of hydrocarbon-soluble soaps, tanning of leather, preparation of artificial leather and the sizing of cellulose materials.

Our invention will be described with reference to the accompanying drawing in which the single figure is a schematic representation, partially in section, of an apparatus for carrying out our improved process.

In this figure a heat interchanger 10 is provided having inlet and outlet pipes 11 for a cooling medium. While we may use any type of heat interchanger, we have, for convenience, shown a type in which the cooling medium passes through a nest of tubes, the fluid to be cooled passing outside the tubes. Baffles 12 may be employed if desired to secure a greater cooling effect. A circulating pump 14 forces an aqueous solution of ammonia through the heat interchanger.

The means for introducing the ethylene oxide into the ammonia solution may take various forms. We have found that a suitable method is to diffuse the ethylene oxide through porous tubes or plates. In the drawing we show a device employing this method, said device consisting of a shell 15, having tube-sheets 17 at the ends thereof. Suitable headers 18—18′ are provided for connecting the device with the circulating pump and a conduit 21 leading from the heat interchanger. Porous tubes 16 extend between the tube sheets. The ethylene oxide is forced into the shell outside the porous tubes through an opening 19.

A still 23 is provided in the system on the delivery side of the circulating pump. This still may be heated by any suitable means but we prefer to use steam coils 24. The vapor from the still consisting of ammonia and steam, is collected in any suitable manner and led by a conduit 25 to a tank 26 containing water which absorbs the ammonia. After enough ammonia has been absorbed it may be transferred, either with or without further treatment, to an ammonia supply tank.

The process may be carried out as follows:

The pump being started, the valve from the ammonia supply tank is opened and the system is filled with a solution of ammonia. At the same time ethylene oxide is forced under pressure into the shell 15 surrounding the porous tubes 16. The ethylene oxide gradually diffuses through the tubes and combines with the ammonia to form ethanol amines. The solution thus treated is circulated through the closed circuit by means of the circulating pump 14 and is cooled in the interchanger. The ethylene oxide is added at such a rate as to maintain the temperature of the solution below 50° C., preferably at

about 40° C. The amount of oxide added depends upon the product desired. If, for example, 50% of the theoretical quantity of oxide for triethanol amine is added, that is to say, ethylene oxide in an amount equal to from about 1.5 to about 2.4 times the total quantity of ammonia present, the final product will contain from 25 to 35% diethanol amine with the balance principally triethanol amine. In other words, ethylene oxide may be added in an amount equal to from about 1.5 to about 2.4 times the total quantity of ammonia present. If 70 to 80% of the theoretical amount of oxide is used the final product will be only the triethanol amine. By using less than 50% of the oxide the final product will contain more of the monoethanol and diethanol amines and less of the triethanol amine. We do not consider it desirable to use the theoretical quantity of ethylene oxide as we have found that in this case undesirable by-products are formed which are difficult to remove. We prefer to operate the processes at temperature of between 40° C., and 50° C., although we have found that the reaction will progress at temperatures as low as 0° C., and as high as 100° C. However, at these extreme temperatures the reaction is more difficult to control and is usually attended by undesirable by-products. The circulation of the liquid medium is desirable in order to prevent localized overheating at the point of contact between the gas and liquid. When the desired amount of oxide has been added valve 27 is opened and the solution is transferred to the still 23 in which excess ammonia and water is removed by distillation, the ammonia evolved during distillation being absorbed in water in the tank 26 and thereby recovered for further use.

While we have described a method in which the gaseous ethylene oxide is diffused into an aqueous solution of ammonia, this reaction may be carried out by adding anhydrous ammonia to an aqueous solution of ethylene oxide or both the ethylene oxide and anhydrous ammonia may be added to water.

We claim:

1. In the process of making ethanolamines involving the operations of reacting ethylene oxide with an excess of aqueous ammonia while cooling and agitating the mixture, the improvements which consist in gradually adding the ethylene oxide to the aqueous ammonia by diffusing the former into the latter at such a rate that the concentration of uncombined ethylene oxide in the resulting reaction mixture is at all times low with respect to the concentration of uncombined ammonia whereby to minimize the formation of by-products in said reaction mixture, and continuously abstracting heat from said reaction mixture whereby to maintain the latter at a temperature below 100° C.

2. The improved process as defined in claim 1, characterized in that the total amount of ethylene oxide added equals from about 1.5 to about 2.4 times the total quantity of ammonia employed.

3. In the process of making ethanolamines involving the operations of reacting ethylene oxide with an excess of aqueous ammonia while cooling and agitating the mixture, the improvements which consist in gradually adding the ethylene oxide to the aqueous ammonia by diffusing the former into a flowing stream of the latter at such a rate that the concentration of uncombined ethylene oxide in the resulting reaction mixture is at all times low with respect to the concentration of uncombined ammonia whereby to minimize the formation of by-products in said reaction mixture, the total amount of ethylene oxide so added equalling from about 1.5 to about 2.4 times the total quantity of ammonia employed, while continuously abstracting heat from said reaction mixture whereby to maintain the latter at a temperature not greater than about 50° C.

In testimony whereof, we affix our signatures.

ERNEST W. REID.
DONALD C. LEWIS.

CERTIFICATE OF CORRECTION.

Patent No. 1,904,013. April 18, 1933.

ERNEST W. REID, ET AL.

It is hereby certified that error appears in the printed specification of the above numbered patent requiring correction as follows: Page 2, line 4, beginning with the words ", that is" strike out all to and including "present," in line 7; lines 10 to 13, strike out the words "In other words, ethylene oxide may be added in an amount epual to from about 1.5 to about 2.4 times the total quantity of ammonia present." and insert the same after "amine." in line 15; and that the said Letters Patent should be read with these corrections therein that the same may conform to the record of the case in the Patent Office.

Signed and sealed this 19th day of June, A. D. 1934.

Bryan M. Battey

(Seal) Acting Commissioner of Patents.