MISCELLANEOUS TARGETS

JAPANESE FUELS AND LUBRICANTS - ARTICLE 5
RESEARCH ON ROCKET FUELS
OF THE HYDROGEN PEROXIDE-HYDRAZINE TYPE

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U. S. NAVAL TECHNICAL MISSION TO JAPAN
CARE OF FLEET POST OFFICE
SAN FRANCISCO, CALIFORNIA

6 February 1946

RESTRICTED

From: Chief, Naval Technical Mission to Japan.
To: Chief of Naval Operations.

Subject: Target Report - Japanese Fuels and Lubricants, Article 5 - Research on Rocket Fuels of the Hydrogen Peroxide - Hydrazine Type.

Reference: (a) "Intelligence Targets Japan" (DNI) of 4 Sept. 1945.

1. Subject report, covering chemical research by the Japanese Navy on rocket fuel of the hydrogen peroxide-hydrazine type as outlined by Targets X-09, X-10 and X-38(N) of Fascicle X-1 of reference (a), is submitted herewith.

2. The investigation of the target and the target report were accomplished by Comdr. G. L. Neely, USNR, Lt. Comdr. C. S. Goddin, USNR, and Lt. W. H. Millet, USNR, assisted by Ens. E. R. Dalbey, USNR, as interpreter and translator.

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30703

JAPANESE FUELS AND LUBRICANTS - ARTICLE 5
RESEARCH ON ROCKET FUELS
OF THE HYDROGEN PEROXIDE-HYDRAZINE TYPE

"INTELLIGENCE TARGETS JAPAN" (DNI) OF 4 SEPT. 1945

FASCICLE X-1, TARGETS X-09, X-10, AND X-38(N)

FEBRUARY 1946

U.S. NAVAL TECHNICAL MISSION TO JAPAN

SUMMARY

MISCELLANEOUS TARGETS

JAPANESE FUELS AND LUBRICANTS - ARTICLE 5
RESEARCH ON ROCKET FUELS OF THE HYDROGEN PEROXIDE-HYDRAZINE TYPE

Japanese naval research pertaining to rocket fuels of the hydrogen peroxide-hydrazine type has been investigated. This report deals primarily with the manufacture of hydrazine and 80% hydrogen peroxide solutions and with combustion studies of the reaction between these two materials. This rocket fuel was to be utilized principally in the newly developed SHUSUI airplane. It was reported that only one flight test was successfully completed before the termination of the war.

TABLE OF CONTENTS

LIST OF ENCLOSURES

REFERENCES

Location of Target:

First Naval Fuel Depot, OFUNA, Kanagawa Prefecture.

Japanese Personnel Interviewed:

H. FUJIMOTO, (Ph. D.) Engineering Commander, Japanese Navy, (very capable research engineer).

S. SHINODA, Naval Chemical Engineer, (designer of hydrogen peroxide concentration plant at the First Naval Fuel Depot, OFUNA).

S. ENDO, Engineering Lieutenant Commander, Japanese Navy, (research engineer - the manufacture of hydrazine).

M. SHIMO, Engineering Lieutenant, Japanese Navy, (research engineer combustion studies of hydrogen peroxide-hydrazine mixtures).

INTRODUCTION

The Japanese Navy became actively interested in the development of rocket fuels in June 1944. It was planned that the fuel to be developed would be utilized in the SHUSUI airplane and in the KAITEN torpedo. This report summarizes the technical information obtained from the First Naval Fuel Depot, OFUNA, relative to such research activities and the application of these activities to the commercial production of rocket fuel of the hydrogen peroxide-hydrazine type.

Pertinent detailed research papers have been prepared in English by Japanese technical personnel, under the direction of the U. S. Naval Technical Mission to Japan. These papers were reviewed with the Japanese authors, revised, and are presented herewith as an integral part of this report, designated as Enclosures (B)1 to (B)10, inclusive. A summary of this work has also been prepared in English for inclusion in this report by Chemical Engineering Commander H. FUJIMOTO (Japanese Navy), and is presented herewith as Enclosure (A).

Since the Japanese research reports, drawings, and other important documents of the First Naval Fuel Depot had been burned during August 1945 at the direction of the Director of the Depot, it was necessary to recall the Japanese technical personnel and to reconstruct this information from laboratory notebooks, laboratory apparatus, and pilot plant equipment. This reconstruction, for both this report and other reports pertaining to the First Naval Fuel Depot, continued for a period of nearly three months. It is to be realized that, in spite of efforts expended in reviewing the reports submitted as Enclosures (A) and (B), they do not conform to American standards, and many errors have inadvertently been included in the translation by the Japanese authors. However, these reports do indicate with considerable accuracy the quality and extent of Japanese research pertaining to the development of the type of rocket fuels which the Japanese Navy planned to use.

The information contained in this report was obtained in connection with an investigation of fuel and lubricant research carried out by the Japanese Navy at the First Naval Fuel Depot. No attempt has been made to supplement these findings by investigating rocket fuel research conducted elsewhere in Japan.

THE REPORT

The rocket fuel which was to have been employed by the Japanese Navy consists of a solution of 80-85% hydrogen peroxide as an oxidizing agent and a 30% solution of hydrazine hydrate in a 8 : 2 methanol-water mixture as a reducing agent. The detailed reports pertaining to the development, improvement, and application of this fuel fall into the following general categories:

1. Laboratory studies on the manufacture, stabilization, and storage of concentrated hydrogen peroxide solutions.

2. Laboratory and pilot plant studies on the synthesis of hydrazine.

3. Design and operation of hydrogen peroxide concentration plants.

4. Combustion studies of peroxide-hydrazine mixtures.

Enclosure (A) summarizes the content of these reports and depicts the role of this research in the overall rocket fuel program. Detailed data, drawings, and flow sheets are presented in the individual reports of Enclosure (B). Of primary interest are the papers on the design and construction of hydrogen peroxide concentration plants (Enclosure (B)-7) and on the combustion studies of hydrogen peroxide-hydrazine mixtures (Enclosure (B)-10).

It was planned to construct a number of hydrogen peroxide concentration plants in Japan capable of producing a total of 3,000 tons of 80% hydrogen peroxide per month. Two units, having a combined capacity of 90 tons per month, had been built at the First Naval Fuel Depot, OFUNA. One of these had been in operation since November 1944 and the other was completed in August 1945. Construction of additional concentration units was underway at other locations, but none of these had been completed at the close of the war, except a 100 ton per month plant at YAMAKITA.

Interesting investigations were carried out in regard to the choice of materials for constructing plants for concentrating hydrogen peroxide. A plant had been built at the Chosen Nitrogen Company (Korea) using aluminum vessels and pipes, but violent decomposition of the concentrated hydrogen peroxide occurred, rendering the plant useless. At OFUNA, after a thorough investigation, tin and porcelain were selected as the available materials which were most resistent to attack by hydrogen peroxide. In the design of the OFUNA plant, tin-lined vessels, tin or porcelain pipes, large porcelain cocks and other porcelain fittings were used exclusively. The fabrication of these porcelain fittings was based upon Japan's ancient technique in the manufacture of porcelain dishes and other household articles. After concentration, the hydrogen peroxide was stored underground in tin-lined steel tanks of 10 kiloliter capacity.

It is of interest that during 1945 the hydrogen peroxide-hydrazine program was one of the two research projects having the highest priority at the First Naval Fuel Depot. The other project was that for obtaining aviation gasoline from pine root oil (NavTechJap Report, "Japanese Fuels and Lubricants" Article 4 - Pine Root Oil Program.) The fact that both of these programs were concerned with aviation fuels serves to emphasize Japan's critical position in regard to this important resource during the final year of the war.

ENCLOSURE (A)

ENCLOSURE (A)

SUMMARY OF THE ROCKET FUEL RESEARCH PROGRAM AT THE FIRST NAVAL FUEL DEPOT, OFUNA

by

CHEM. ENG. COMDR.
H. FUJIMOTO

Prepared for and Reviewed with Author
by U. S. Naval Technical Mission to Japan

December 1945

ENCLOSURE (A)

TABLE OF CONTENTS

ENCLOSURE (A)

I. INTRODUCTION

The appearance of the V-1 rocket in the European theatre stimulated the Japanese to investigate rocket fuels. Research on the SHUSUI airplane, the KAITEN torpedo, and rocket fuels was started simulutaneously in June 1944 at the First Naval Technical Depot, Naval Technical Institute and the First Naval Depot, respectively. At first, concentrated hydrogen peroxide and sodium permanganate solutions were used as rocket fuels; afterwards they were supplanted by a hydrogen peroxide and hydrazine hydrate-methanol combination, as it was shown that some detonation occurred at the initial period of the injection of a permanganate solution.

There were two hydrogen peroxide manufacturing companies in Japan, the Edogawa Technical Co. at YAMAKITA and the Nippon Dye-stuff Co. at OSAKA, producing 120 tons per month and 70 tons per month of a 30% hydrogen peroxide solution by the ammonium persulphate method. In June 1944 only the former was in operation.

The production of 3000 tons per month of 80% hydrogen peroxide was planned on the basis of designs made by the Edogawa Technical Co. obtaining the necessary supplies of platinum anodes, porcelain cells and towers, and pure sulphuric acid, and the training of operators sufficiently qualified to deal with this particular industry were among the difficulties confronting this expansion. Another problem was to construct rapidly about 300 standard units producing 40 tons of 30% H_2O_2 monthly. Further studies were made on new processes for producing 30% H_2O_2 without using platinum and also on the problems concerning the concentration of H_2O_2 from 30% to 80%. Neither new processes, however, nor substitutes for existing processes were developed, and the actual production of concentrated hydrogen peroxide at the termination of the war was about 100 tons monthly, according to the author's estimate.

With regard to hydrazine hydrate, no large scale production was available in 1944. Laboratory experiments on the synthesis of hydrazine from ammonia and from urea, respectively, based on Rassig's method, were carried out promptly in this depot. The ammonia process was selected for commercial use, after comparing the results with the urea process (see Enclosures (B)8 and (B)9). Commercial plants were erected by the Nippon Chemical Synthesis Co. at KUROSAKI, Mitsui Dye-stuff Co. at OMUTA, Chosen Nitrogen Co at KONAN, Toa Synthesis Co. at NAGOYA, and Dainippon Chemicals Co. at KAWASAKI, each having capacities of 100, 30, 100, 50 and 30 tons of 80 wt% hydrazine hydrate solution, respectively. The construction of each plant was making steady progress without any serious difficulties, and a total monthly production of about 100 tons was reached at the end of the war.

At OFUNA, research was done only on rocket fuel, since the production there was supervised by the Rocket Fuel Department of the Supply Bureau of the Navy Ministry.

II. HYDROGEN PEROXIDE PRODUCTION

There were two major research subjects concerning the hydrogen peroxide problem. One was to solve the problem of the shortage of anodic platinum, which was estimated to be about 2000 kilograms to realize the monthly production plan of 3000 tons of conc. H_2O_2, and the other was to determine a suitable hydrogen peroxide concentrating method.

Many kinds of metallic electrodes were tested as a substitute for platinum, but almost all of them were dissolved by anodic oxidation during electrolysis, precipitating metallic oxides in the electrolyte. Tungsten electrodes having a

coated oxide film did not dissolve, but lost conductivity after a short time. On the bases of these experiments, PbO_2, which did not dissolve and had a good conductivity, was selected and tested for application in the electrolysis of $(NH_4)_2S_2O_8$. Results were satisfactory as reported in Enclosure (B)1, showing a current efficiency of 40% and an electrolytic potential of 5 volts, compared with current efficiency of 75% and 6 volts for platinum electrodes. The electrolyte, however, could not be treated by the Lowenstein and Riedel process, as it contained volatile HF, and the concentration of $(NH_4)_2SO_4$ was so high that crystals deposited in the pipe-still on decomposition. Therefore, it had to be filtered after cooling and then further decomposed in a batch type still. A pilot plant test was planned by the Nippon Carbide Co. at UOZU. but this test was not completed.

Similar experimental studies on the synthesis of H_2O_2 were carried out by means of electric discharge, which did not use platinum in the process. At first, a mixed gas of hydrogen and oxygen (5%) was passed through an ozonizer tube under silent electric discharge with 30,000 volts of tension, and fairly satisfactory results were obtained. About 80% of the oxygen was reacted, yielding 50% by wt of H_2O_2 solution in one pass through the tube. Energy consumption was below 100 kwh per kg of H_2O_2, against that of 30 kwh by the $(NH_4)_2S_2O_8$ method. However, the production per unit volume of the apparatus was very small, yielding about 0.5 grams of H_2O_2 per liter of ozonizer tube per hour, and would have required a large amount of materials and glass works to erect a commercial unit. To avoid these disadvantages, the same experiments were carried out using arc discharge instead of silent discharge. The procedure and the results are reported in Enclosures (B)3 and (B)4. Here a dilute H_2O_2 solution was obtained with a power consumption of about 300 kwh per kg of H_2O_2. Although these figures were not satisfactory for commercial development, the fact that over 100 m/sec of reacting gas velocity passing through the arc gave better results suggested a key point of further developments on this subject. The author also thought that the experiments on the action of the electric arc on water vapour would be promising.

Concentration of H_2O_2 from 30% to 80% as reported in Enclosure (B)7, was accomplished at first by means of vacuum evaporation, and finally to concentrations over 70% by means of vacuum distillation. Experiments on the evaporation of 30% H_2O_2 solution showed that it was not effective to evaporate to concentrations over 60%. From these considerations the commercial plant was designed to concentrate in two steps, first by evaporation and finally by distillation. Phosphoric acid was added as a stabilizer to the feed stock, and oxyquinoline, plus phosphoric acid to the final product.

The procedure was as follows: The feed stock was neutralized by NaOH until it was only slightly acidic, since it contained usually about 0.5 grams per liter of H_2SO_4, which was entrained in the $(NH_4)_2S_2O_8$ electrolyte. Then, 0.3 grams per liter of $Na_4P_2O_7$ was added, producing phosphoric acid by double decomposition with the remaining H_2SO_4 and acting as a stabilizer. In this case, oxyquinoline was not used because it would be oxidized in the course of evaporation. Porcelain and tin gave the best results as the materials of construction for the plant. Aluminium was used for towers and vessels in the commercial plant at Chosen Nitrogen Co., but it was unsuccessful due to the violent decomposition of H_2O_2.

III. HYDRAZINE HYDRATE

Hydrazine hydrate was made by Rassig's method using ammonia and sodium hypochlorite. In laboratory experiments, ammonia was converted to hydrazine with a yield corresponding to 55% of active chlorine in hypochlorite, and the hydrazine was actually obtained in the form of hydrazine sulphate with a yield of 40%. In the commercial scale operation, the yield of concentrated hydra-

zine hydrate was about 10%, although that of hydrazine in the diluted solution immediately after the reaction was about 55% as determined by laboratory tests. The reason for this was the decomposition of hydrazine in the course of concentration, caused by impurities such as ions and oxides of heavy metals. In this industry, therefore, it was necessary to avoid the entrance of all the traces of impurities, using distilled water, pure raw materials, etc. and stainless steels to construct the commercial plant. Gelatines used in the reaction are believed to serve as protectors for the impurities.

