Jan. 14, 1936. F. C. BERSWORTH 2,028,041

PRODUCTION OF ETHYLENE DIAMINE

Filed Aug. 14, 1931 2 Sheets-Sheet 1

Fig. 1.

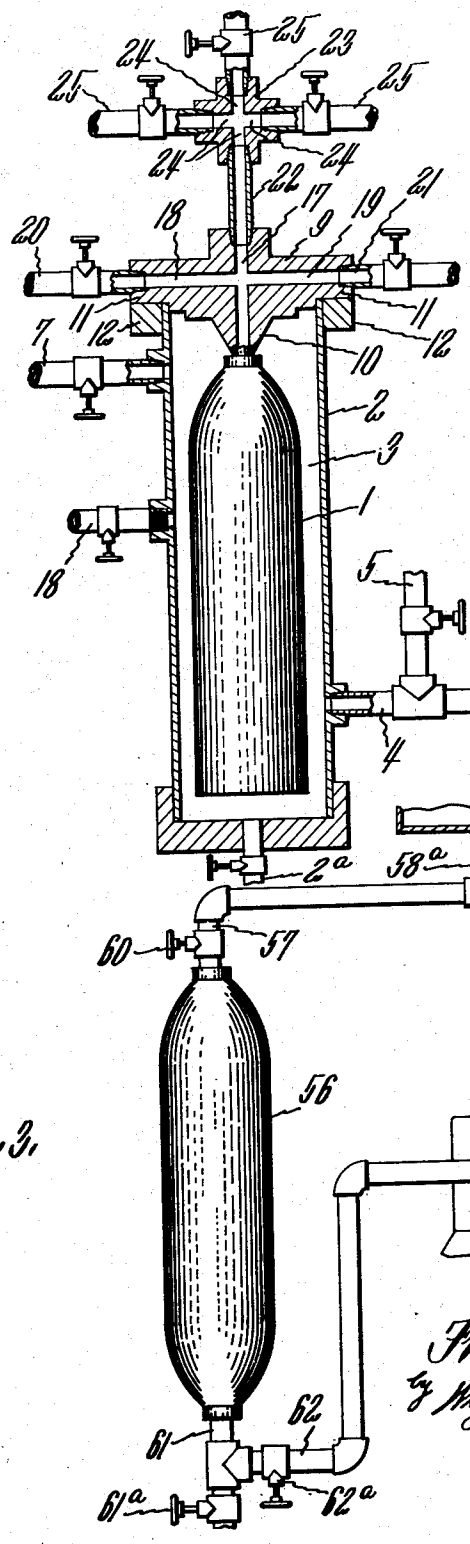


Fig. 2.

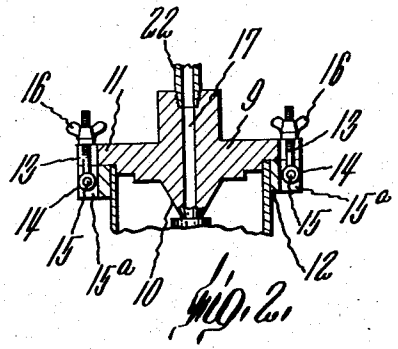


Fig. 3.

