ITEM No. 22
FILE No. XXII—18

# PRODUCTION OF HYDRAZINE HYDRATE
# I.G. FARBEN A.G., LEVERKUSEN, GERMANY

COMBINED INTELLIGENCE OBJECTIVES
SUB-COMMITTEE

4200/7/45.

LONDON — H. M. STATIONERY OFFICE

# PRODUCTION OF HYDRAZINE HYDRATE

## I.G. FARBEN, A.G. LEVERKUSEN, GERMANY

27 April 1945

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18 May 1945

CIOS BLACK LIST ITEM - 22
Miscellaneous Chemicals

COMBINED INTELLIGENCE OBJECTIVES
SUB-COMMITTEE
G-2 DIVISION, SHAEF (REAR) APO 413

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# PRODUCTION OF HYDRAZINE HYDRATE

## I.G. FARBEN. A.G. LEVERKUSEN, GERMANY

## 1. INTRODUCTION.

a. In interviewing Drs. Klebert, Konrad, and Redies, Directors of I.G. Farbeindustrie A.G. at Leverkusen, on 27 April 1945, it was learned that a plant was in operation at Leverkusen for the manufacture of hydrazine hydrate ($NH_2NH_2.H_2O$) for jet propulsion and rocket fuels. Production was started in April, 1944, when 20 tons were produced. This was increased to 40 to 45 tons per month and a total of 280 tons were produced in 1944. Only about 45 tons were produced in 1945.

b. The plant was under strict governmental control and all product was shipped to the Chemische Fabrik Transehe at Gersthofen (near Augsburg). This project was classified by the German Military as secret and all documents at Leverkusen marked "Geheime Kommandosache" were ordered to be destroyed in August, 1944. The German government financed a plant for production of 300 tons per month of hydrazine hydrate at Gersthofen. This plant was built by the Elect. Chem. Werke of Hollriegelskreuth (near Munich) acting as contractors. The plant was operated by Chemische Fabrik Transehe. Transehe is the director in charge. The plant operated first in October, 1944, and produced only 50 tons. Little more has been made since because of various troubles, according to information at Leverkusen. The I.G. at Leverkusen furnished technical information for construction and operation of the Gersthofen plant. They have a number of men in the operating force who were trained at Leverkusen.

## 2. INSPECTION OF PLANT.

The plant at Leverkusen had a rated capacity of 60 tons hydrazine hydrate per month. It is housed and the apparatus is in good condition. There are two parts. In the one NaOCl and $NH_3$ solutions are reacted in pressure equipment at 40 to 50 atmospheres pressure to form $NH_2NH_2.H_2O$. The time of the solutions in the reaction coils which are kept at 180°C is only a matter of seconds, when it is let down through a reducing valve to the concentrating system. This section of the plant is small and was protected by a special brick house within the plant building proper. The other part of the plant is for concentrating the 5% hydrazine hydrate solution from the reactor. A standard evaporator removes the NaCl and distills over the solution of hydrazine hydrate. The hydrazine hydrate is concentrated in two sets of distillation columns, the first producing about 46% solution and the final 95 to 97% solution of hydrazine-hydrate. Complete sets of drawing and specifications necessary to build the plant are available at Leverkusen.

## 3. PROCESS.

A discussion of the reaction and description of the process with accompanying flow sheet as given by Dr. Hempel at Leverkusen follows:

a. Reaction Mechanism - According to the discovery of Raschig, it is possible to prepare $NH_2NH_2 \cdot H_2O$ from alkali hypochlorite and excess $NH_3$ (in aqueous solution) conveniently in the presence of such materials as gelatin, glue, etc., which raise the viscosity.