IV. STORAGE, HANDLING AND TESTING

Laboratory storage tests were carried on in regard to the vessels for shipping and handling these fuels (See Enclosure (B)6). Stainless steel and tin were found to be best for both H_2O_2 and N_2H_4. Twenty five liter vessels and 1000 liter tank cars made from steel, lined with tin, were fabricated for transportation and 5000 liter tanks of similar construction for storage.

Bench tests on the rocket fuel burning characteristics were carried on at OFUNA (See Enclosure (B)10) and the Naval Technical Institute at MEGURO, and satisfactory results with regard to its use in actual planes were obtained. Only one actual flight test was successful before the termination of the war.

ENCLOSURE (B)

ENCLOSURE (B)1

STUDIES ON THE SYNTHESIS OF $(NH_4)_2 S_2O_8$ BY PbO_2 ANODE

by

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Research Period: 1944-1945

Prepared for and Reviewed with Authors
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December 1945

ENCLOSURE (B)1

LIST OF TABLES AND ILLUSTRATIONS

ENCLOSURE (B)1

SUMMARY

A 15-20% $(NH_4)_2S_2O_8$ solution is produced with a current efficiency of ca. 60% by decreasing the anode current density, increasing the current concentration*, changing the concentration of $(NH_4)_2SO_4$ and H_2SO_4 in the electrolyte, and adding HF to the electrolyte. On cooling the electrolyted solution to ca. 0°C., $(NH_4)_2S_2O_8$ crystals (purity of 99%) are prepared with a yield of ca. 70%.

I. DETAILED DESCRIPTION

A. Electrolysis of Ammonium Persulfate

Details of the PbO_2 anode and the electrolysis vessel are shown in Figure 1(B)2. Various electrolyte compositions and conditions of electrolysis were tried. In each case, the current efficiency and yield were obtained and recorded. Details of the conditions and results of each experiment are given below.

1. The Effect of Current Density and Addition of Fluorides. In the case of Pt anode, the current density is as high as 100 amp/dm^2, but for PbO_2 anodes this is too high to obtain good current efficiency. The current density in this case must be limited to ca.10-20 amp/dm^2 as may be seen in the following experiment.

The Composition of Electrolyte:

Anode electrolyte: $(NH_4)_2SO_4$, 28gm H_2SO_4, 30gm dissolved in water to 100cc total volume.

Cathode electrolyte: The same composition as anode electrolyte.

Electrolysis Conditions: Volume of anode electrolyte, 100cc current, 2.5 amp; current density of anode, D_A, 5 - 80 amp/dm^2, current concentration in anode electrolyte, C_A, 2.5 amp/100cc; temperature of bath, 15°C; time, 1 hr.

Results are given in Table I(B)1 and are plotted in Figure 2(B)1.

From this data, a current density, D_A, between 5 and 20 Amp/dm^2, appears to be adequate.

2. The Effect of Electrolyte Composition on Yield of $(NH_4)_2S_2O_8$. The relationship between current efficiency and composition of electrolyte was studied in the following tests:

a. The effect of concentration of H_2SO_4. H_2SO_4 is necessary in the electrolyte, but its concentration should not exceed 40% or it will accelerate the decomposition of synthesized $(NH_4)_2S_2O_8$. Results are shown in Table II(B)1

From this data, it appears that the concentration of H_2SO_4 in the electrolyte should be 20-30 gm/cc.

b. The effect of concentration of $(NH_4)_2SO_4$. The concentration of $(NH_4)_2SO_4$ affects the current efficiency remarkably. The results are shown in Table III(B)1.

The $(NH_4)_2SO_4$ saturated solution gives the best yield and the highest current efficiency.

c. The effect of the quantity of HF added. Varying the quantity of HF added to the electrolyte, the optimum quantity was determined to be 1.0-1.5gm/100cc. Results are given in Table IV(B)1 and are plotted in Figure 3(B)1.

3. The Effect of Impurities in Electrolyte. When a PbO_2 anode is used, the effect of impurities in the electrolyte is greater than when a Pt anode is used. Hence, pure H_2SO_4, $(NH_4)_2SO_4$, and HF must be used as raw materials. For instance, the electrolyte made from industrial H_2SO_4 gives only a current efficiency of 10% even under the best conditions as described previously. The impurities are assumed to be Fe^{++}, Fe^{+++}, Cu^{++} and other metallic ions.

4. The Effect of Increasing the Quantity of Added HF. From precise measurements, the remarkable rise of anode decomposition voltage by the addition of HF was observed. Therefore, it was attempted to determine the effect of increasing quantities of added HF. The electrolysis conditions of the experiment and a summary of the results were as follows:

Anode Electrolyte (107cc)

$(NH_4)_2SO_4$	61gm
H_2SO_4	9.6gm
HF	5.0gm
H_2O	54.4gm

Cathode Electrolyte

$(NH_4)_2SO_4$ saturated solution 32cc.

Electrolysis Conditions

Current	4 Amp
D_A	10 Amp/dm^2
CA	4 Amp/107cc
Temp	25-30°C
Time	1 hr

Results

$(NH_4)_2S_2O_8$ produced	11.36gm
Concentration of $(NH_4)_2S_2O_8$	10.82gm/100cc
Current Efficiency	66.6%

The current efficiency was augmented exceedingly by the increased quantity of HF. Increasing the quantity of HF five times to 5gm HF/100cc gave a current efficiency of ca. 67%. Further increasing the quantity did not effect appreciably the current efficiency.

5. The Effect of Concentration of H_2SO_4 in Electrolyte Containing an Increased Quantity of HF. Fixing the quantity of HF at 5-6gm/100cc, the effect of various concentrations of H_2SO_4 and $(NH_4)_2SO_4$ on current efficiency was examined. The effect of varying the electrolyte concentration is shown in Table VI(B)1 Figure 4(B)1.

From these data the following electrolyte appears to be the best composition:

100cc electrolyte containing:

$(NH_4)_2SO_4$	58.0gm
H_2SO_4	8.0 - 12.0gm
HF	5.5 - 6.0gm

B. Crystallization of Ammonium Persulfate

By electrolysis, a solution containing 15 - 20% $(NH_4)_2S_2O_8$ is obtained, and when this solution is cooled to ca. 0°C, $(NH_4)_2S_2O_8$ crystals deposit. Typical data pertaining to the crystallization of $(NH_4)_2S_2O_8$ is as follows: A 15.5% $(NH_4)_2S_2O_8$ solution (87.0cc) which contained 13.5gm of $(NH_4)_2S_2O_8$ was cooled to 4°C, and the deposited $(NH_4)_2S_2O_8$ crystals were filtered off from the mother liquor. The yields were as follows:

Weight of wet $(NH_4)_2S_2O_8$ crystals	12.4gm
Purity of wet $(NH_4)_2S_2O_8$ crystals	78.7%
Weight of dry $(NH_4)_2S_2O_8$ crystals (Purity of 99%)	9.7gm
Volume of filtrate	77cc
Concentration of $(NH_4)_2S_2O_8$ in filtrate	5.13%
Weight of $(NH_4)_2S_2O_8$ in filtrate	3.9gm
Yield of $(NH_4)_2S_2O_8$ crystals from electrolyte	71.8%

The filtrate could be electrolyzed again after adjusting its composition.

C. Yields and Operating Difficulties

1. Total Yields By electrolysis, 16gm of $(NH_4)_2S_2O_8$ in solution are obtained from 100cc of the electrolyte containing $(NH_4)_2SO_4$ 58gm H_2SO_4 8.5gm and HF 6.0gm per 6 ampere-hours and 11.6gm of $(NH_4)_2S_2O_8$ crystals deposit from it on cooling. The total yield is ca. 42%. The mother solution can be separately electrolyzed. The conditions of the process which proved to be best are given in Figure V(B)1.

2. Operating Difficulties

a. HF corrodes the porcelain diaphragm and is consumed gradually, causing the porcelain to interfere with the electrolysis.

b. PbO_2 is slowly attacked by HF, and contaminates the electrolyte considerably. Accordingly, the electrolyte must be filtered before cooling to obtain pure white $(NH_4)_2S_2O_8$ crystals.

II. CONCLUSIONS

For the electrolytic synthesis of $(NH_4)_2S_2O_8$, a PbO_2 anode can be substituted for a Pt anode under the proper conditions.

The addition of HF to the electrolyte presents problems, since the materials for the electrolysis vessels and diaphragms are ordinarily made of porcelain, which is attacked by HF.

When HF is present in the electrolyte, $(NH_4)_2S_2O_8$ must be immediately separated from the solution by cooling.

ENCLOSURE (B)1

PbO_2 is gradually attacked by HF. Therefore, the contaminated electrolyte must be filtered before cooling to obtain stable and pure $(NH_4)_2S_2O_8$ crystals.

The difficulty of regulating the composition of the mother liquor, the problem of materials for the apparatus, and the decomposition of PbO_2 require still further studies before this process can be applied to industry.

Table I(B)1
EFFECT OF CURRENT DENSITY ON YIELD OF AMONIUM PERSULFATE

	Number						
	1	2	3	4	5	6	7
D_a (Amp/dm^2)	80	60	40	20	15	10	5
$(NH_4)_2S_2O_8$ Produced (gm)	0.22	0.35	0.42	0.62	0.80	0.83	0.81
Current Efficiency (%)	2.1	3.3	4.0	5.8	7.5	7.8	7.6

Table II(B)1
EFFECT OF VARYING CONCENTRATIONS OF H_2SO_4
ON YIELD OF $(NH_4)_2S_2O_8$

No.	$(NH_4)_2SO_4$ sat'sol.	Water	H_2SO_4	$(NH_4)_2SO_4$	Conc. $(NH_4)_2S_2O_8$ (gm/100cc)	Current Efficiency
1	in water	63.7	0	53.7	0.606	9.76
2	in 20% H_2SO_4	57.3	14.3	53.0	2.591	41.74
3	in 30% H_2SO_4	55.1	23.1	49.7	2.809	45.25
4	in 40% H_2SO_4	50.9	33.0	47.6	2.899	46.70
5	in 50% H_2SO_4	43.2	43.2	52.6	2.734	44.04

Note: 1.6gm HF present in all cases

Effect of varying concentration of H_2SO_4 on Yield of $(NH_4)_2S_2O_8$
Anode Electrolyte: Volume, 100cc; Composition is shown below
Cathode Electrolyte: The same as anode electrolyte
Electrolysis Conditions:

Current ..... 3.5 Amp
D_A ..... 10Amp/dm^2
C_A 3.5Amp/100cc
Temp. ..... 25-28°
Time ..... 1 hr

ENCLOSURE (B)1

Table III(B)1
EFFECT OF VARYING CONCENTRATION
OF $(NH_4)_2SO_4$ ON YIELD OF $(NH_4)_2S_2O_8$

No.	Compositions of Electrolyte 100cc of Each Anode Electrolyte Contains (gm).				Yield and Current Efficiency		
					$(NH_4)_2S_2O_8$		Current efficiency (%)
	Water	H_2SO_4	$(NH_4)_2SO_4$	HF	Produced (gm)	Concen. (gm/100cc)	
1	60.2	15.0	55.5(Sat. Sol)	2.0	14.43	14.43	32.3
2	65.8	16.5	46.1	2.0	12.37	12.37	27.7
3	71.1	17.8	35.6	2.0	9.74	9.74	21.8

Anode Electrolyte: $(NH_4)_2SO_4$ dissolved in 20% H_2SO_4 The composition is given below.
Cathode Electrolyte. $(NH_4)_2SO_4$ saturated solution.
Electrolysis Conditions:

Current ..... 3.5Amp.
D_A ..... 10Amp/dm^2
C_A 3.5Amp/100cc
Temp. ..... 25-30°C
Time ..... 3 hr

Table IV(B)1
EFFECT OF VARYING CONCENTATION OF HF ON YIELD OF $(NH_4)_2S_2O_8$

HF(gm)	$(NH_4)_2S_2O_8$ Produced (gm)	Concentration of $(NH_4)_2S_2O_8$ (gm/100cc)	Current Efficiency (%)
1.50	8.02	9.22	34.2
0.75	7.96	9.04	34.0
0.50	8.04	9.24	34.3
0.35	6.28	7.21	26.8
0.25	7.06	8.12	30.2
0.10	5.24	6.02	22.4

Anode Electrolyte: $(NH_4)_2SO_4$ sat'd in 20% H_2SO_4 soln. 90cc.
Cathode Electrolyte: $(NH_4)_2SO_4$ saturated aqueous solution, 30cc
Electrolysis Conditions

Current ..... 5.5Amp.
D_A ..... 10 Amp/dm^2
C_A 5.5Amp/90cc
Temp. ..... 25-28°C
Time ..... 1 hr

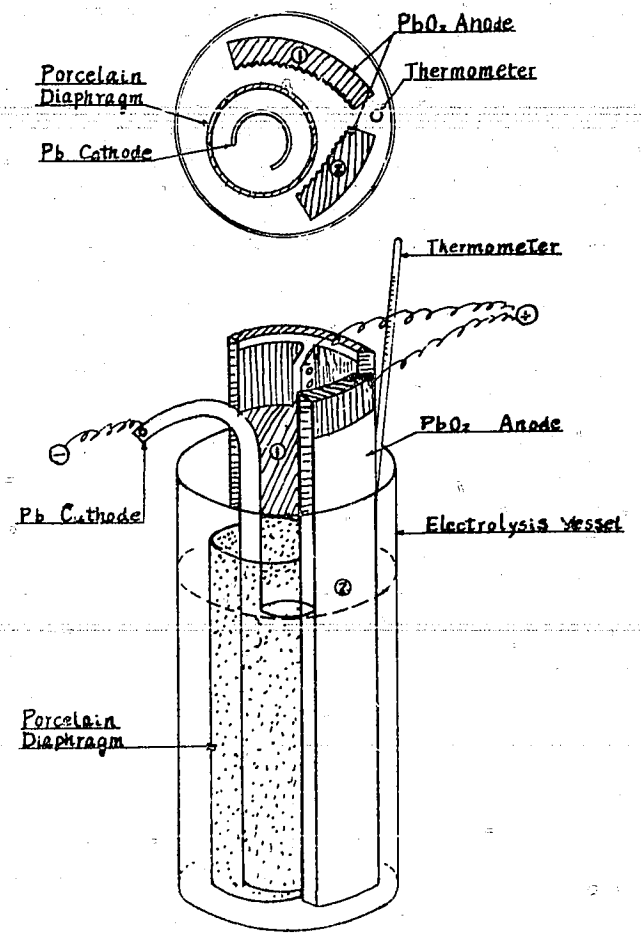
ENCLOSURE (B)1

Table V(B)1
EFFECT OF VARYING ELECTROLYTE CONCENTRATIONS
ON YIELD OF $(NH_4)_2S_2O_8$ (AMMONIUM PERSULFATE)