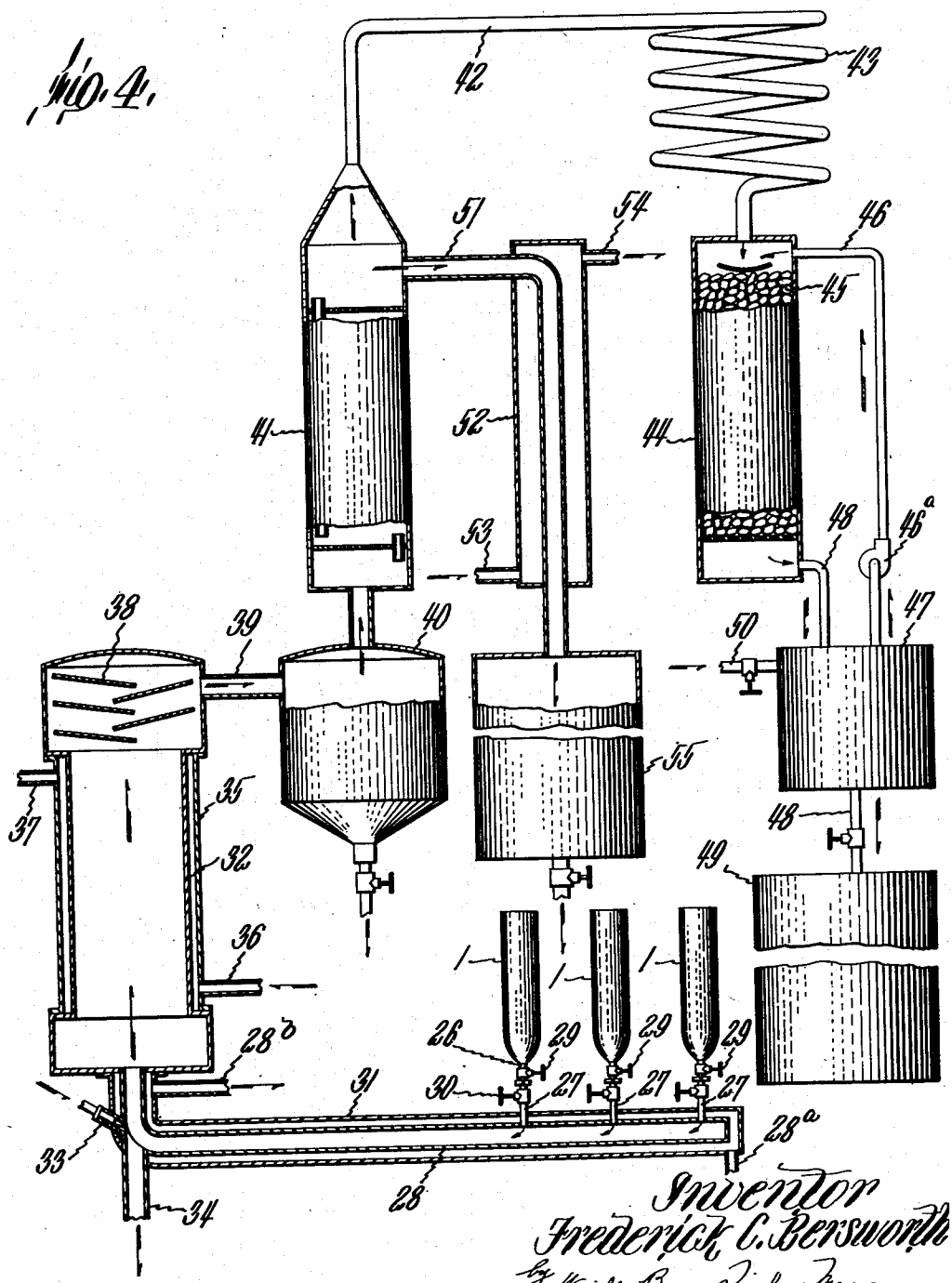
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Fig. 4.



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PRODUCTION OF ETHYLENE DIAMINE

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Application August 14, 1931, Serial No. 556,999

3 Claims. (Cl. 260—127)

This invention relates to a reaction between ammonia and ethylene dichloride to form ethylene diamine hydrochloride and the liberation from its hydrochloride of ethylene diamine as a chemical of high purity and suitable for a variety of uses.

I shall describe my invention in detail in conjunction with the accompanying drawings, wherein:

Figure 1 represents a section through one form of reaction bomb such as can be employed in carrying out the reaction.

Figure 2 is a sectional detail through the upper or charging end of the bomb.

Figure 3 shows another type of reaction bomb in combination with other instrumentalities for charging the starting chemicals.

Figure 4 illustrates more or less diagramatically and conventionally a recovery system designed to receive the reaction products from a reaction bomb.