Raschig suggested the following overall equation:

$$NaOCl + 2NH_3 \longrightarrow N_2H_4 + NaCl + H_2O$$

The first step of the reaction is:

$$NaOCl + NH_3 \longrightarrow NH_2Cl + (NaOH)$$

The second step:

$$NH_2Cl + NH_3 \longrightarrow NH_2NH_2 + (HCl)$$

The following undesirable side-reaction appreciably diminishes the yield:

$$2NH_2Cl + N_2H_4 \longrightarrow 2NH_4Cl + N_2$$

It has now been found that $NH_2NH_2 \cdot H_2O$ is produced in good yield, without the addition of glue, etc., if the chloramine solution is heated with excess $NH_3$ under pressure at a temperature of 150°-200°C; this process is best carried out as rapidly as possible. For this purpose it is not necessary to start with pure chloramine solutions, but instead solutions containing NaOCl and $NH_3$ (for the formation of $NH_2Cl$) may be conveniently employed. The reaction is carried out in a pressure tube through which the reaction mixture flows.

Since, under the indicated conditions, the reaction is complete in a few seconds, an apparatus of very small dimensions is all that is required, if it is so constructed, that the heating takes place correspondingly quickly. After the reaction has taken place, a reduction in pressure on the solution allows the greater part of the excess $NH_3$ to escape; the heat needed to raise the temperature of the mixture to the boiling point is almost completely supplied by the heat evolved in the reaction. The remaining amount of $NH_3$ is driven off by further heating in a column, and the vaporization is so regulated, that an ammonia solution results from the cooling of the driven-off $NH_3$ and water vapor and from the $NH_3$ resulting from release of pressure on the solution which can be directly used again in the reaction. A crude hydrazine hydrate solution (concentration about 3%) is obtained. The yield (based on the active chlorine in the NaOCl solution) is 70-75%.

The presence of impurities, especially heavy metals, has an especially bad effect on the yield; this is particularly true of copper. In addition, the amount of iron should be as low as possible. In case the NaOCl solution contains large amounts of iron, it is advisable to filter it after dilution. The $NH_3$ solution must be continually tested for its copper content.

Since the crude $NH_2NH_2 \cdot H_2O$ solution contains 5-6% NaCl and some NaOH, it cannot be directly concentrated; those substances must first be removed. This is conveniently carried out in a "Salt-Evaporator", in which, after vaporization, the resulting 6%-8% hydrazine hydrate water vapor mixture is driven over into a fractionating column; the separated NaCl, which contains some NaOH, is periodically washed out into a suction filter and removed from the process.

The pure dilute $NH_2NH_2 \cdot H_2O$ solution which condenses in the fractionating column is concentrated in two steps by means of two distillation columns. In the first step a concentration of 40-50% is obtained; the second step gives a concentration of 95-98%. The second step is carried out under a nitrogen atmosphere in order to avoid the possibility of explosions.

### b. Description of apparatus and working procedure. (See chart. Numbers refer to this chart.)

The NaOCl solution (contains 12.7% active Cl, 0.4g free alkali per liter) is adjusted to a content of about 70g active Cl per liter in container No. 1 with permutit-water from container No. 2.

The $NH_3$ solution is adjusted to a concentration of about 20-25% (sp.gr.0.910). Both solutions flow through measuring meters and then to a high pressure pump (No. 6), which is provided with mixing ducts. The regulating valves controlling the inlet flow of each solution are so adjusted that the ratio of NaOCl-solution to $NH_3$-solution is 1 to 2. The pump compresses the reaction mixture to about 40-50 atmospheres and drives it into the reaction pressure tube (No. 7) heated to about 180°C. The time required in the reaction pressure tube is a matter of a few seconds. The pressure on the solution (after reaction) is reduced to atmospheric in the evaporation pot (No. 8). The resultant vapor and the residual liquid, in order that thermodynamic equilibrium can be established, first flows through a packed column (Fullkorper-saule) (No. 9) that is connected from below to the evaporator pot (No. 8). The vapor, removed from below, is rectified in a second packed column (No. 10) by means of $NH_3$ water, in order to avoid hydrazine losses. The solution mixed with the reflux from the second column (No. 10) then enters the separating column (No. 11). For the production of vapor, a circular tube evaporator (No. 12) is employed. A part of the heated vapor is obtained from the vaporization of the high-pressure condensate from the heater. In the upper part of the separating column (No. 11) the necessary amount of $NH_3$ (as 100 percent $NH_3$) is continuously introduced. The separating column (No. 11) is operated in such a way that the $NH_3$ water vapor mixture produced has the proper composition for use again in the process. The $NH_3$-water vapor mixture is condensed in two tube condensers (13a and 13b) and flows back into storage container (No. 5). The $NH_3$-free crude $NH_2NH_2$ solution is collected in storage container (No. 14) and from this is led to the further steps in the process.