No.	Composition of Electrolyte (gm)				Yield and Current Efficiency		
					$(NH_4)_2S_2O_8$		Current efficiency (%)
	H_2SO_4	$(NH_4)_2SO_4$	H_2O	HF	Produced (gm)	Concen. (gm/100cc)	
1	2.8	56.5	64.8	5.2	9.96	10.19	58.6
2	8.4	59.1	59.6	5.6	11.25	11.48	66.1
3	11.5	58.0	58.1	5.3	11.00	11.23	64.6
4	14.7	58.3	56.2	5.1	11.96	12.00	68.0
5	18.3	56.4	54.7	5.5	10.48	10.70	61.5

Anode Electrolyte: volume. 100cc
Cathode Electrolyte: $(NH_4)_2SO_4$ saturated solution 32-35cc
Electrolysis Conditions:

Current 4Amp
D_A ..... 10Amp/dm^2
C_A 4Amp/100cc
Temp. .....20-30°C
Time ..... 1 hr



(Dimensions)

- ① Electrolysis Vessel
  - Internal Diameter 6.0 cm
  - Height 12.0 cm
- ② Porcelain Diaphragm
  - Internal Diameter 2.8 cm
  - Height 9.2 cm
  - Thickness 1.0~1.5 mm
- ③ PbO_2 Anode
  - Height (=Depth of Electrolyte)
    - ① 8.4 cm
    - ② 8.4 cm
  - Width
    - ① 4.3 cm
    - ② 2.2 cm
  - Thickness
    - ① 0.5~1.0 cm
    - ② 0.7~0.9 cm