Referring first to Figure 1 of the drawings,—1 represents a reaction vessel or bomb, which, as shown, is of cylindrical shape and has an opening at its upper end to receive the starting chemicals. The bomb is loosely received in a second cylindrical container 2, whose bottom and side walls are spaced sufficiently therefrom to provide a jacket 3 through which a suitable medium may be passed for controlling the temperature inside the bomb. Leading into the jacket 3 near the bottom of the container 2 is a pipe 4 having two valved branches 5 and 6. The branch 5 can be used to deliver water at seasonable temperature upwardly through the jacket 3, wherefrom it leaves through a valved discharge pipe 7 near the upper end of the container 2. The branch 6 may be used to deliver steam or other suitable heating medium through the jacket, wherefrom it is discharged through a valved pipe 8 shown below the pipe 7. The bottom of the container 2 may be provided with a valved drain pipe 2a, which may be opened to discharge cooling water or condensate from the jacket. The upper end of the jacket, as well as the bomb itself, can be confined by a closure 9, from whose bottom projects centrally a cone-shaped plug 10 which may be in tight-threaded engagement with the charging end of the bomb 1. The marginal portion 11 of the closure may be formed to fit nicely over a bearing ring 12 affixed to or made integral with the upper end of the container 2. The closure may be fastened to the jacket as by a plurality of bolts 13 whose lower ends 14 are pivoted on pins 15 bridging recesses 15a in the ring 12 and which can be swung upwardly and then sidewise through recesses in the marginal portion 11 of the closure, registering with the recesses 15a. With the bolts 13 in the upright position shown in Figure 2, wing nuts 16 may be engaged on the bolts and turned down to clamp the closure into seal-proof engagement with the ring 12. In order to permit the feeding of the chemicals into the assembled reaction bomb, the closure may have a vertical feed channel 17 leading to the charging end of the reaction bomb and side feed channels 18 and 19 merging with the central channel. The outer ends of the channels 18 and 19 may have received therein the terminal ends of feed pipes 20 and 21, respectively. The channel 17 may lead to a pipe 22 which, in turn, may be fitted into a threeway block 23, in each way 24 of which is engaged the end of a valved feed pipe 25 which can serve to deliver a particular chemical into the reaction bomb.

In using the apparatus hereinbefore described for the production of ethylene diamine, the procedure may be substantially as follows. The ethylene dichloride may be delivered through any one of the supply pipes, say the pipe 20, into the bomb. The ammonia may then be fed through another supply pipe, say the pipe 21, into the bomb. After the reaction bomb has been charged with the requisite amount of chemicals, the valves of the various feed pipes are closed. The main reaction product consists of ethylene diamine hydrochloride, but along with this reaction product there may be residual amount of ammonia, together with such secondary reaction products as may have been formed. The residual ammonia can be discharged from the reaction bomb by opening one of the pipes 25 to a recovery system presently to be described. The primary reaction product exists as a mass of loose needles containing entrained therein such secondary reaction products as the higher boiling point amines. The reaction product may be easily removed from the bomb, as it does not cake on or stick to the walls of the bomb. After it has been removed from the bomb, the ethylene diamine may be liberated from its hydrochloride by the use of any suitable base, such as caustic soda. To this end, the hydrochloride may be placed, together with dry caustic soda, in a still preferably provided with agitating means, as a result of which reaction takes place to liberate the free amine. This reaction is exothermic, so that external heat need not be supplied to the mixture, although the reaction may be

hastened by the application of heat. The reaction is quite rapid and results in a liquid reaction product containing sodium chloride. The freed liquid amine existing in the reaction product may be distilled at, say, 110° to 130° C., under which conditions the distillate is a water-white liquid consisting substantially of ethylene diamine. As is well known, ethylene diamine is quite hygroscopic, and the water-white distillate is inevitably associated with more or less water of hydration. The water of hydration results from the water produced during the liberation of the amine from the hydrochloride. The presence of additional water can be avoided by the use of substantially anhydrous caustic soda. One may, therefore, by the use of perfectly dry caustic soda, avoid any water in the amine other than that which ensues from the reaction to free the amine from its hydrochloride. By the use of a substantially anhydrous caustic soda, one can secure a distillate made up of approximately 62% of the amine. One may, as will hereinafter be described, remove practically all of the water in the amine. The diamine containing more or less water of hydration has a slippery feel characteristic of solutions of bases such as caustic soda. Depending upon the amount of water present therein, the diamine may have a boiling point varying from as low as about 110° C. to as high as 125° C. When the amine is substantially anhydrous, its boiling point is about 116° to 118° C. A product which contains about 20% of the free diamine has a boiling point of approximately 113° C.

