ENCLOSURE (B) 8

SYNTHESIS OF HYDRAZINE

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LIST OF TABLES AND ILLUSTRATIONS

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SUMMARY

The synthesis of hydrazine by Raschig's method was studied and the following raw materials were used:

2.5~30 % water solution of ammonia
1~2 N water solution of sodium hypochlorite
10% water solution of glue

The results of the experiments were as follows:

To increase the yield of hydrazine, much excess of NH_3 should be used. The mol-ratio of NH_3/ NaOCl should be more than 20.

The temperature of materials should be 0°C-10°C before mixing, and the time required for mixing must be short.

It is sufficient to heat the mixture of materials to 50°C to complete the reaction, but it is necessary to heat it to about 100°C to recover the excess of NH_3.

If the glue is absent, the yield of hydrazine is much reduced. The glue should be added previously to the solution of NH_3, and it is sufficient to use 0.05 gm of glue per 100cc of the mixture of materials.

All types of glue, gelatine, cerisine of silk, peptone, or a solution of chrysalis were found to be suitable.

If traces of heavy metal ions are present, the yield of hydrazine is much reduced.

In the laboratory test, 95% of the excess of NH_3 can be recovered.

I. INTRODUCTION

A. History of the Project

In July 1944, we were ordered to study the synthesis of hydrazine from NH_3 and NaOCl. This reaction was reported by Raschig(1) in 1907, and the equations are as follows:

$$NH_3 + NaOCl \longrightarrow NH_2Cl + NaOH$$
$$NH_3 + NH_2Cl \longrightarrow NH_2\text{-}NH_2HCl$$

$$2NH_3 + NaOCl \longrightarrow NH_2\text{-}NH_2H_2O + NaCl$$

R. A. Joyner(2) also made a detailed report of this reaction. It was desired to reproduce their experiments and decide on the conditions for the large scale production of hydrazine. When our laboratory experiments were finished, the large scale production of hydrazine was being carried out in a civilian factory, so the plan was abandoned.

The flow sheet of the pilot plant for hydrazine synthesis is shown in Plate I(B)8, but this pilot plant was not used. Small amounts of 80% solution of hydrazine hydrate were made as samples.

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B. Key Research Personnel Working on Project

Chem. Engr. Lieut. Comdr. Y. KOMOTARI
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II. DETAILED DESCRIPTION

A. Description of Test Apparatus

In this study only glass beakers, flasks and porcelain dishes were used.

B. Test Procedures

1. Preparation of Raw Materials

a. Water solution of NH_3. Ordinary commercial solution of NH_3 (chem. pure) was used.

b. A water solution of NaOCl was prepared as follows: Put 500 grams of bleaching powder in 2.5 liters of water, and add 500 grams of Na_2SO_4. After a few hours, filter the solution of NaOCl through a filter-paper, and measure the concentration of NaOCl with iodine.

c. A water solution of ordinary glue was prepared.

2. The details of test procedures and conditions were as follows: Mix 1000cc of a 3.1% NH_3 solution and 15cc of a 10% glue solution, then add 500cc of a 1.6 N NaOCl solution in a porcelain dish. Heat the mixture quickly, boil it for about 20 minutes, when it will have evaporated to about 1/3 of its original volume. When cold, add an excess of conc. H_2SO_4 solution, and cool. Hydrazine sulphate crystallizes out. Filter the crystals, wash with alcohol, dry in an air bath at 100°C, weigh, measure the purity with iodine, and calculate the yield of hydrazine based on the consumption of NaOCl.

C. Experimental Results

1. The effect of mol-ratio of NH_3/NaOCl on the yield of hydrazine (shown in Table I(B)8).

From Table I(B)8, it is obvious that to increase the yield of hydrazine a large excess of NH_3 must be used. In large scale production of hydrazine, the ratio of NH_3/NaOCl should be 20~40.

2. Effect of the temperature of mixing on the yield of hydrazine. The mixture of NH_3 and glue was kept at constant temperature in a 3-necked flask, and the solution of NaOCl was added at the same temperature, then heated to 50°C and kept at this temperature for 5 minutes. The solution was divided into two parts and the yield of hydrazine was measured by iodometry on one portion and the other portion was boiled as stated above.

The results of the experiments are tabulated in Table II(B)8.

From this table, it is obvious that when the temperature of mixing is as high as 25°C, the yield of hydrazine decreases.

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3. Effect of Mixing Time on the Yield of Hydrazine. The yield of hydrazine prepared under two conditions was compared. In Exp. No.14 the materials were mixed rapidly, (in this case the temperature of the mixture rose from 10°C to 17°C). In Exp. No. 15 the temperature of the solution of NH_3 (containing glue) was kept at 10°C and the solution of NaOCl was added slowly at the same temperature, (it took about 1 hr. to complete the reaction), and then treated as stated above. The results of these experiments are recorded in Table III(B)8.