PbO_2 ANODE

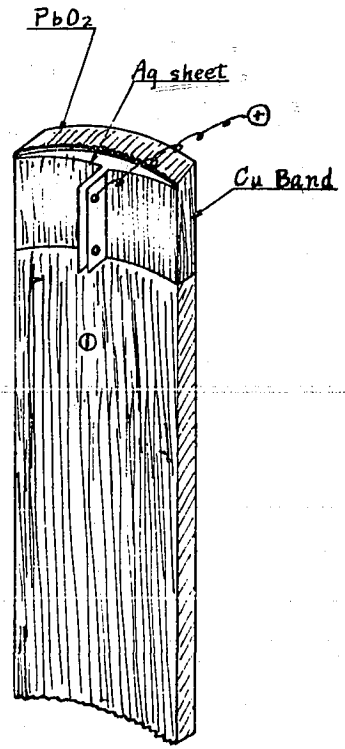


Figure 1(B)1
DRAWING OF ELECTROLYSIS VESSEL AND PbO_2 ANODE

ENCLOSURE (B)1

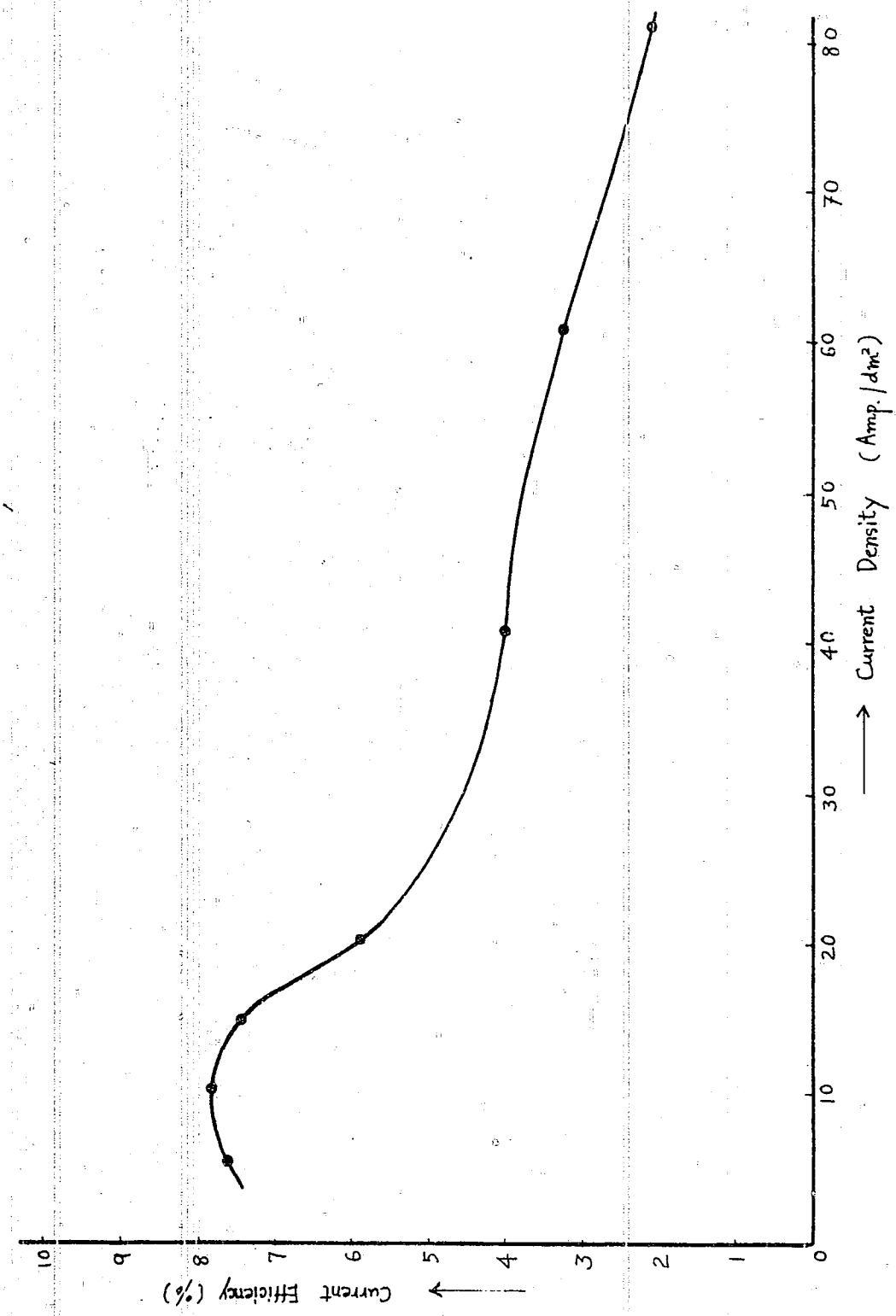


Figure 2(B)1
CORRELATION CURVE BETWEEN
CURRENT DENSITY AND CURRENT EFFICIENCY

ENCLOSURE (B)1

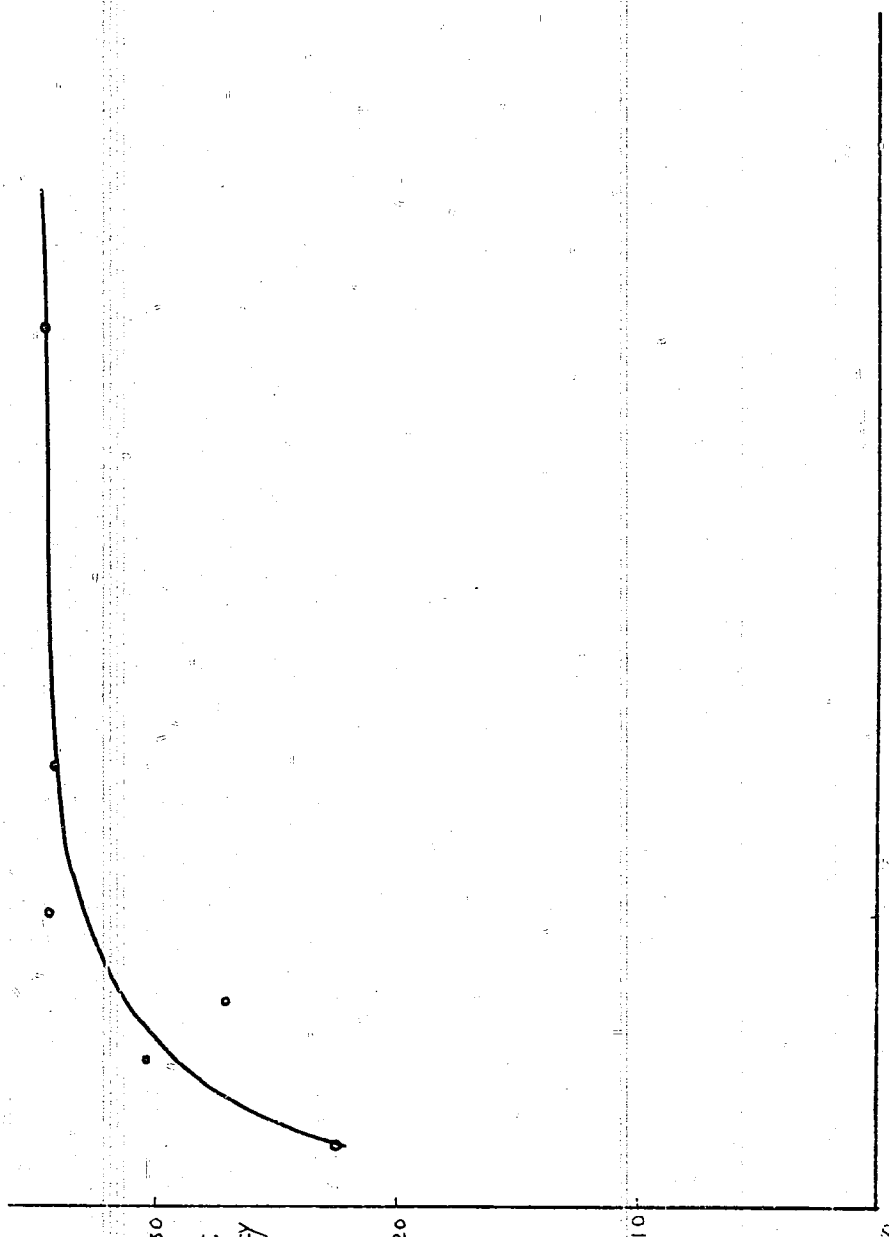


Figure 3(B)1
CORRELATION CURVE BETWEEN
THE QUANTITY OF ADDED HF AND CURRENT EFFICIENCY

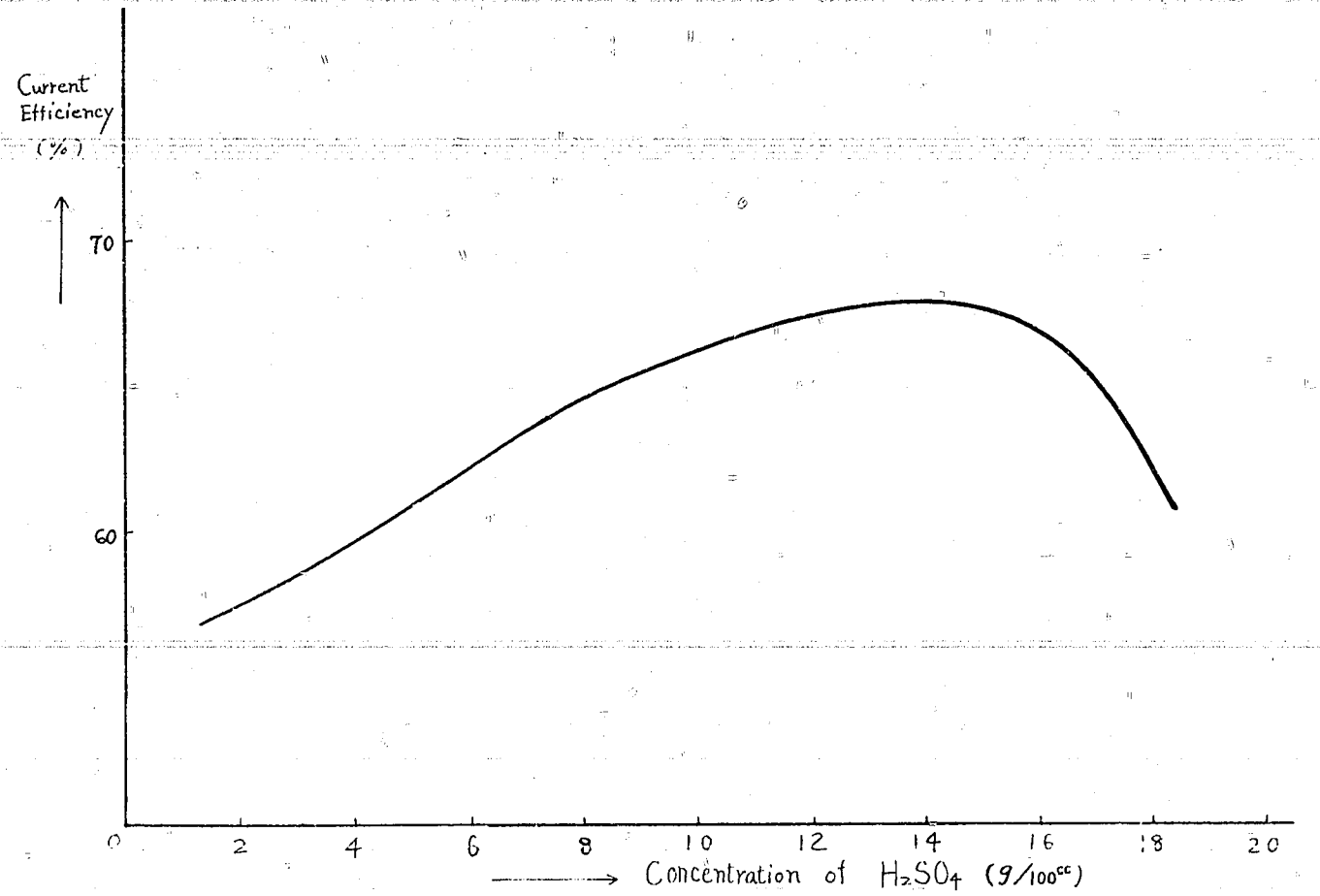


Figure 4(B)1
CORRELATION CURVE BETWEEN
THE CONCENTRATION OF H_2SO_4 AND CURRENT EFFICIENCY

ENCLOSURE (B)1

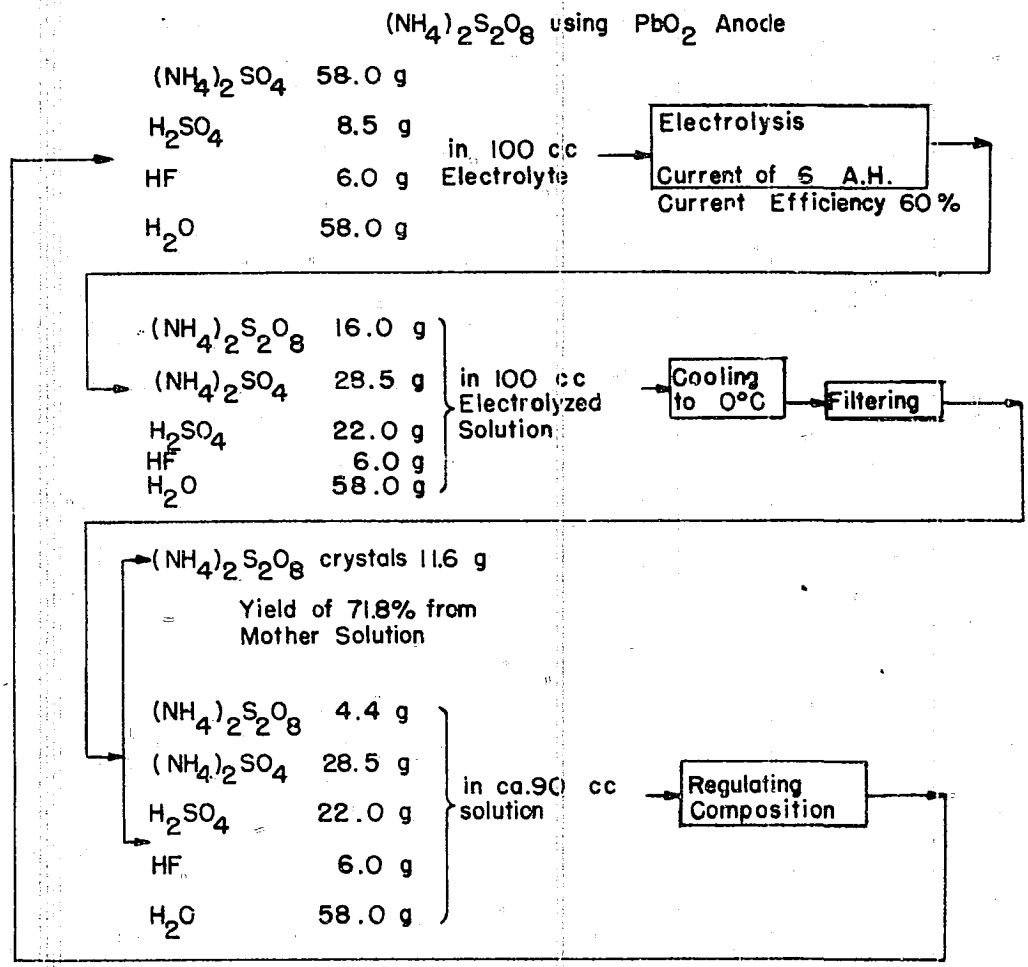
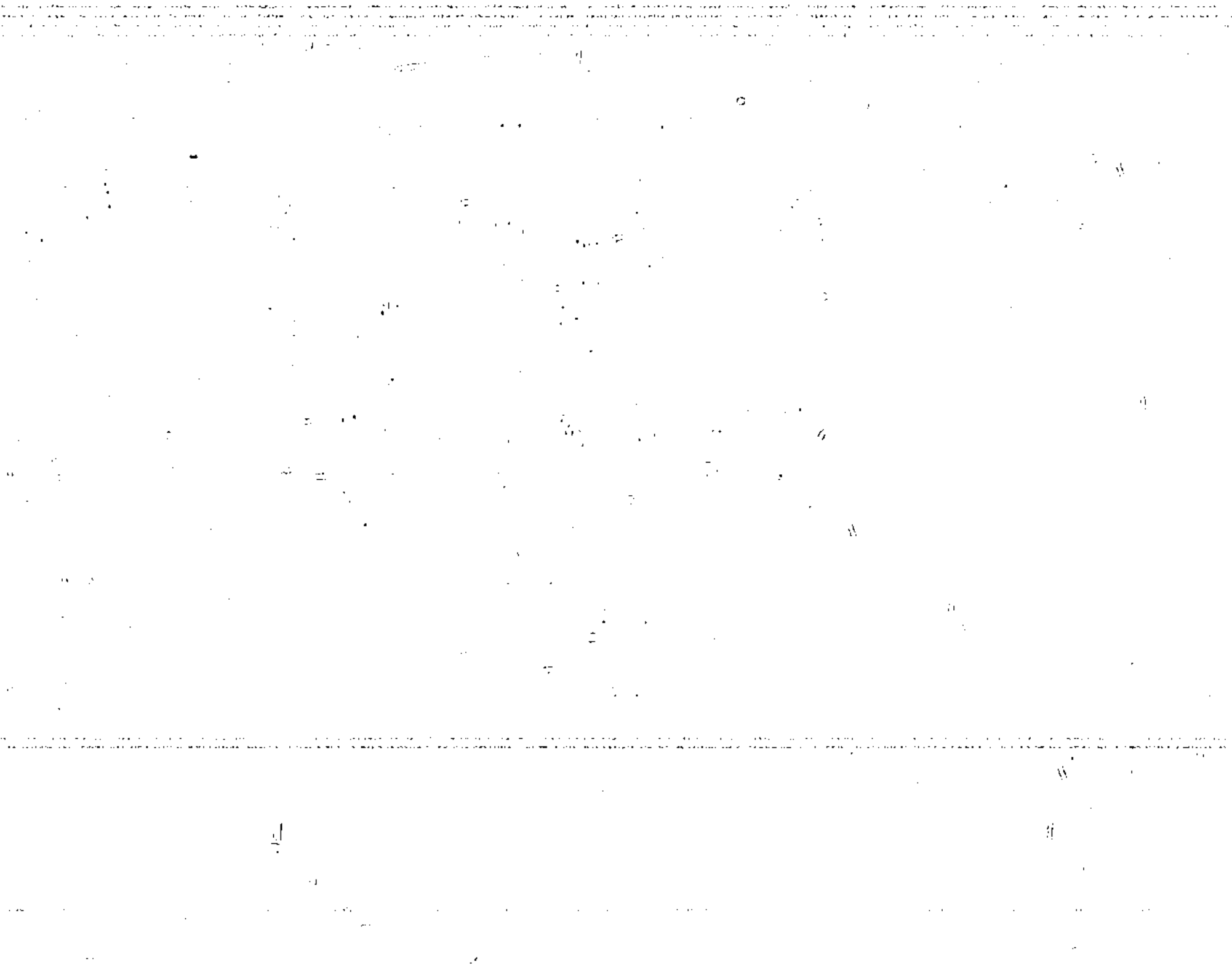


Figure 5(B)1
OPTIMUM CONDITIONS FOR PREPARATION
OF $(NH_4)_2S_2O_8$ USING PbO_2 ANODE



ENCLOSURE (B)2

STUDIES ON MATERIALS OF ANTI-CORROSIVE REACTION TUBE FOR PRODUCING HYDROGEN PEROXIDE BY HYDROLYSIS OF AMMONIUM PERSULPHATE

by
CHEM. ENG. LIEUT.
J. UETA

Research Period: 1944-1945

Prepared for and Reviewed with Author
by U. S. Naval Technical Mission to Japan

December 1945

ENCLOSURE (B)2

LIST OF TABLES AND ILLUSTRATIONS

ENCLOSURE (B)2

SUMMARY

The object of this study was to determine suitable materials and working methods for the reaction tube with a long life.

Significant results were:

Lead which contains from 0.2% to 2.0% antimony is best as the material of the reaction tube.

In preparing the tube it is best that the lead be melted at less than 350°C during preparation in order to avoid the formation of lead oxide. Using these materials and this procedure, the reaction tube becomes very anti-corrosive and can be used perfectly for more than two months.

I. INTRODUCTION

A. History of Project

In producing hydrogen peroxide by the hydrolysis of ammonium persulphate, the so-called pure lead tubes had been used previously in service as the reaction tube, but these tubes were corroded rapidly and damaged after a week. Therefore, we tried to make the reaction tube more anti-corrosive and obtained one which seemed to be more satisfactory.

These tubes are now in use in all the plants of this type in Japan. A flow sheet of a typical plant of this type is presented in Plate I(B)2.

B. Key Research Personnel Working on the Project

Chemical Engineering Lieutenant UETA
Chemical Engineering Sub-Lieutenant A. MOCHIZUKI

II. DETAILED DESCRIPTION

A. Test Procedures

The reaction tube is shown in Figure 1(B)2.

At first, the state of corrosion was observed microscopically in a pure lead tube which had been damaged. It was recognized that in the pure lead tubes, lead grains were very large and lead oxides were developed on the boundaries of lead grains; and that the corrosion only occured in the lead oxide zones, or the boundaries of lead grains. (See Figure 2(B)2)

In order to avoid corrosion it is necessary that the eutectoid be compactly filled between lead grains and that lead oxide be eliminated.

From the above point of view, it was supposed that lead containing from 0.2% to 2.0% antimony is more anti-corrosive than pure lead. And also, from the metalluragical point of view, lead seems to combine with oxygen in the atmosphere at temperatures in excess of 350°C, and this lead oxide is readily corroded by the fluid.

From these points of view, it was supposed that lead tubes containing from 0.2% to 2.0% antimony and melted at less than 350°C during working up would be the best. (See Appendix). Therefore, various tubes were used in the plant of Edogawa Manufacturing Co., Ltd.

B. Experimental Results

Lead tubes containing 0.2%-2.0% antimony were very good and could be used in service perfectly for more than two months.

These tubes were observed microscopically and the following observations were made.

The lead grains were very small and lead-antimony alloy filled up the space between lead grains compactly so that intercrystalline corrosion did not occur.

III. CONCLUSION

A. The best material for the reaction tube is lead containing 0.2-2.0% antimony.

B. The melting temperature of lead should be maintained at less than 350°C in order to avoid the oxidation of lead.

The reaction tube which was made under these conditions has a long life and was used in service perfectly more than two months.

The study was not complete, since proper percentage of Sb in the alloy has not been investigated.

APPENDIX

1. As shown in the above phase-diagram, Figure 5, lead begins to form a eutectoid with antimony at the point of 0.2% antimony.

2. At high temperatures, the greater the amount of antimony, the smaller the tensile strength of Pb-Sb alloy becomes, and at the same time the easier the alloy is oxidized.

3. When the amount of antimony is less than 0.2%, the tensile strength of the alloy is small, the alloy is easily oxidized, and intercrystalline corrosion occurs.

4. Thus it was assumed that 0.2-2.0% antimony lead alloys would be proper for this purpose.

ENCLOSURE (B)2

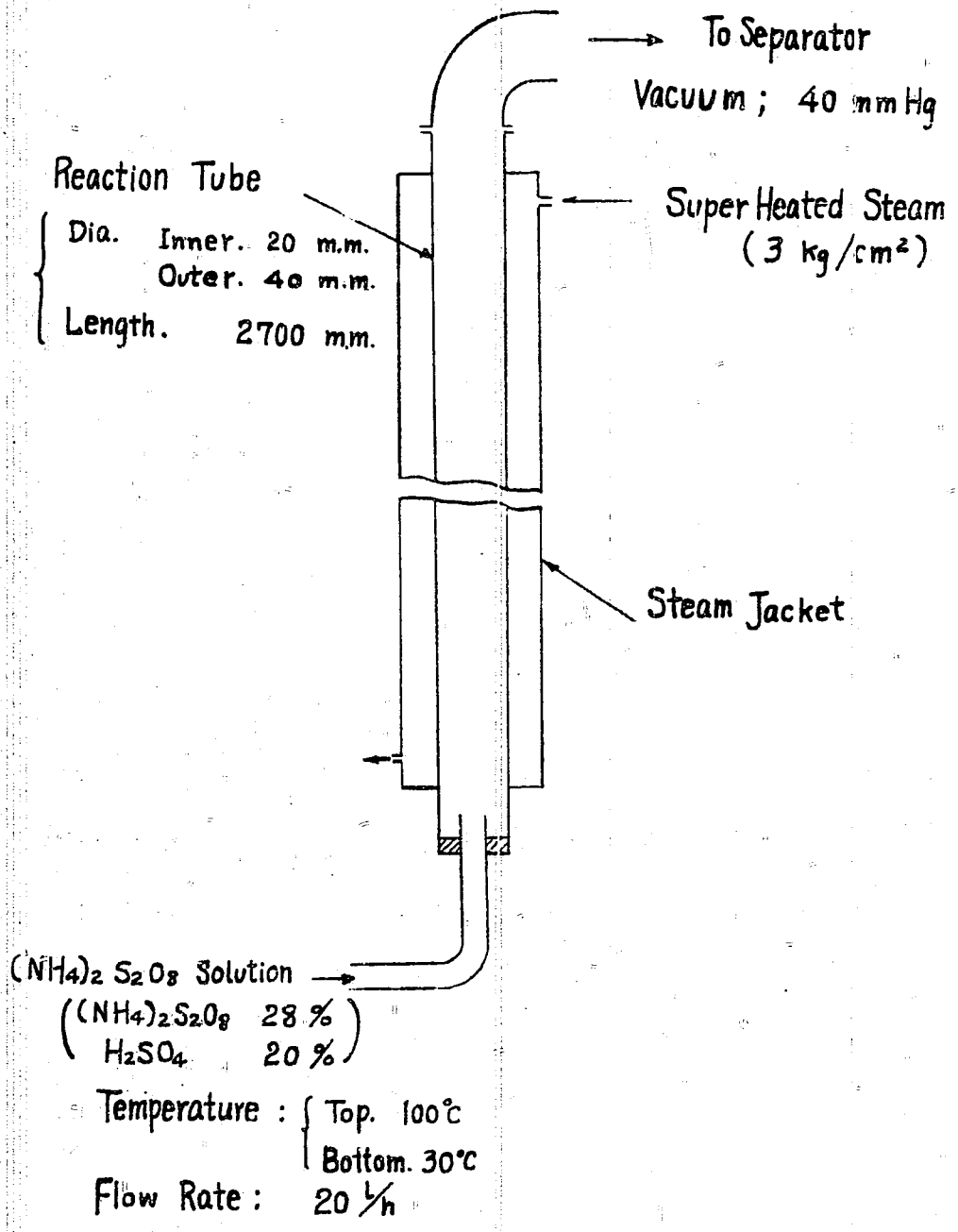


Figure 1 (B)2
REACTION TUBE

ENCLOSURE (B)2

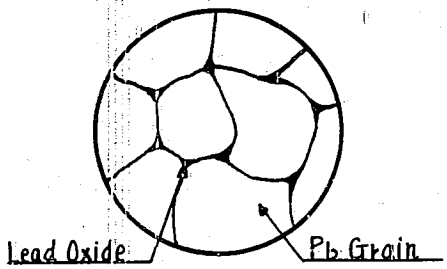


Figure 2 (B)2
PURE LEAD (0·016% Sb)
(x300)