The bomb is discharged into a suitable receiving and recovery system, such as that illustrated in Figure 4. The bomb may be equipped with only a single valved inlet pipe **26**, through which the starting chemicals may be fed into the bomb. The inlet pipe **26** of the bomb may be tightly engaged in any one of a series of valved discharge pipes **27** entering a manifold **28**. The valve **29** in the pipe **26** and the valve **30** in the pipe **27** may be opened to permit the discharge of the reaction products into the manifold **28**. This discharge being effected at elevated temperature and under high pressure through a small orifice, such residual ammonia and dichloride vapors as issue from the bomb undergo intimate admixture while passing at high velocity from high pressure stage in the bomb to the low pressure stage in the manifold **28**, with the result that complete reaction is ensured. The manifold **28** is preferably encompassed by a jacketing wall **31** so as to provide a jacket through which a suitable heating medium, such as steam, may be passed to maintain the discharged reaction products at the temperature required for separation and recovery. The steam may be delivered into the jacket through an inlet pipe **28***a* and may leave the jacket through an outlet pipe **28***b*. The reaction products are preferably discharged at about 150° C., which temperature is above the boiling point of the amine. Consequently, the temperature of the heating medium passed through the jacket may be below 150° C., for instance, at as low as 100° C., particularly if the reaction products are to be treated in the manifold **28** with caustic soda or equivalent base to liberate the free amine, as such liberation is accompanied by the evolution of heat. As shown, the reaction products pass horizontally through the manifold **28** and thence upwardly into an expansion chamber **32**, wherein the gaseous reaction vapors are brought down to atmospheric pressure. Immediately before passing into the expansion chamber, the vapors may undergo treatment with a solution of a suitable base, say a caustic soda solution, injected into the manifold, preferably as a spray from a spray nozzle **33**. At this point, it is to be remarked that the amine hydrochloride is carried along with the steam and residual ammonia gas as fine particles or as a solution in the steam, the pressure in the manifold being sufficient to sweep the amine hydrochloride past the nozzle **33** whereat it undergoes reaction to form the liquid amine and sodium chloride. The sodium chloride tends to precipitate out at the region where the reaction takes place, so that a trap **34** may lead off from the manifold immediately below the spray nozzle **33** to permit removal of the sodium chloride. In the reaction chamber **32** the amine, water, and residual ammonia vapors are heated, if necessary, to a temperature above the boiling point of the amine, say, 130° C. For this purpose, the expansion chamber may have a spaced outer wall **35** forming with the inner wall a jacket through which may be circulated a suitable heating medium coming from an inlet pipe **36** near the lower end of the chamber and leaving through an outlet pipe **37** near the upper end of the chamber. A series of suitable baffles **38** may be arranged near the upper end of the expansion chamber so that such sodium chloride and other solid particles as are present in the vapors will tend to separate out and to fall through the expansion chamber into the trap **34**. The vapors flow from the upper end of the expansion chamber through a pipe **39** into a receiver **40**, wherein higher boiling amines and residual solid impurities tend to accumulate. The remaining vapors, made up essentially of the desired amine, water, and ammonia, are passed upwardly through a dehydrating column **41**. The more volatile constituents, namely, the ammonia and steam, are taken off at the upper end of the column through a pipe **42** and a coil **43** emitting into a tower **44** filled with inert interstitial material **45**, such as spiral brick or the like. While passing downwardly through the tower **44**, the steam and ammonia are scrubbed with water delivered onto the inert interstitial material from a pipe **46** communicating with a water-supply tank **47**. The steam is condensed and the ammonia vapor is dissolved in the water trickling downwardly through the tower, the ammonia water falling to the bottom of the tower being returned by a drain pipe **48** to the tank **47**. The water in the tank **47** is recirculated by a pump **46***a* included in the pipe **46** until the concentration of ammonia has reached saturation, namely, 26° Baumé, whereupon the concentrated ammonia water is discharged from the tank **47** through a pipe **48** into a storage tank **49** for reuse in preparing new amine. Such fresh water as is needed in the tank **47** may be had from a valved water-feed pipe **50** discharging into the tank **47**. Returning again to the dephlegmating column **41**, a vapor conduit **51** leads off from the tower somewhat below its upper end and conducts the less volatile amine vapors downwardly through a condenser or water jacket which is shown encompassed by an outer wall **52**. Cold water may be fed upwardly through the jacket from a pipe **53** and be removed near the upper end of the jacket through a pipe **54**. The condensed amine may be discharged into a tank **55** from which it may be removed for use as such or for further treatment.