It appears that better yields of hydrazine are obtained when the solutions are mixed rapidly then when they are mixed slowly.

4. Effect of the Temperature of Heating on the Yield of Hydrazine. The solutions were mixed at 10°C, heated at constant stirring, kept at a fixed temperature for 30 minutes, and the yield of hydrazine measured by iodometry. From this experiment, it appears that the reaction is completed at 60°C, but that when it is necessary to heat the solution to 90°C~100°C to recover excess NH_3, small amounts of hydrazine are evaporated with NH_3 and water. The results are shown in Table IV(B)8.

5. Effect of Concentration of Glue on the Yield of Hydrazine. If the glue is absent in the mixture, the yield of hydrazine is much reduced. To examine the necessary amount of glue, from 0.001 to 1 gram of glue per 100cc of total solution was added to the mixture of raw materials. When the glue is previously added to the solution of NaOCl, the yield is much smaller than the case in which glue is previously added to the solution of NH_3.

6. Various types of glue, gelatine, cerisine of silk, peptone, and a solution of chrysalis are all useful and have the same effect in this reaction. (No experimental datum is available).

7. If even traces of heavy metal ions (especially Cu^{++}, Fe^{++}, Fe^{+++} etc.) are present, the yield of hydrazine is much reduced. (No experimental datum is available).

8. Recovery of excess ammonia and generation of nitrogen by side reactions.

To measure the amount of N_2 generated by the side reactions, a 3-necked flask was used as a closed reaction vessel, and all the gas generated from the reacting solutions was gathered. The gas was washed with dilute H_2SO_4 solution to recover the excess of NH_3, and the amount of N_2 was measured by gas analysis. The results of this experiment were as follows:

Raw materials NH_3 solution 31% 178cc (NH_3 49.5gm)

NaOCl solution 1.44 N 100cc

Glue solution 10% 2.8cc

Yield of $N_2H_4H_2SO_4$ 45.2%

Recovered NH_3 44.17gm

Gathered N_2 0.8gm

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Material balance of NH_3

~~Raw Material~~	~~49.5gm~~	~~100.00%~~
As product ($N_2H_4H_2SO_4$)	2.3gm	4.65%
Recovered	44.17gm	89.32%
Loss	3.03gm	6.03%
As N_2	0.8gm	1.6 %

From this data, it is the opinion of the authors that N_2 is generated as follows:

$$NH_3 + NaOCl \longrightarrow NH_2Cl + NaOH$$
$$NH_3 + NH_2Cl \longrightarrow NH_2NH_2HCl$$
$$NH_2NH_2HCl + 2NH_2Cl \longrightarrow 2NH_4Cl + HCl + N_2$$

III. CONCLUSIONS

The synthesis of hydrazine by Raschig's method was studied. The necessary conditions to obtain hydrazine with high yield were as follows:

The mol-ratio of $NH_3/NaOCl$ must be greater than 20.
The raw materials should be mixed quickly at temperature below 10°C.
Before mixing the reagents, 0.05 gram of glue per 100cc of total solution must be dissolved in the solution of NH_3.
All materials must be completely free from heavy metal ions.

In this way the yield of hydrazine is 35~45% (calculated from the consumption of NaOCl). It is thought that in large scale production of hydrazine there will be technical difficulties in regard to the following:

Purity of raw materials.
Recovery of excess of NH_3.
Reaction vessel. (Metal vessels are all inadequate for this reaction.)

Notes

Physical and Chemical Properties of Products.

The 80% solution of hydrazinehydrate is a colourless, corrosive liquid which fumes in air and smells like NH_3. Specific gravity of solution is about 1.03, and b.p. is about 113°C. This solution absorbs moisture and CO_2 from air, and is slowly attacked by O_2 with the liberation of N_2, and miscible with water in all proportions.

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Table I(B)8
EFFECT OF NH_3/NaOCl RATIO ON YIELD OF HYDRAZINE

Exp. No.	NH_3 Soln.**		NaOCl Soln.**		NH_3/NaOCl	Glue Soln.**		$(NH_2)_2H_2SO$	
	(cc)	Conc(%)	(cc)	conc(N)	mol-ratio	(cc)	conc(%)	(gm)	Yield(%)
1	1000	31	500	1.60	20.2	15	10	36.2	35.0
2	500	31	500	1.60	10.1	10	10	27.3	26.4
3	125	31	250	1.60	35.0	4	10	4.4	9.5
4	595	31	100	2.22	40.0	7	10	13.3	45.9
5	595	31	200	2.22	20.0	6	10	20.1	35.8
6	208	31	200	2.22	7.0	4	10	8.9	15.5
7*	326	29	50	1.24	80.0	4.5	10		61
8*	90	29	100	0.052	186	5.0	1		65
9*	90	29	100	0.0052	1860	5.0	1		69