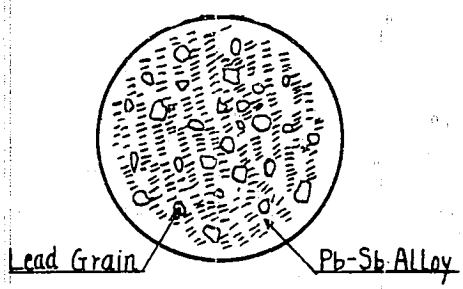


Figure 3 (B)2
LEAD CONTAINING 2% ANTIMONY
(x300)

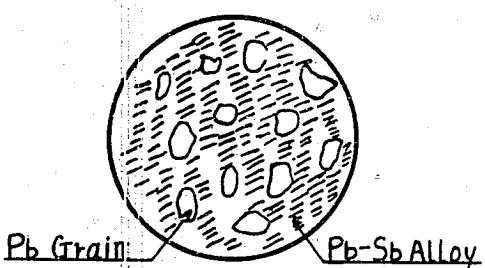


Figure 4 (B)2
LEAD CONTAINING 0.2% ANTIMONY
(x300)

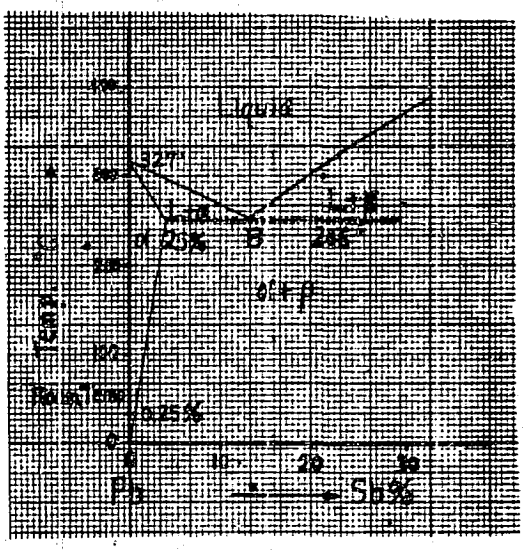
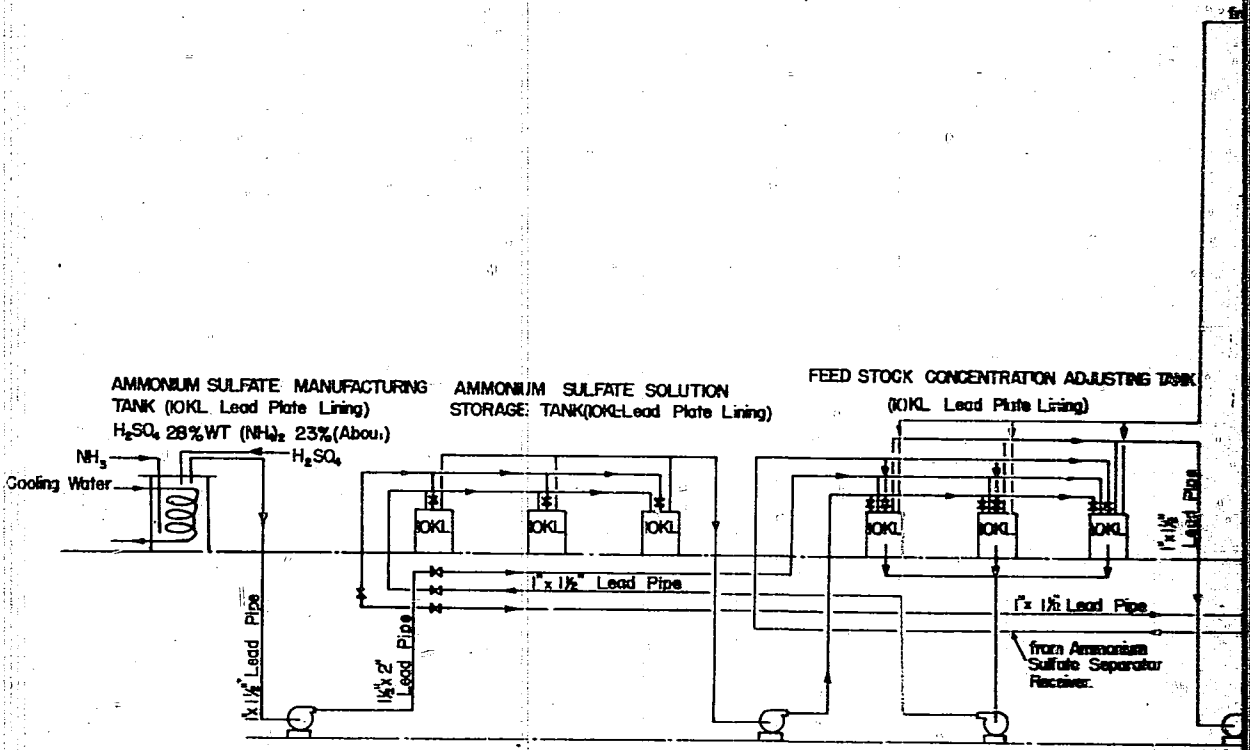
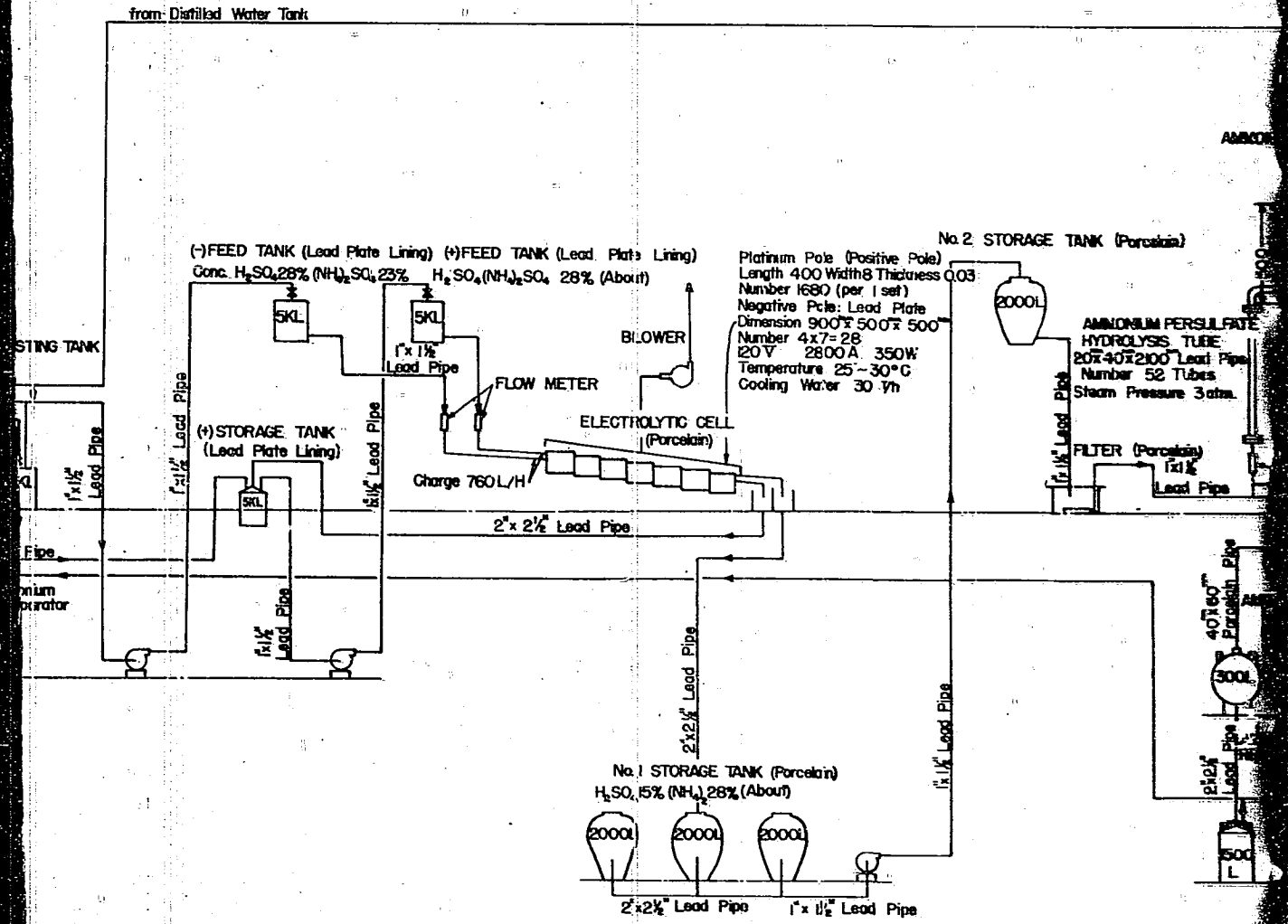
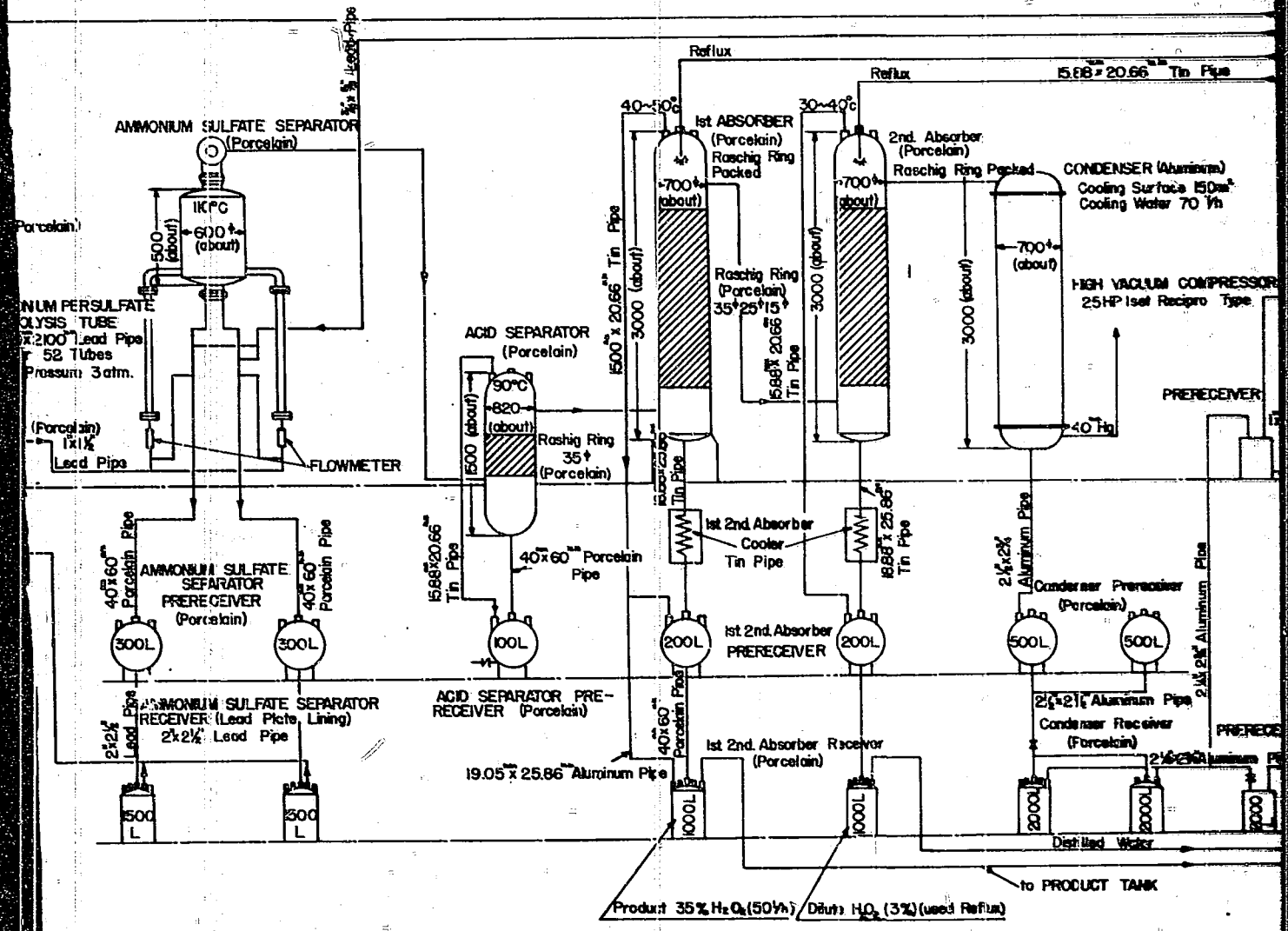


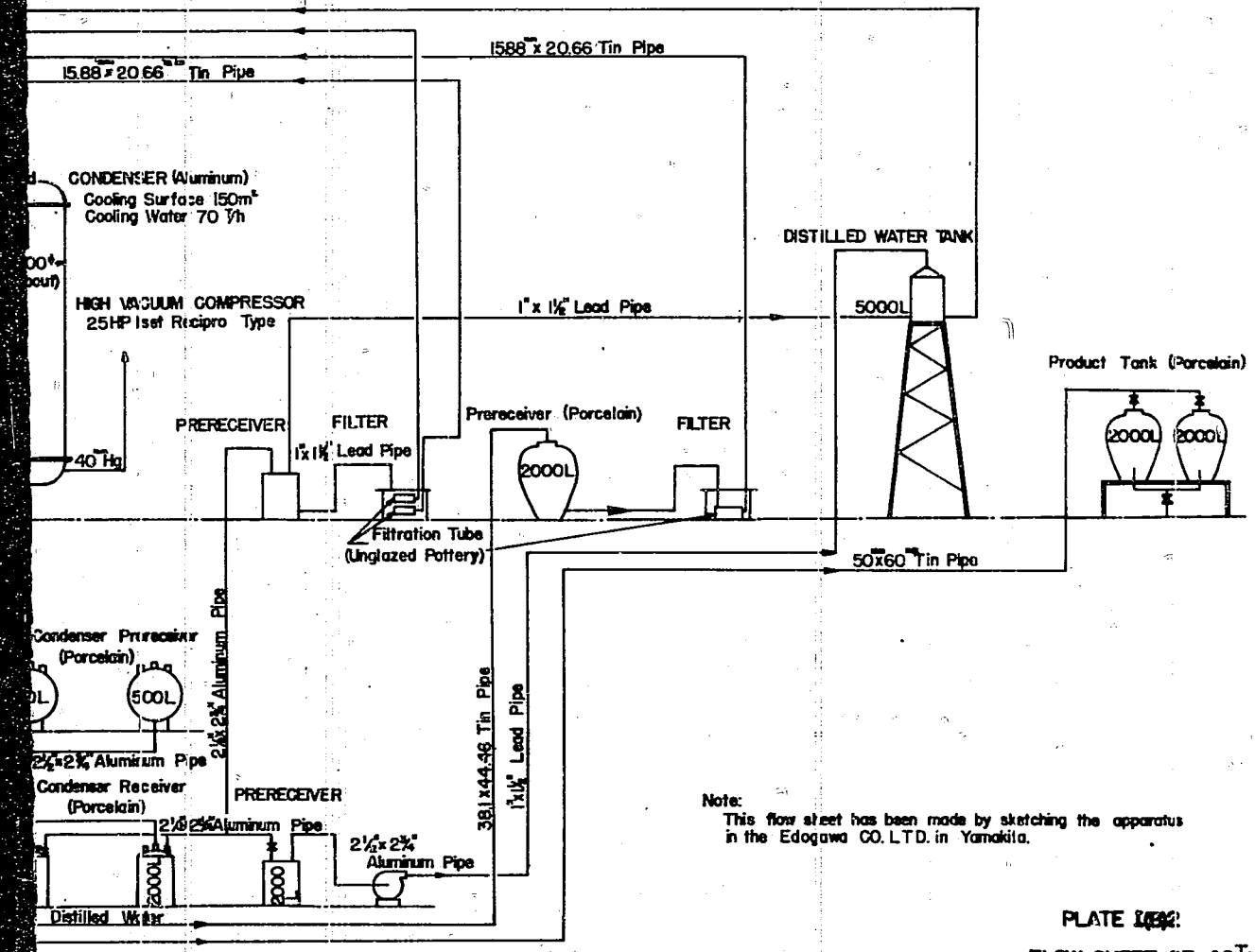
Figure 5 (B)2
PHASE DIAGRAM


AMMONIUM SULFATE MANUFACTURING TANK (10KL Lead Plate Lining)
H_2SO_4 28%WT $(NH_4)_2$ 23%(About)
NH_3
H_2SO_4
Cooling Water
AMMONIUM SULFATE SOLUTION STORAGE TANK(10KL-Lead Plate Lining)
10KL
1" x 1½" Lead Pipe
1½"x 2" Lead Pipe
FEED STOCK CONCENTRATION ADJUSTING TANK (10KL Lead Plate Lining)
1" x 1½" Lead Pipe
from Ammonium Sulfate Separator Receiver.