Since $NH_2NH_2$ in high concentration attacks iron, it is essential that all the subsequent apparatus be constructed of VA-steel (18-8 Cr-Ni Steel). First, in order to remove NaCl and NaOH from the crude solution, the solution is worked up in the "Salt-Evaporator" (No. 15). The "Salt-Evaporator" consists of a column with a circular tube evaporator (No. 15a); at the base of the column is connected a suction filter (No. 15b). The solution is concentrated to the point where crystallization of the NaCl begins; a $NH_2NH_2$-water vapor mixture (% $NH_2NH_2$ = 8-12) escapes. The solution in the "Salt-Evaporator" has a $NH_2NH_2 \cdot H_2O$ concentration of 15-20 percent and boils about 112-114°C. The NaCl containing NaOH, which is collected in the suction filter, is periodically removed after thorough washing. Special attention must be devoted to the washing process in order that large losses of $NH_2NH_2$ do not occur at this stage. The vapor mixture driven off from the "Salt-Evaporator" is led into the bottom of a packed fractionating column (No. 16); in the upper part of the column a portion of the condensate is introduced as reflux. The fractionated, pure hydrazine hydrate solution (concentration 6-8 percent) is pumped into distillation column (No. 17) and is concentrated here to about 40-50 percent. In the middle section of the distillation column is a perforated plate, and the lower part is filled with VA rings. In the condensers (17a and 17b) attached over the column, the vaporized $H_2O$ is recondensed. A part of the condensate, which should contain only traces of $NH_2NH_2 \cdot H_2O$, is led into the upper part of the column where it comes in contact with the rising vapors. The temperature in this step is about 108-110°C. The 40-50 percent solution from this column is pumped into the second distillation column (No. 18), which is just the same in principle as the first column. Since hot, concentrated $NH_2NH_2 \cdot H_2O$

solution reacts explosively with oxygen, all access of air to the product in the final step must be carefully avoided. The column is connected through the condenser (No. 18a) to a nitrogen gasometer (No. 19), and must be carefully flushed out with nitrogen at the start of the operation or at an interruption of the process. In addition, in the upper part of the column an "explosion-damper", made of 5mm thick lead sheet, is provided. The boiling point of the resultant 95-98% $NH_2NH_2 \cdot H_2O$ solution is 119-120°C. The final concentrated solution runs continuously out of the column by means of an overflow tube into a measuring vessel (No. 20) provided with a cooler, and is then pumped into a storage vessel (No. 21), lined with Mipolam (Polyvinyl resin).

