

Oct. 25, 1966

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3,281,211

PROCESS OF FORMING HYDRAZINE

Filed July 26, 1963

Fig. 1

NaCl in liquid NH_3 NaCl in liquid NH_3

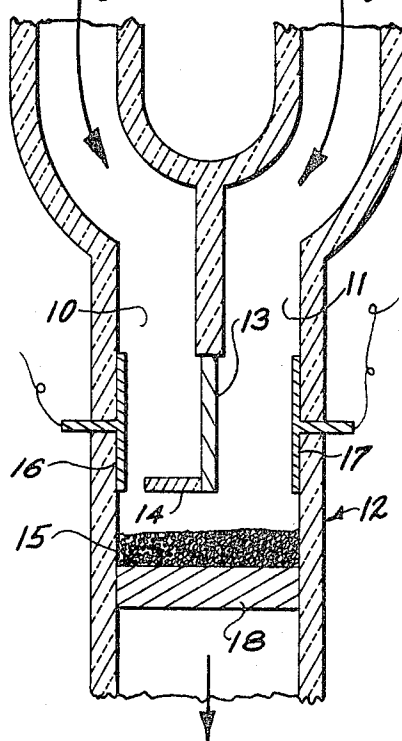


Fig. 2

KCl in liquid NH_3 KCl in liquid NH_3

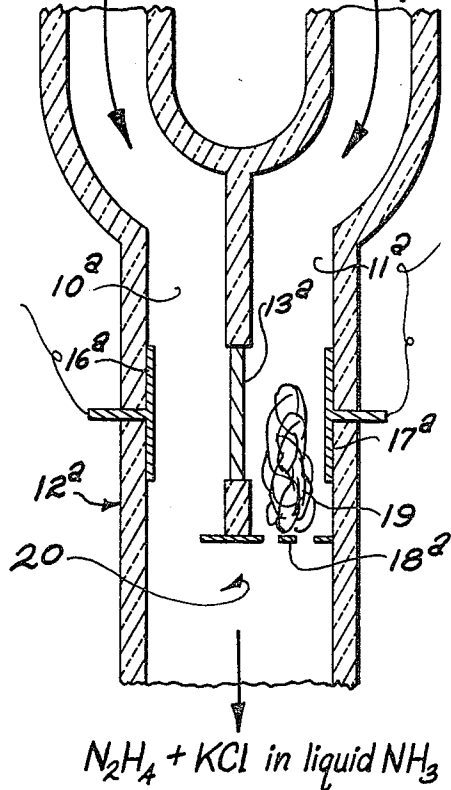
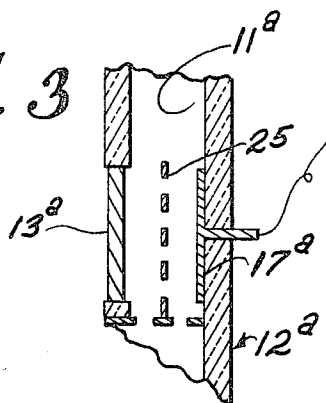


Fig. 3



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1

3,281,211

PROCESS OF FORMING HYDRAZINE

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Filed July 26, 1963, Ser. No. 297,894
5 Claims. (Cl. 23—190)

This invention relates to a process of forming hydrazine by the electrolysis of an electrolyte consisting of an alkali metal chloride in liquid ammonia.

A primary object of my invention is to provide a process of producing anhydrous hydrazine in which the hydrazine is produced in liquid ammonia in such a manner that the separation of the anhydrous hydrazine from the ammonia is simple and economical.

Another object of my invention is to provide an electrolytic process for forming hydrazine in which the negative ions formed in the cathode compartment of an electrolytic cell are prevented from entering the anode compartment thereof, thereby preventing the formation of hydrazine in the anode compartment where it would be decomposed by anodic oxidation.

As is well known in the art to which my invention relates, various processes have been devised for producing anhydrous hydrazine, such as the conventional Raschig synthesis (sodium hypochlorite plus aqueous ammonia). In this process, a dilute aqueous solution of hydrazine is formed and the hydrazine is recovered by separating the hydrazine from the water solution. This separation is difficult and expensive due to the formation of the azeotrope, hydrazine hydrate.

Another well known process of making hydrazine has included the formation of chloramine by the reaction of ammonia with chlorine in the gas phase followed by condensation of the chloramine-ammonia gas mixture in liquid ammonia, where reaction occurs to form anhydrous hydrazine. A mixture of hydrazine and ammonium chloride in liquid ammonia is thus produced. The hydrazine is difficult and expensive to separate from this mixture because of an equilibrium between NH_4^+ and N_2H_5^+ ions in the presence of the Cl^- anion.

Hydrazine has also been produced from ammonia by a fission-chemical reaction wherein hydrazine is produced in liquid ammonia. While there is no problem in separating these two components, there are problems encountered in the separation of the traces of radioactive contaminants.