For many technical uses, the amine is valuable with an inclusion of water. For some purposes, however, it is desirable to have substantially anhydrous amine. I have found caustic alkalies, such as caustic soda and caustic potash, are excellent dehydrating chemicals. Thus, caustic soda may be intimately admixed with the aqueous solution of the amine and the mixture allowed to stand. The caustic soda selectively absorbs the water and settles out, leaving a supernatant layer of water-free amine, which may be decanted or otherwise removed from the underlying hydrated caustic soda. This particular dehydrating treatment can be considered as a salting-out operation, since a saturated solution of caustic soda is a non-solvent of the amine.

The recovery system shown in Figure 4 may be operated in connection with a number of reaction bombs in which the reaction has been completed. That is to say, a number of bombs may be discharged in succession into the recovery system to constitute in effect continuous recovery operation. From an economical standpoint, I have found it preferable to utilize small bomb units for effecting the reaction, but it is obvious that large autoclaves might be used in lieu of small bombs and that the autoclaves might be permanently tied up with the recovery system in such a way that the reaction is effected while the autoclaves are closed off from the recovery system and the autoclaves containing the reaction products then exhausted into the recovery system. A procedure of this sort is illustrated in Figure 3, wherein a bomb **56** whose charging end may be made to communicate selectively through a valved pipe **57** with either a supply of ethylene dichloride in a tank **58** having a valved outlet **58***a* or a source of ammonia in a tank **59** having a valved outlet **59***a*. A valve **60** in the pipe **57** may be opened to feed the starting chemicals successively into the bomb **56** after a previous charge of reacted chemicals has been discharged through a valved discharge pipe **61** permanently connected with the recovery system. The charging of fresh chemicals into the bomb may be facilitated by a valved pipe **62** leading off from the pipe **61** to a vacuum pump **63** or other suitable evacuating means. After the reaction bomb has been charged with the starting chemicals, the valve **60** is closed. At this time, too, the valve **61***a* in the pipe **61** is closed and the valve **62***a* leading to the vacuum pump is closed. At the end of the reaction, the valve **61***a* is opened to permit the discharge of the reaction products into the recovery system. The discharge tends to create a partial vacuum in the bomb **56**, particularly when it is permitted to cool for some time and condensation of such steam as remains therein takes place. The extent of the vacuum created, however, may be augmented by closing the valve **61***a* after the discharge of the reaction products and connecting the bomb with the vacuum pump **63**.

A preferred method of effecting the reaction using, for example, the apparatus shown in Figure 1 may consist in charging the bomb initially with the appropriate amount of liquid ammonia. The bomb may then be heated to about 100° C. to vaporize the ammonia and to create pressure in the bomb, whereafter the ethylene dichloride may be fed or injected thereinto under pressure into the bomb to effect the reaction. So, too, while the reaction is in progress or before the reaction has commenced, one may feed into the bomb shown in Figure 1 an amount of caustic soda or other base sufficient to liberate the free amine and thus avoid the necessity of carrying out such liberation as a separate subsequent step. In such latter case, the bomb may be discharged to advantage in the recovery system shown in Figure 4, so as to accomplish a separation of the free amine from the sodium chloride, higher amines, and other reaction products. This method also has an advantage, in that the free amine is produced in situ in the bomb, thereby utilizing the heat of the reaction products to promote a liberation of the amine.