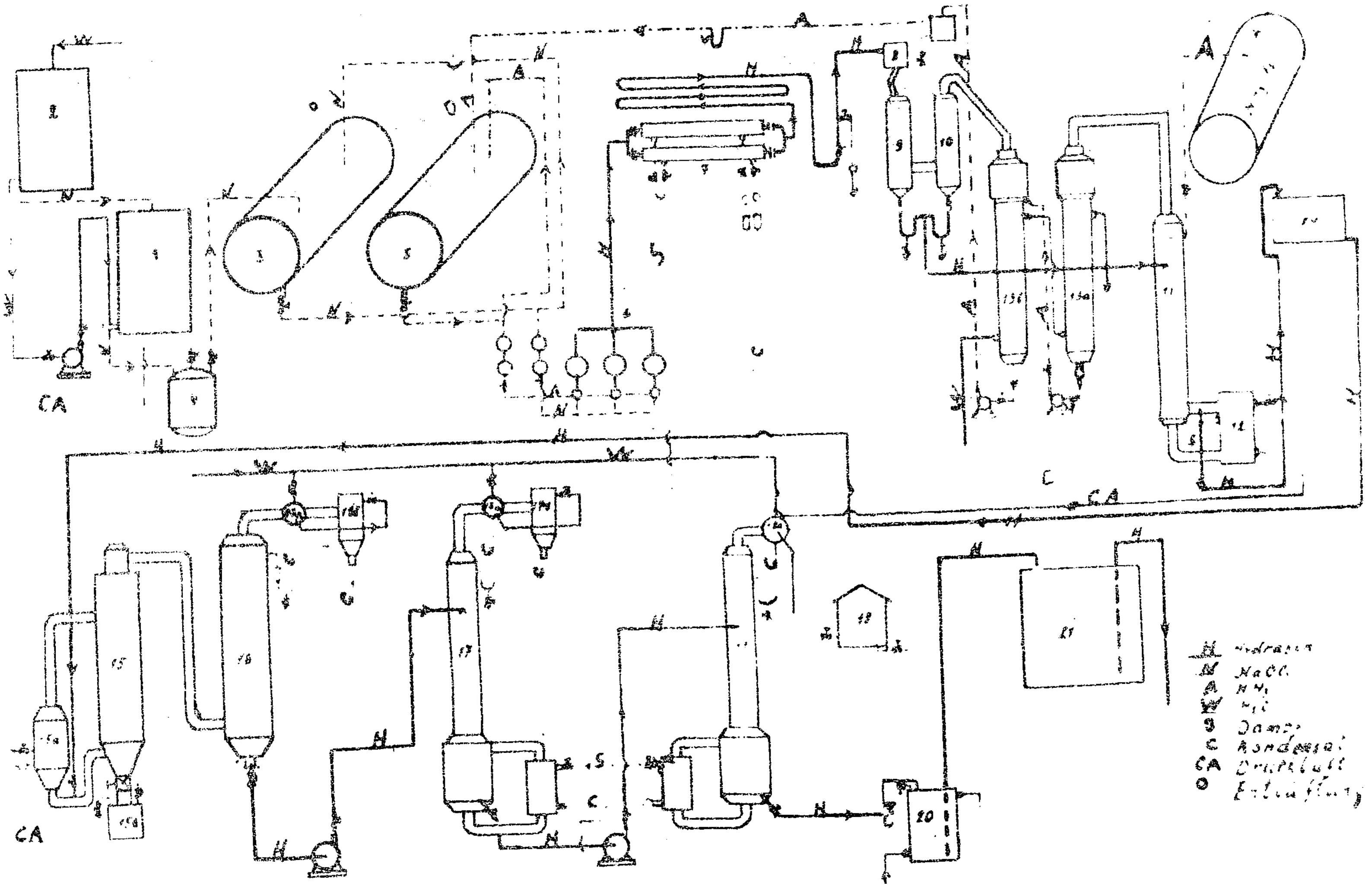
The yield in the distillation based on the amount of crude solution employed, is 80-85 percent. The sources of loss are:

a. Oxidation by air oxygen.
b. Loss during removal of NaCl
c. Catalytic decomposition according to the equation:
$$3N_2H_4 \cdot H_2O \longrightarrow N_2 + 4NH_3 + 3H_2O$$
d. Losses in run-off condensate.

Concentrated $NH_2NH_2 \cdot H_2O$ vapors are a little known blood poison; it is therefore necessary to take great pains to avoid leaks in the apparatus, and to provide good ventilation for the room in which the apparatus is located. Moreover, the solution and vapors of $NH_2NH_2 \cdot H_2O$ act as a skin-poison, depending somewhat on the individual; it is especially important to protect the eyes from spray or mist of the solution.

## 4. RECOMMENDATION.

The plant at Gersthofen and the Electro. Chem. Werke near Munich should be visited for further process and manufacturing information.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