from Distilled Water Tank
(-)FEED TANK (Lead Plate Lining)
Conc. H_2SO_4 28% $(NH_4)_2SO_4$ 23%
(+)FEED TANK (Lead Plate Lining)
H_2SO_4 $(NH_4)_2SO_4$ 28% (About)
5KL
5KL
1"x1½" Lead Pipe
BLOWER
FLOW METER
ELECTROLYTIC CELL (Porcelain)
Charge 760 L/H
Platinum Pole (Positive Pole)
Length 400 Width 8 Thickness 0.03
Number 1680 (per 1 set)
Negative Pole: Lead Plate
Dimension 900"x 500"x 500"
Number 4x7=28
120 V 2800 A 350 W
Temperature 25°~30°C
Cooling Water 30 l/h
No.2 STORAGE TANK (Porcelain)
2000L
AMMONIUM PERSULFATE HYDROLYSIS TUBE
20"x40"x2100" Lead Pipe
Number 52 Tubes
Steam Pressure 3 atm.
FILTER (Porcelain)
1"x1½" Lead Pipe
(+)STORAGE TANK (Lead Plate Lining)
5KL
1"x1½" Lead Pipe
1"x1½" Lead Pipe
1"x1½" Lead Pipe
2"x2½" Lead Pipe
2"x2½" Lead Pipe
1"x1½" Lead Pipe
No.1 STORAGE TANK (Porcelain)
H_2SO_4 15% $(NH_4)_2$ 28% (About)
2000L
2000L
2000L
2"x2½" Lead Pipe
1"x 1½" Lead Pipe
40"x60" Porcelain Pipe
300L
500 L

ENCLOSURE (B)2





Note:
This flow sheet has been made by sketching the apparatus in the Edogawa CO. LTD. in Yamakita.

PLATE [illegible]:
FLOW SHEET OF 40 T/M
30WT% H_2O_2 APPARATUS

ENCLOSURE (B) 3

STUDIES ON THE SYNTHESIS OF HYDROGEN PEROXIDE FROM WATER VAPOUR BY THE ELECTRIC DISCHARGE METHOD

by
ENG. COMDR. DR. H. FUJIMOTO
ENG. LT. COMDR. Y. MOMOTARI
ENG. LIEUT. T. KONOSU

Research Period: 1945

Prepared for and Reviewed with Authors
by U. S. Naval Technical Mission to Japan

December 1945

ENCLOSURE (B)3

LIST OF TABLES AND ILLUSTRATIONS

ENCLOSURE (B)3

SUMMARY

Using superheated steam at about 125°C, H_2O_2 was not synthesized by the 50 cycle A.C. Tesla discharge. Using superheated steam at about 125°C and 500 kilocycles, H_2O_2 could be synthesized. The power consumption was about 300 kwh/kg of H_2O_2 and its concentration was about 0.08%. When two reaction tubes were used in series, there was no improvement in the yield of H_2O_2.

I. INTRODUCTION

The synthesis of H_2O_2 from water vapour has been carried out with the high frequency silent discharge under reduced pressure. However, by this method, the operation of the apparatus is difficult owing to the reduced pressures and the extremely small volume treated per unit. To improve this point, this experiment was begun under such conditions that gaseous superheated steam was used and the high frequency discharge took place at atmospheric pressure followed by rapid cooling. Commercial frequency discharge was also tried but results were unsatisfactory. This research was carried out from January to July 1945 by Eng. Lt. T. KONOSU

II. DESCRIPTION

A. Apparatus

The apparatus is shown in Figure 1(B)3.

B. Procedure

As shown in Figure 1(B)3, the water is boiled in the water boiler (B). The steam formed is superheated by the heating coil (H) and flows into reaction tube (R). At this point discharge occurs. The products then flow into cooling tube (C) and are condensed. The condensed water containing the synthesized H_2O_2 is collected in receiver (D). When the experiment is over, the product is titrated with $\frac{1}{10}$ N $KMnO_4$ to determine the concentration of synthesized H_2O_2. The discharge voltage is generated by the Tesla coil shown in Figure 1(B)3.

C. Results

Results are shown in Table I(B)3.

III. CONCLUSIONS

When commercial frequency discharge was used, the formation of H_2O_2 was negligible. When high frequency discharge was used, the quantity of H_2O_2 increased with increasing steam volumes, but its concentration was decreased.

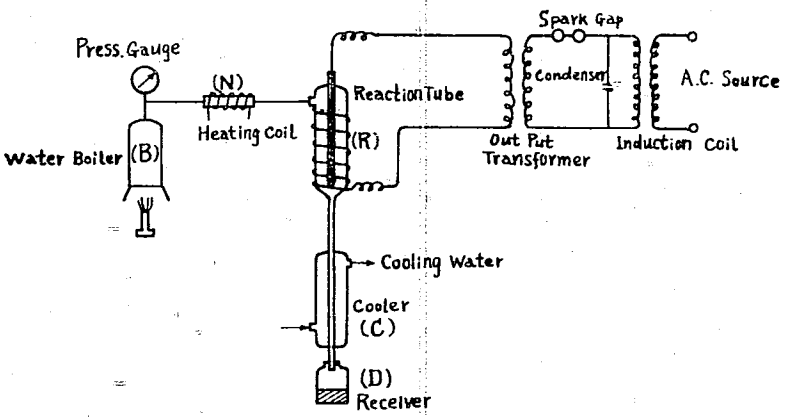
The synthesis of H_2O_2 by this method offers many difficulties, since the power consumed per quantity of H_2O_2 is high and the concentration of product is low.

ENCLOSURE (B)3

Table I(B)3
RESULTS OF TESIA DISCHARGE ON STEAM

Discharge	Condensed Water (cc/10 min)	Superheated temp (°C)	Prim Voltage (volts)	Prim Current (amps)	Powerr (watts)	H_2O_2		Power Consumption (kwh/kg H_2O_2)
						Total (gm/hr)	Concentration (%)	
Commercial frequency	10	125	15	5	75	Trace	---	---
	30	130	20	5	100	Trace	---	---
	50	125	30	5	150	Trace	---	---
	100	125	40	5	200	Trace	---	---
High frequency	10	130	15	4	60	0.02	0.03	3.000
	15	125	17	5	85	0.04	0.05	2.000
	20	125	17	5	85	0.05	0.04	1.500
	30	125	22	5	110	0.11	0.05	1.500
	60	125	35	5	165	0.17	0.05	1.000
	100	125	40	5	200	0.40	0.06	500
	150	125	42	5	210	0.70	0.08	300
	200	125	45	5	225	0.45	0.04	500

ENCLOSURE (B)3



Reaction Tube Detail

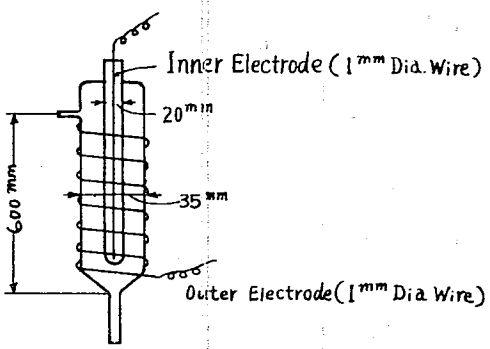


Figure 1 (B)2
APPARATUS FOR H_2O_2 SYNTHESIS
BY TELSA DISCHARGE

ENCLOSURE (B)4

STUDIES ON SYNTHESIS OF HYDROGEN PERCXIDE FROM HYDROGEN-OXYGEN MIXTURE BY ELECTRIC ARC DISCHARGE METHOD

by

CHEM. ENG. COMDR. DR. H. FUJIMOTO

CHEM. LIEUT. COMDR. Y. MOMCTARI

CHEM. ENG. LIEUT. T. KCNOSU

Prepared for and Reviewed with Authors
by U. S. Naval Technical Mission to Japan

December 1945

ENCLOSURE (B)4

LIST OF TABLES AND ILLUSTRATIONS

ENCLOSURE (B)4

SUMMARY

When the flow rate of the hydrogen-oxygen mixture (O_2 about 5%) through the electric arc exceeded 100 m/sec, the power consumed by the hydrogen peroxide synthesis was about 300 kwh/kg H_2O_2.

To obtain the synthesized hydrogen peroxide, the following three methods were used. Among them, Method 1 was the best.

1. Distilled water at the end of the reaction tube was used to absorb the H_2O_2.

2. Distilled water was allowed to contact the reacted gas directly and absorb the H_2O_2.

3. Synthesized H_2O_2 was condensed directly by cooling.

I. INTRODUCTION

The synthesis of hydrogen peroxide from hydrogen-oxygen mixtures by electric discharge previously had been effected with an ozonizer tube. However, the treated volume per unit in this method, was so small that to improve this point, arc discharge was tried by Lieutenant T. KONOSU from September to December 1944. When the arc discharge was used, the flow speed in the reaction tube was most important, and it was found necessary that the flow speed be above 100 m/sec. To obtain the synthesized products, distilled water was injected at the end of the reaction tube, and the products absorbed.

II. DESCRIPTION

A. Apparatus

The apparatus is shown in Figure 1(B)4

B. Procedure

In Figure 1(B)4, the mixed hydrogen oxygen gases are stored in the gas tank (T) and the O_2 content is maintained at about 5%. By means of the gas recycling pump (P), the gases are forced into the reaction tube (R). Their volume is measured by the flow meter (F_1) and their pressure by the manometer (P_1). In the reaction tube they contact the arc and the cooling water, which is recycled by the recycling pump (I), and flow into the cooling tube (C). Then the cooling water flows into the receiver (E), and residual gases are recycled into the gas tank (T) by the gas recycling pump (P) after their volume is measured by the flow meter (F_2), and their pressure by the manometer (P_2). When the experiment is over, the product is removed and titrated with 1/10 N $KMnO_4$ to determine the concentration of H_2O_2.

C. Results

The results are shown in Table I(B)4

The apparatus in which the cooling water was used so as to contact directly with reacted gases, is shown in Figure 2(B)4, and its results are shown in Table II(B)4.

ENCLOSURE (B)4

The apparatus in which the synthesized H_2O_2 was condensed directly by cooling is shown in Figure 3(B)4, and its results are shown in Table III(B)4.

II. CONCLUSIONS

When the cooling method was used as shown in Figure 1(B)4, the power consumption was about 300 kwh/kg H_2O_2, and the H_2O_2 concentration was about 0.5%. This concentration may be increased by reducing the volume of initial cooling water. In this case, however, the materials of the cooling water recycling pump, which is made of iron and copper, are not suitable. Hence, it will be necessary to select a material that will minimize the decomposition of H_2O_2 synthesized.

It was the object of this research to develop a commercial method of producing H_2O_2 which would eliminate the use of platinum and which could be used as a substitute for the $(NH_4)_2S_2O_8$ method. In this experiment it was hoped that the power consumption would be below 100 kwh/kg H_2O_2 and that the concentration of H_2O_2 produced be at least one percent. Additional experiments will be necessary to develop this method commercially.