*Yield determened by iodometry
**Raw materials cooled to 10°C before mixing

Table II(B)8
EFFECT OF TEMPERATURE OF MIXING ON YIELD OF HYDRAZINE

Raw material NH_3 31% 178cc
NaOCl 1.44N 100cc
NH_3/NaOCl = 20
Glue 10% 2.8cc

Exp.No.	Mixing		Yield	
	Temp °C	Required Time min	Before Condensation	After Boiling
10	-6	13	48.7	34.4
11	10	13	48.4	35.3
12	0	14	49.4	39.5
13	24.5	11	42.3	31.7

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Table III(B)8
YIELDS OF HYDRAZINE

Raw Materials NH_3 29% 163cc
NaOCl 1.25 N 100cc
} $NH_3/NaOCl = 20$
Glue 10% 4.5cc

Exp.No.	Method of Mixing	Temperature	Yield
14	mix. solns. at a time	10-17°C	46.5
15	mix. solns. slowly	100C	38.7

Table IV(B)8
EFFECT OF HEATING TEMPERATURE ON YIELD OF HYDRAZINE

Raw materials NH_3 31% 189cc
NaOCl 1.5 N 100cc
Glue 10% 4.5cc

Exp. No.	Temp. of Heating °C	Last Volume cc	Strength of Alkalis Normality	Yield of Hydrazine %
16	10	257	5.6 N	37.0
17	30	250	4.15	41.2
18	50	238	3.80	42.6
19	70	199	1.10	42.0
20	90	159	0.59	40.8
21	100	97	0.74	36.0
22*	100	116	0.67	35.6

*Solution heated quickly

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Table V(B)8
EFFECT OF GLUE CONCENTRATION ON YIELD OF HYDRAZINE

Raw material NH_3 31% 134cc

NaOCl 1.8 N 66cc

Glue 10%

(I) Glue previously added to solution of NH_3

Exp.No.	23	24	25	26	27	28
Glue gm/100cc	0.001	0.01	0.05	0.1	0.5	1.0
$N_2H_4H_2SO_4$ Yield (%)	36.2	37.8	42.8	42.1	41.7	42.6

(II) Glue previously added to solution of NaOCl.

Exp.No.	29	30	31	32	33	34
Glue gm/100cc	0.001	0.01	0.05	0.1	0.4	0.8
$N_2H_4H_2SO_4$ Yield (%)	24.8	30.7	36.0	40.1	26.4	4.2

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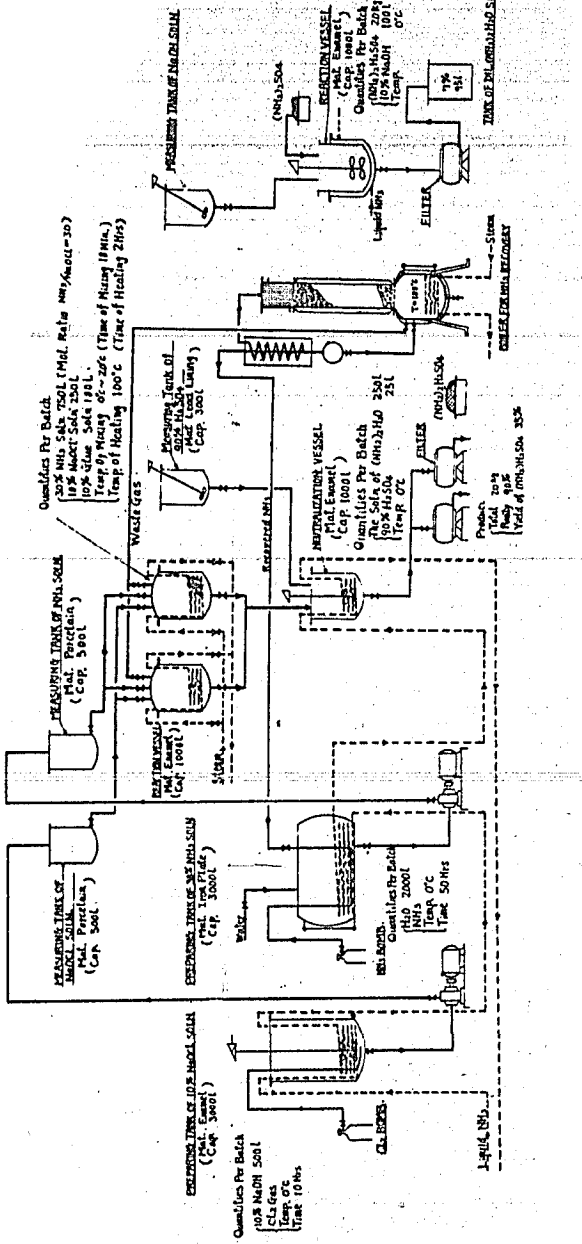

Figure 1 (B)8

FLOW SHEET OF PILOT PLANT FOR HYDRAZINE SYNTHESIS