To overcome the difficulties encountered in the production of hydrazine, I have devised a process of forming hydrazine in which an electrolyte consisting of sodium chloride or potassium chloride in liquid ammonia is introduced into separate anode and cathode compartments of an electrolytic cell. The electrolyte is then electrolyzed while the negative ions formed in the cathode compartment are prevented from entering the anode compartment. Chloramine and ammonium chloride are formed in the anode compartment. A reaction of the electrolyte of the cathode compartment is catalyzed by the presence of iron, cobalt or nickel to form an alkali metal amide. The products of the anode and cathode compartments are brought together to form a solution of hydrazine and an alkali-metal chloride in liquid ammonia. The hydrazine is then recovered from the solution thus formed.

Apparatus which may be employed to carry out my improved process is shown in the accompanying drawing, forming a part of this application, in which:

FIG. 1 is a diagrammatic view of an electrolysis cell and reactor in which sodium chloride in liquid ammonia is introduced into the anode and cathode compartments;

FIG. 2 is a diagrammatic view of an electrolysis cell and reactor in which potassium chloride in liquid ammonia is introduced into the anode and cathode compartments; and,

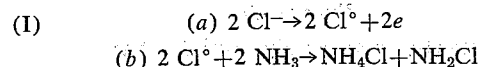
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FIG. 3 is a fragmental view showing a still further modified form of my invention.

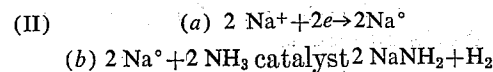
Referring now to the drawing for a better understanding of my invention, and more particularly to FIG. 1, I introduce an electrolyte consisting of sodium chloride in liquid ammonia into the anode compartment 10 and the cathode compartment 11 of an electrolysis cell indicated generally at 12. The anode compartment 10 is separated from the cathode compartment 11 by a porous diaphragm 13 or other suitable means to prevent migration of negative ions from the cathode compartment 11 to the anode compartment 10. A cation permeable diaphragm may be employed instead of a porous diaphragm. Preferably, a baffle 14 or other suitable means is provided adjacent the lower end of the anode compartment 10 to restrict the flow of the electrolyte from the lower end thereof whereby there is a continuous flow of a portion of the electrolyte through the diaphragm 13 from the anode compartment to the cathode compartment. Accordingly, there is no net flow of negative ions from the cathode compartment 11 to the anode compartment.

As the electrolysis proceeds, the reactions are as follows:

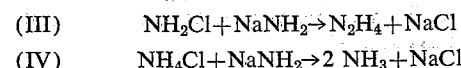
At the anode=



At the cathode=



When the anolyte and catholyte are mixed=



Chloramine and ammonium chloride are formed by reactions I at the anode and simultaneously therewith sodamide is formed by the catalytic reactions II at the cathode. Reaction II (b) is catalyzed by the presence of iron, cobalt or nickel. The catalyst may be absorbed onto a carbon electrode, or a catalytic metallic screen may be placed adjacent a carbon electrode, or the cathode itself may be made of the catalytic metal. As shown in FIG. 1, the anode is indicated at 16 and the cathode is indicated at 17, both of which may be formed of carbon.

A porous filter diaphragm 18 extends across the lower portion of the electrolysis cell 12 beneath the diaphragm 13, as shown. The insoluble amide is carried as a slurry downwardly to the porous filter diaphragm 18 where the solid material is retained as at 15.

The chloramine and ammonium chloride formed at the anode are carried in solution to the solid bed of sodamide on the porous filter diaphragm 18 whereupon reactions III and IV occur to form hydrazine and sodium chloride in liquid ammonia solution. This solution passes through the porous filter diaphragm 18 and is removed from the electrolysis cell for subsequent separation. The separation of the anhydrous hydrazine from the solution may be carried out by conventional processes well known in the art, such as distillation of the ammonia followed by evaporation and condensation of the hydrazine from the sodium chloride. The sodium chloride and the liquid ammonia may be recycled to the electrolysis cell 12.

A critical feature of my improved process is that the products formed at the cathode must be prevented from entering the anode compartment 10. That is, if the NH_2^- ions enter the anode compartment, hydrazine will be formed near the anode and will be decomposed by anodic oxidation. Accordingly, to the extent that the NH_2^-

ions enter the anode compartment, the yield of hydrazine will be reduced. The cathodic products may be prevented from reaching the anode compartment 10 by providing the porous diaphragm 13 and baffles 14 which restrict the downward flow of the anodic products whereby there is a continuous and sufficient flow of the solution through the porous diaphragm 13 from the anode compartment 10 to the cathode compartment 11 to prevent the migration of NH_2^- ions to the anode compartment 10. Instead of employing a porous diaphragm, the member 13 may be in the form of a cation-permeable membrane whereby there is no flow of negative ions from the cathode compartment 11 to the anode compartment 10.

Where my process is carried out at temperatures above 33.35°C , the electrolytic cell is maintained under pressure in order to prevent the escape of gaseous ammonia.