Table I(B)4
RESULTS OF ARC DISCHARGE ON MIXED H_2, O_2 GAS

Gas volumes (F_1) (lit/min)	Pressure (P_1) (mm Hg abs)	Primary		Secondary		Power Factor	Power (watts)	Total H_2O_2 (gm/hr)	Power Consumption (KWH/kgH_2O_2)	H_2O_2 Concentration (%)
		Voltage (volts)	Current (amps)	Voltage (kilo – volts)	Current (milli– amps)					
15	740	45	20	15.6	35	0.6	540	0.19	2,800	0.004
20	740	43	20	11.0	45	0.6	516	0.26	2,000	0.005
30	730	42	19	11.0	42	0.6	480	0.48	1,000	0.01
75	730	44	20	10.5	50	0.6	528	1.42	400	0.3
100	730	45	20	10.6	50	0.6	540	1.56	350	0.4
120	720	50	20	12.0	50	0.6	600	1.98	300	0.5
135	720	50	20	13.3	45	0.6	600	1.86	320	0.4

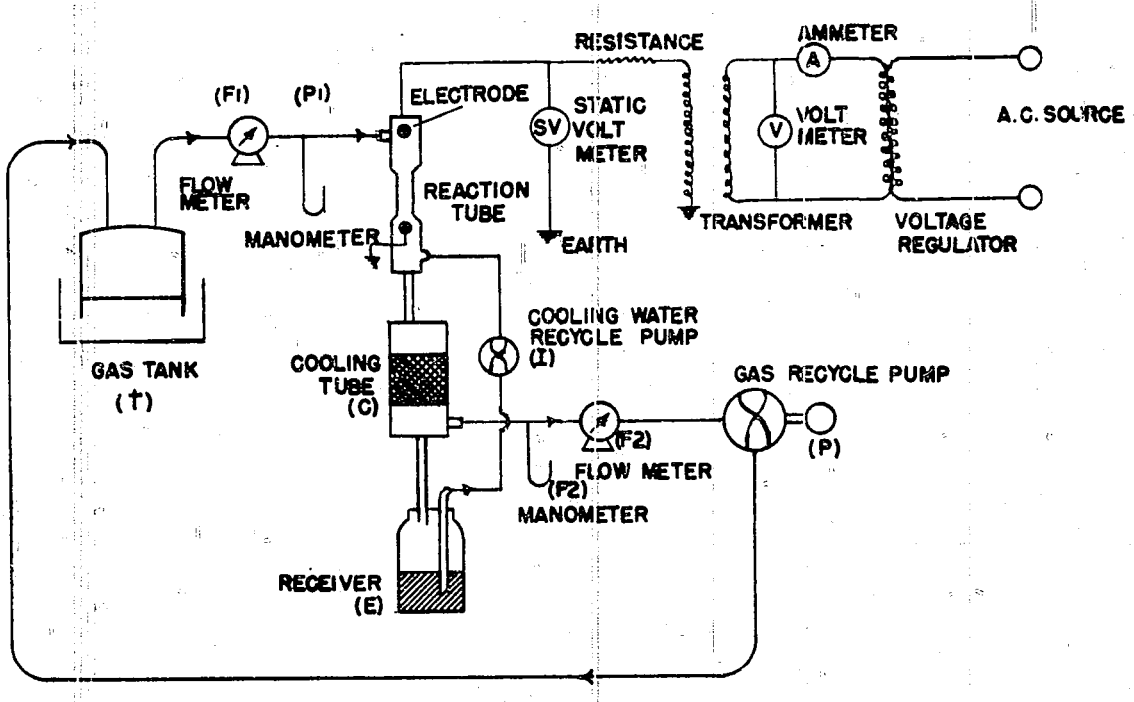
Table II(B)4
RESULTS OF ARC DISCHARGE ON MIXED H_2, O_2 GAS

Gas volumes (lit/min)	Pressure (mm Hg abs)	Primary		Secondary		Power factor	Power (watts)	Total H_2O_2 (gm/hr)	Power consumption (KWH/kgH_2O_2)	H_2O_2 concentration (%)
		Voltage (volts)	Current (amps)	Voltage (kilovolts)	Current (milliamps)					
75	740	45	20	10.8	50	0.6	540	0.97	550	0.6
100	740	46	20	11.0	50	0.6	552	1.37	400	0.8
120	740	48	20	11.5	50	0.6	576	1.34	420	0.7

Table III(B)4
RESULTS OF ARC DISCHARGE ON MIXED H_2, O_2 GAS

Gas volumes (l/min)	Pressure (mm Hg abs)	Primary		Secondary		Power factor	Power (watts)	Total H_2O_2 (gm/hr)	Power consumption (KWH/kgH_2O_2)	H_2O_2 concentration (%)
		Voltage (volts)	Current (amps)	Voltage (kilovolts)	Current (milliamps)					
75	740	45	20	10.8	50	0.6	540	0.7	700	1.0
100	740	45	20	10.8	50	0.6	540	1.1	500	1.2
120	740	48	20	11.5	50	0.6	576	1.0	550	1.0

ENCLOSURE (B)4



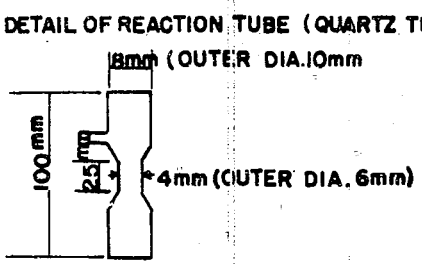


Figure 1 (B)4
APPARATUS FOR H_2O_2 SYNTHESIS BY ARC DISCHARGE

ENCLOSURE (B)4

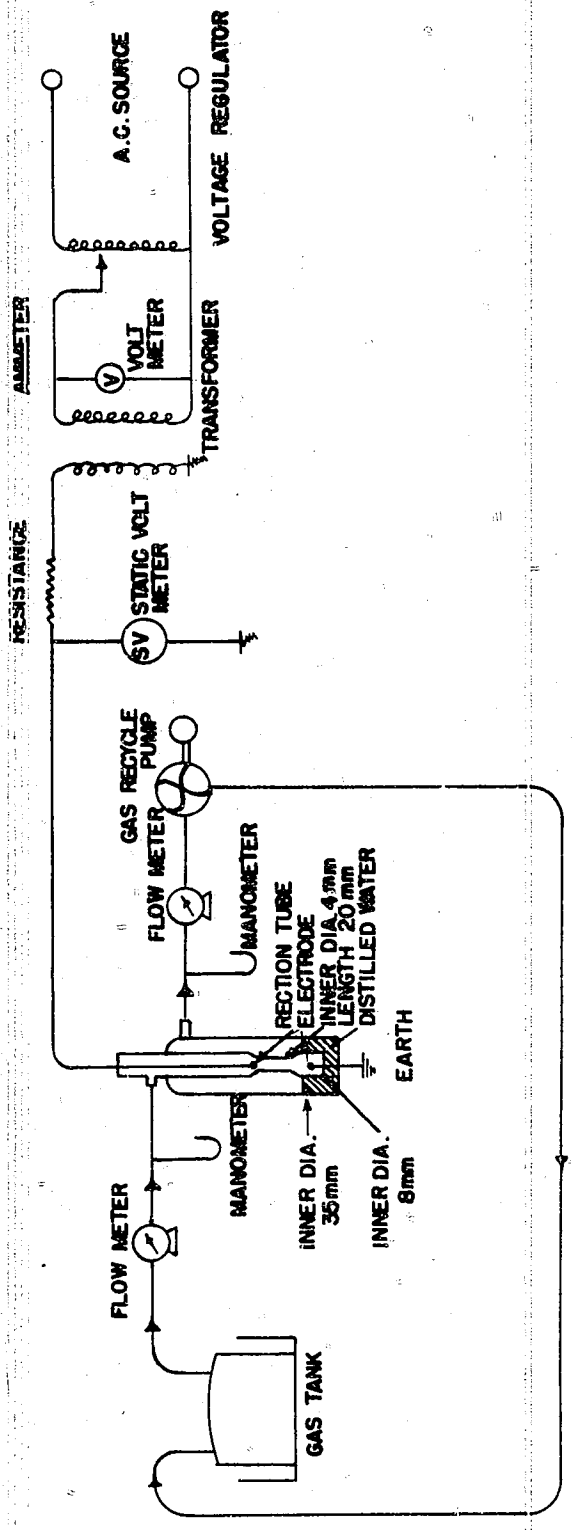


Figure 2 (E)4
APPARATUS FOR H_2O_2 SYNTHESIS BY ARC DISCHARGE

ENCLOSURE (B)4

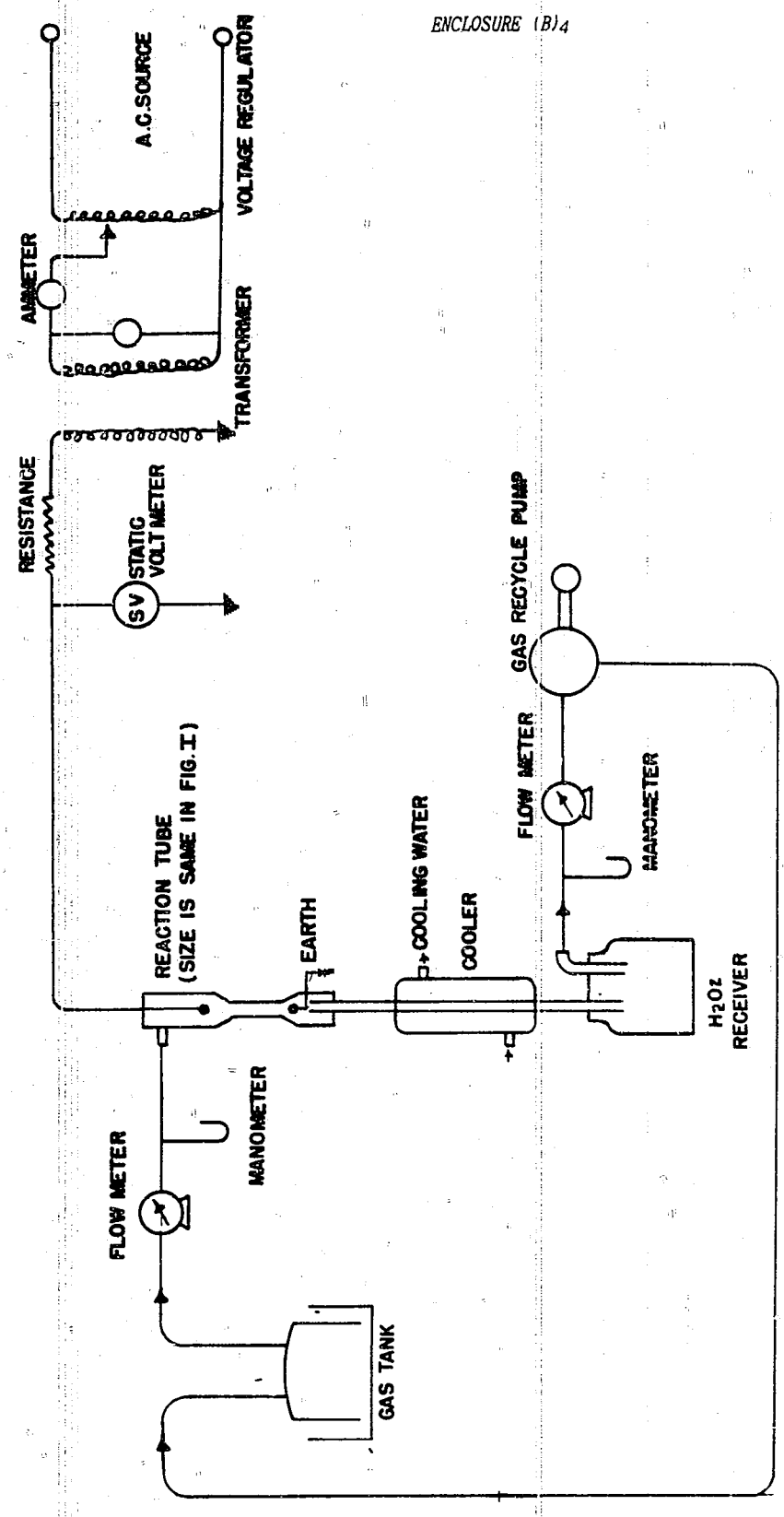


Figure 3 (B)4
APPARATUS FOR H_2O_2 SYNTHESIS BY ARC DISCHARGE

ENCLOSURE (B) 5

RESEARCHES ON ORGANIC STABILIZERS FOR HYDROGEN PEROXIDE

by
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Research Period: 1944-1945

Prepared for and Reviewed with Author
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December 1945

ENCLOSURE (B)5

LIST OF TABLES AND ILLUSTRATIONS

ENCLOSURE (B)5

SUMMARY

Organic stabilizers for concentrated hydrogen peroxide solutions have been required ever since the use of hydrogen peroxide for rockets was developed. Inorganic substances are rather unsatisfactory for this application.

In order to discover appropriate stabilizers from the point of view of effectiveness and durability, some preliminary experiments were conducted which show the superiority of quinoline and its derivatives, although no general conclusions have been reached.

I. INTRODUCTION

A. History of Project

As very few investigations have been carried on in Japan on this subject, it was intended to search for the appropriate types of organic compounds by several experiments.

Consequently, it was discovered that aniline, 8-Hydroxy-quinoline, etc., are quite effective, but that they were apt to be oxidized and lose their effectiveness.

Therefore, although superior and more stable substances were desired and searched for in the subsequent experiments, it was in vain and the quinolines remained the best known stabilizers.

One portion of each sample was maintained at 90°C, and its concentration titrated at intervals. Another portion of each sample was maintained at room temperature and titrated in the same manner.

Glycerine is necessary for the production of 8-Hydroxy-quinoline. Since glycerine was difficult to obtain, it was necessary to use its methyl derivatives which were easy to obtain, and are as excellent as the former. These researches were carried on from August, 1944, to the present.

B. Test Procedures

1. A sample containing a definite quantity (0.02gm) of each of several compounds was dissolved in 50cc of concentrated H_2O_2 in a glass bottle which was kept in a water bath at 90°C., and the time to fill a 50cc gas burette with the evolved oxygen gas was measured.

It was assumed that the longer the time to fill it, the more effective the inhibitor was.

2. Equimolecular quantities, equivalent to 0.5 gram 8-hydroxy-quinoline per liter of several organic compounds were added to conc, H_2O_2, heated to 90°C as before, and the concentration of peroxide was titrated with 0.1N potassium permanganate solution at intervals.

Other portions of each of these same samples were kept at room temperature and titrated in the same manner.

C. Experimental Results

No data is available except the concentration drop curves. Table I(B)5 is written from memory and indicates the effectiveness of

of various inhibitors as judged by the time required to liberate 50 cc of oxygen at 90°C.

Table II(B)5 shows the change of H_2O_2 concentration with time at 90°C in the presence of various inhibitors. Table III(B)5 shows the results using the same solutions, but maintaining them at an average temperature of 18°C.

The data recorded in Table II(B)5 and III(B)5 is presented in Figures 1(B)5 and 2(B)5 in the form of curves, showing the decrease in the concentration of H_2O_2 with time at 90°C and at room temperature, respectively.

Table I(B)5
EFFECTIVENESS OF H_2O_2 INHIBITORS AT 90°C*

Excellent	Good	Ineffective
Pyridine	Sodium Pyrophosphate	Salicylic acid
Phosphoric acid	Phenacetine	Tannine
Aniline	a-Naphthylamine	Urea
Diphenylamine	Hippuric acid	Acetanilide
8-Hydroxyquinoline	Hydroquinone	Benzoic acid
		Centralit
		Triphenylamine
		Acetic acid

* Excellent: More than 20 minutes needed.
Good: 10-20 min. needed.
Ineffective or Harmful: less than 10 min. needed.

Table II(B)5
CHANGE IN H_2O_2 CONCENTRATION IN PRESENCE OF VARIOUS INHIBITORS

H_2O_2 Solution	Inhibitor	Time (hr)													
		0	5	7	8	10	11	15	16	17	19	20	21	24	25
No. 1	Phenol	75		70			64		15			6			
	Pyrocathechine	75	66			29		2							
	Oxalic acid	75		16								0			
	Phthalic anhydride	75	73			69		30							
	Urea	75			65					34		22			
	Pyridine	75	64			49						4			
No. 2	Blank	75	69			49		5				4			
	Phosphoric acid (0.01 gm/lit)	79	77			74		72							
	Resorcinol	79	75					68				46			
	Aniline	79	70			59		47					30		19
	Quinoline	79	78			77		76				75			73
	8-Hydroxy-quinoline	79	79			77		76						75	
	2-Methyl-Oxy-q	79	79			78		78			76			76	
	2-4-Dimethyl-Oxy-q	79	79			78		78			77				
	Blank	79	76			74		69			61				

Temperature 90°C
Concentration of Inhibitor, 0.0034 moles/lit
Concentrations are given in percent

Table III(B)5
CHANGE IN H_2O_2 CONCENTRATION IN PRESENCE OF VARIOUS INHIBITORS

H_2O_2 Solution	Inhibitor	Days 0	60	63	64	67	68	69	70	71	72	74	96	103	105	106	112	115	119	120	122	123
No. 1	Pyrocathechine	79										72										68.2
	Oxalic acid	79									74									54.3		
	Phthalic-anhydride	79						76											73.3			
	Urea	79								70.5											46.0	
No. 2	Phosphoric acid (Conc.)	79							71										68.6			
	Resorcinol	79					74									71.6						
	Aniline	79												77.0								
	Quinoline	79	79												78.0							
	8-Hydroxy-quinoline	79															78.3					
	2-M-8-Q	79												78.3								
	2-4-D.M.-8-Q	79											78.3									
	Blank	79			78													76.3				

Temp. Room temp. (March-August 1945), Average temp. 18°C.
Concentration of inhibitor, 0.0034 moles/lit
Concentrations are given in percent.