The step of dehydrating the amine by the use of dehydrating agents, and more especially caustic soda, at low temperatures is an important one. Heretofore, it has been the practice to remove the water content of amines by repeated distillation, which, however, is expensive and objectionable because of degradation or decomposition of the amine itself. I have found that the treatment of the water-containing amine resulting from my process with caustic soda at room temperature not only ensures a substantially complete removal of the water content from the amine, but is attended by no undesirable side reaction whatever, as attested by the fact that the resulting amine retains its water-white appearance and freedom from malodors. In fact, the amine is purified or refined by the removal of its water content, which content is apparently associated with malodors and coloring matter. Thus, a water-containing amine is characterized by an opalescent and slightly yellow appearance, whereas the water-free amine has a crystal-clear appearance and complete freedom from malodors of the pyridine type.

There are other important phases of the procedure hereinbefore outlined. First of these may be mentioned the fact that, according to my process a high yield of excellent quality amine is made possible. This result is attributable to the particular temperature under which I effect the reaction, namely, 150° C. After considerable experimentation, I have found that, irrespective of the amount of heat externally applied and furnished by the reacting chemicals themselves, it is highly desirable, in forming ethylene diamine, to react the chemicals at about 150° C. Under the conditions of operation hereinbefore outlined, a temperature of reaction of 150° C. is attained when the starting chemicals are heated to 100° C., but in any case, the chemicals should be maintained at a reacting temperature of about 150° C. If this temperature is understepped considerably, there is a high residium of unreacted material, which is reflected in low yield of desired primary reaction product. On the other hand, if this temperature is considerably overstepped, considerable undesirable side reactions conducive to high boiling point amines ensue, with an attendant low yield of desired primary reaction product. The utilization of the heat of the reaction and the heat supplied to initiate the reaction in the liberation of the amine is also of value. In other words, by adding a suitable base, such as caustic soda, to the reaction bomb, or during the discharge of the reaction products from the bomb, one does away with the necessity of using separate apparatus and of supplying additional heat in securing the free amine. The discharge of a bomb under high pressure while hot is of value for the reason that, should the reaction be uncompleted in the bomb, the reaction tends to go to completion during the discharge of the bomb at optimum reacting temperature. The fact is, that in such

instances where the chemicals have been kept at reacting temperatures for an insufficient period of time to complete the reaction, the reaction will be more nearly completed if the bomb contents are discharged at reacting temperature. Should the bomb with incompletely reacted chemicals be permitted to cool and then be discharged, it is found that there is a greater residium of unreacted chemical. The feature of discharging the bomb into a recovery system makes possible the utilization of the heat content of reaction products in effecting the distillation and recovery of the amine from the undesirable diluents and contaminations included therewith. After the amine associated with more or less water is recovered, by the simple expedient of adding suitable salting-out agents thereto, I am enabled to secure the water-free amine. The salting-out agents which are operative in my process are those which are insoluble in the amine, which do not react upon the amine, and which tend to take on water to form solutions which are immiscible with the water-free amine. Caustic soda and caustic potash are chemicals which are comparatively cheap and which answer well the desiderata of salting-out agents for liquid amines containing water, as they are unreactive with the amines at about room or lower temperature. The step of salting-out or dehydrating a water-free amine is, however, applicable not only to amines prepared by my process, but such amines containing water as have heretofore appeared on the market.

I claim:

1. A process which comprises confining ammonia in vaporized condition at a temperature of about 100° C. and under superatmospheric pressure and injecting ethylene dichloride under pressure into the hot, compressed ammonia vapor, thereby forming ethylene diamine hydrochloride.

2. A process which comprises confining liquid ammonia, heating the confined liquid ammonia sufficiently to vaporize it and to generate superatmospheric pressure, and injecting ethylene dichloride under pressure into the hot, compressed ammonia vapor, thereby forming ethylene diamine hydrochloride.

3. A process which comprises confining liquid ammonia, heating the confined liquid ammonia sufficiently to vaporize it and to generate superatmospheric pressure, injecting ethylene dichloride under pressure into the hot, compressed ammonia, thereby forming ethylene diamine hydrochloride, emitting the hot, compressed reaction products as a stream under atmospheric pressure, treating the stream of hot reaction products with a base of the character of caustic soda to liberate the ethylene diamine from its hydrochloride and to form a chloride of the base, and recovering the ethylene diamine from the chloride of the base.

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