Example I

As an example of my improved process, liquid ammonia at -78°C . was saturated with sodium chloride. The sodium chloride solution was electrolyzed in an electrolytic cell as shown in FIG. 1 and described hereinabove at a current density of 300 to 400 amp/sq. ft. Appreciable quantities of hydrazine were detected in the effluent solution from the electrolysis cell by a conventional method of analysis that makes use of the highly colored compound formed by the reaction of p-dimethyl amino-benzaldehyde with hydrazine.

Example II

My improved process was also carried out as described in Example I with the exception that the current density was from 120 to 200 amps/sq. ft. Hydrazine was detected in the solution leaving the cell, but the amounts were less than in Example I.

Referring now to FIG. 2 of the drawing, I show another embodiment of my invention in which potassium chloride is dissolved or slurried in liquid ammonia and introduced into both compartments of a two-compartment electrolytic cell 12^a.

Chloramine and ammonium chloride are formed at the anode 16^a in the anode compartment indicated at 10^a, similarly to reaction I (b). Potassium metal is formed at the cathode 17^a in the cathode compartment indicated at 11^a and goes into solution where it is carried downwardly toward a retaining screen indicated at 18^a. A catalytic metal, such as iron, cobalt or nickel wire, gauze, or wool 19 is supported by the retaining screen 18^a, as shown in FIG. 2. When the solution of potassium metal comes into contact with the catalytic metal 19, potassium amide is formed as sodamide is formed in reaction II (b). The soluble potassium amide flows with the solution to a space indicated at 20 downstream from the wire mesh 19 where it mixes with the products from the anode compartment. In the space 20 reactions similar to reactions III and IV occur. Accordingly, hydrazine and potassium chloride are produced by reactions similar to reactions II (b), III, and IV in space 20 and leave with the liquid ammonia.

After removal of the hydrazine and potassium chloride in liquid ammonia from the electrolysis cell 12^a, the hydrazine is recovered by conventional means and the potassium chloride and liquid ammonia may be recycled.

It is also critical that the cathodic product be prevented from entering the anode compartment 10^a for the reasons pointed out hereinabove. The means 13^a employed to prevent the migration of negative ions from the cathode compartment 11^a to the cathode compartment 10^a may be in the form of a porous diaphragm with solution flow from the anode compartment 10^a to the cathode compartment 11^a. Also, a cation-permeable membrane may be employed to separate the anode compartment from the cathode compartment.

Where potassium chloride in liquid ammonia is employed as the electrolyte in the electrolytic cell 12^a catalytic metal grids or meshes 25 may be placed in the cathode compartment 11^a, as shown in FIG. 3 so that the soluble potassium amide is formed in the cathode compartment 11^a and is carried in solution to the bottom of the electrolytic cell 12^a to be reacted similar to reactions III and IV to form hydrazine, as described hereinabove.

From the foregoing, it will be seen that I have devised an improved process for forming hydrazine. By forming the hydrazine in liquid ammonia whereby the anhydrous hydrazine may be recovered in a simple and inexpensive manner, I eliminate the formation of the azeotrope, hydrazine hydrate, and the difficult and expensive separation procedures required. By preventing the migration of the negative ions from the cathode compartment to the anode compartment, hydrazine is not formed near the anode, thereby preventing decomposition of the hydrazine by anodic oxidation.

I wish to be understood that I do not desire to be limited to the exact details of the process shown and described, for obvious modifications will occur to the person skilled in the art.

What I claim is:

1. A process of forming hydrazine which comprises,
 - (a) introducing an electrolyte consisting of an alkali metal chloride selected from the group consisting of sodium chloride and potassium chloride in liquid ammonia into separate anode and cathode compartments of an electrolytic cell,
 - (b) electrolyzing said electrolyte while preventing the negative ions formed in the cathode compartment from entering the anode compartment to form chloramine and ammonium chloride in the anode compartment,
 - (c) catalyzing a reaction of the electrolyte of the cathode compartment to form an alkali metal amide,
 - (d) bringing together the products of the anode and cathode compartments to form a solution of hydrazine and an alkali metal chloride in liquid ammonia, and
 - (e) recovering hydrazine from the solution thus formed.

2. The process as defined in claim 1 in which sodium chloride is the alkali metal chloride employed and sodamide is formed in that cathode compartment.

3. The process as defined in claim 1 in which potassium chloride is the alkali metal chloride employed and potassium metal is formed in the cathode compartment where it goes into solution and is catalyzed to form potassium-amide.

4. The process as defined in claim 1 in which the reaction of the electrolyte of the cathode compartment is catalyzed by a catalytic metal selected from the group consisting of iron, cobalt and nickel.

5. The process as defined in claim 1 in which the products formed in the cathode compartment are prevented from entering the anode compartment by separating the anode compartment from the cathode compartment by a porous diaphragm and causing a continuous flow of a portion of the electrolyte from the anode compartment to the cathode compartment.

References Cited by the Examiner

UNITED STATES PATENTS

586,236	7/1897	Hulin	204—258 X
2,841,543	7/1958	Haller	204—59
3,082,158	3/1963	Lefrancois et al.	204—59

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