ENCLOSURE (B)5

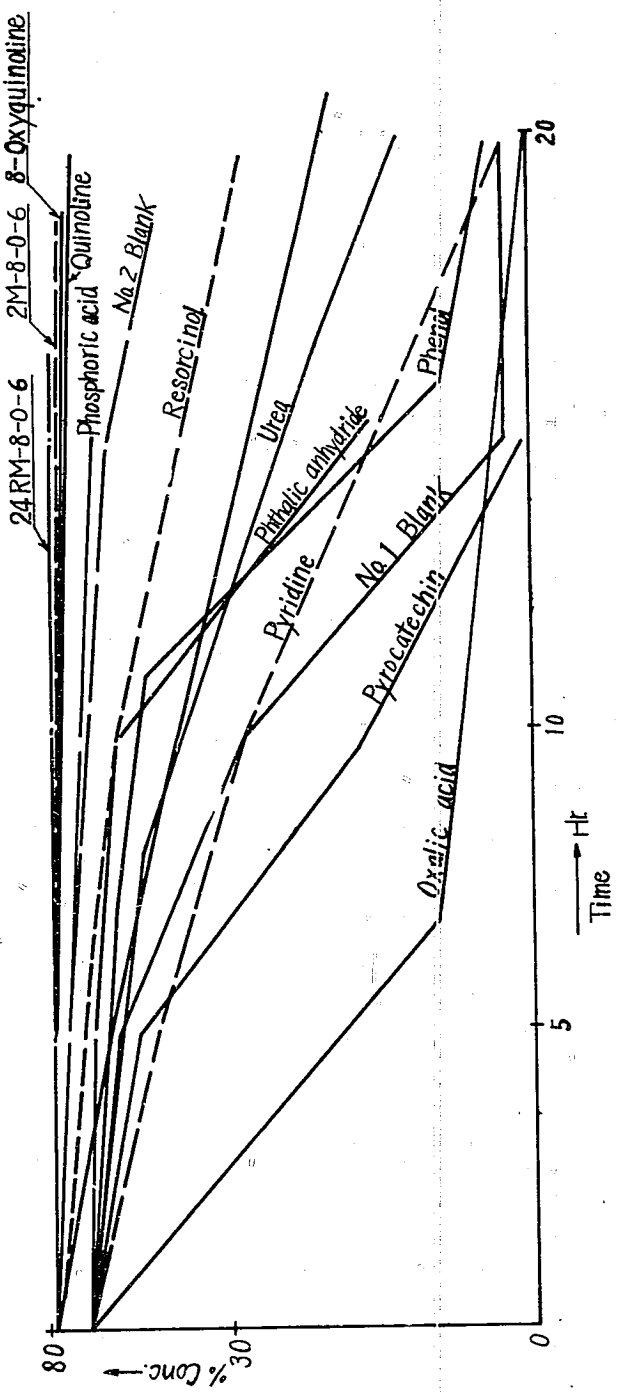

Figure 1 (B)5

CONCENTRATION DROP CURVES WHEN HEATED AT 90°C

ENCLOSURE (B)5

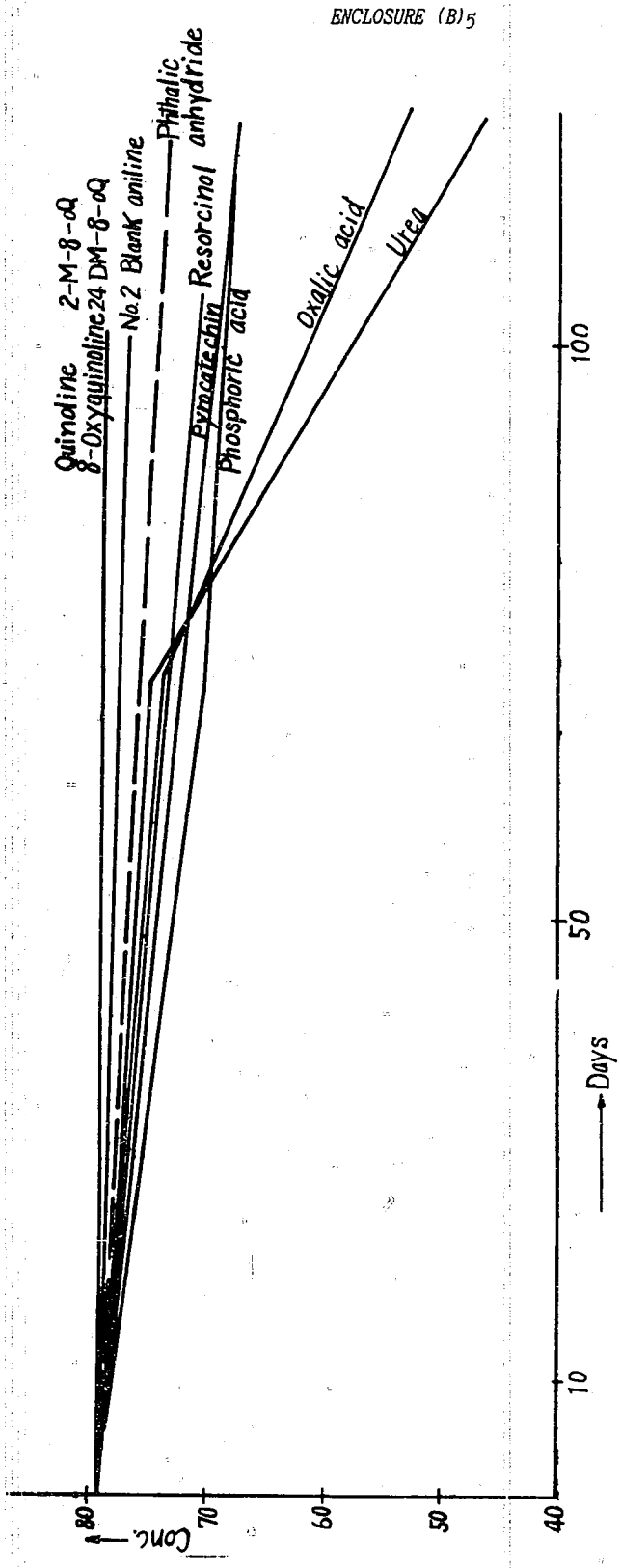

Figure 2 (B)5

CONCENTRATION DROP CURVE WHEN PLACED AT ROOM TEMP

ENCLOSURE (B)6

STUDIES ON THE METALLIC MATERIALS IN THE MANUFACTURING, STORING, AND TRANSPORTING OF THE HYDROGEN PEROXIDE SOLUTION

by

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Research Period: 1944-1945

Prepared for and Reviewed with Authors
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December 1945

ENCLOSURE (B)6

LIST OF TABLES AND ILLUSTRATIONS

ENCLOSURE (B)6

SUMMARY

Suitable metallic materials for the manufacturing apparatus, storing-tank, and transporting-vessel of hydrogen peroxide solution were investigated and the following results were obtained.

1. For the manufacturing apparatus of hydrogen peroxide, tin and stainless steel may be used.

2. It is satisfactory to use tin for the transporting-vessels.

3. It is satisfactory to use tin for the storing-tank.

I. INTRODUCTION

A. History of Project

It is known that glass, porcelein, paraffin, etc., are good materials in regard to non-corrosion and non-decomposition of hydrogen peroxide, but it is difficult to use them practically because of their low strength and plasticity. We were obliged to investigate metallic materials for the above purpose.

B. Key Research Personnel Working on Project

Chem. Eng. Lieut. M. OKAZAKI
Chem. Eng. Lieut. T. ONO

Date of the beginning: August 1944
Date of the finish: July 1945

II. DETAILED DESCRIPTION

A. Description of Test Apparatus

For the test apparatus a water-bath, controlled to hold a constant temperature at 60°C, was used. In this bath were placed many glass bottles in which the corrosivity of liquid H_2O_2 to various metallic test pieces and the decomposition of hydrogen peroxide were tested.

B. Test Procedure

1. All test pieces of various metals made to have the same form of about 30mm in length, 15mm in width, and 1-2mm in thickness, were polished with various polishing-powders until they became glassy, then partially immersed in the bottles full of hydrogen peroxide solution.

The temperature of liquid was held at 60°C in the water-bath and the initial concentration of H_2O_2 solution was 80%.

The term of the test was always 10 days. During the experiment, the initial concentration of hydrogen peroxide in the 80% solution was measured by titration with potassium permanganate solution and each test piece was weighed. The degree of decomposition of hydrogen peroxide (Table I(B)6) and the corrosion of the metallic test pieces (Table II(B)6) were calculated and recorded.

At the same time, the surfaces of the test pieces and the liquid were examined for evidences of corrosion. Observations are recorded in Table III(B)6.

Some non-metallic materials were tested by the same method but only for comparative purposes.

2. To examine the materials for the storing-tank and transporting vessel, some vessels were produced by way of experiment, each 20 liters in capacity, and after pouring in 15 liters of the liquid, initial concentration of 80%. The vessels were kept for 20 days at 40°C to observe the existence of something unusual on the surface of the vessel and liquid (Table IV(B)6). Also, for the examination of transporting, some of the vessels were carried for about 12 hours at room temperature on a truck (Figure 1(B)6).

C. Experimental Results

The results of the experiments are tabulated in the following tables. The results of the test for transporting were very good. That is, none of them showed anything unusual on the wall of vessel and in the liquid.

The kinds of materials or the structure of vessels used for the test were as follows: Aluminium vessel with one outlet, steel vessel lined with tin plate, and glass bottle, 20 liters in capacity. Details of the vessels used in practice are shown in Figure 1(B)6 and Figure 2(B)6.

III. CONCLUSION

The conclusions from the tests are as follows:

A. For the material in the manufacturing apparatus of hydrogen peroxide solution, porcelain is suitable; but it is hard to use practically because of its mechanical strength and plasticity. If metallic materials are to be used for the purpose, stainless steel containing chromium and nickel, tin, and pure aluminium, are suitable for practical use. From the viewpoint of ease of obtaining a large amount in practice, tin is the most suitable and stainless steel is the next.

B. For the transporting vessel and storage tank, it is better to use tin plate for the lining material. This is better than using a steel vessel.

Table I(B)6
DEGREE OF DECOMPOSITION OF HYDROGEN PEROXIDE

No	Name of Materials	Surface Area (cm^2)	Vol. of Liquid in the bottle (cc)	Number of Testing Days	Temp. of Liquid (^oC)	Concentration of H_2O_2 (%)		Degree of Decomposition of H_2O_2 (%/cm^2/day)
						Initial	Final	
1	18-8-Ni-Cr Stainless steel	10.2	50	10	60	80.0	65.0	0.15
2	13-Cr Stainless steel	10.0	50	10	60	80.0	55.0	0.25
3	Tin (99%)	10.0	50	10	60	80.0	74.0	0.06
4	Aluminium (99.99%)	10.3	50	10	60	80.0	74.0	0.06
5	Aluminium (99.8%)	10.3	50	10	60	80.0	70.0	0.10
6	Paraffin	10.0	50	10	60	80.0	75.0	0.05
7	Smoked sheet	10.0	50	10	60	80.0	75.0	0.05
8	Rubber	10.0	50	10	60	80.0	74.5	0.055
9	Blank Det'n		50	10	60	80	76	0.04

ENCLOSURE (B)6

Table II(B)6
CORROSION VALUE OF METALS

No.	Name of Materials	Surface Area (cm^2)	Vol. of the Liquid in the Bottle (cc)	Number of Testing Days	Temp. of Liquid (°C)	Weight of Test Piece (gr)		Corrosion Value ($\%/cm^2$/day)
						Initial	Final	
1	18-8-Ni-Cr Stainless steel	10.2	50	10	60	14.0230	14.0228	$2X10^{-6}$
2	13-Cr Stainless steel	10.0	50	10	60	13.9524	13.9515	$9X10^{-6}$
3	Tin (99%)	10.0	50	10	60	13.3552	13.3545	$7X10^{-6}$
4	Aluminium (99.99%)	10.3	50	10	60	4.8240	4.8238	$2X10^{-6}$
5	Aluminium (99.8%)	10.3	50	10	60	4.8155	4.8165	$10X10^{-6}$
6	Paraffin	10.0	50	10	60	1.7432		
7	Smoked sheet	10.0	50	10	60	1.6531		
8	Rubber	10.0	50	10	60	1.6772		

Table III(B)6
APPEARANCE

No.	Name of Materials	Ap. of Liquid	Ap. of Surface of Test Pieces
1	18-8-Ni-Cr Stainless steel	Usual	Vapor-exposed surface-slight violet tarnish
2	13-Cr Stainless steel	Usual	Vapor-exposed surface-slight violet tarnish
3	Tin (99%)	Usual	Usual
4	Aluminium (99.99%)	Usual	Usual
5	Aluminium (99.8%)	White turbidity	White substance on the entire surface
6	Paraffin	Usual	Usual
7	Smoked sheet	Slightly cloudy	Bleached in liquid phase
8	Rubber	Decomposed rubber	Bleached in liquid phase

ENCLOSURE (B)6

Table IV(B)6
STORAGE FOR 20 DAYS AT 40°C

No.	Name of material of vessel	Concentration of H_2O_2(%)		Degree of decomposition of H_2O_2 (%/10 days)	Observation of liquid	Observation of vessel
		initial	final			
1	Aluminium (99.99%)	80.0	79.0	0.5	Usual	Usual
2	Aluminium (99.8%)	80.0	75.0	2.5	White sub. in bottom	White sub. on the wall of vessel
3	Tin-lined steel	80.0	79.5	0.025	Usual	Usual
4	Paraffin lined steel	80.0			Excessive decomp.	There may be crack or pinhole in paraffin layer
5	Rubber lined steel	80.0	79.8	0.01	White slight sub.	Rubber layer is bleached and corroded.
6	Glass bottle	80.0	80.0	0.0	Usual	Usual

ENCLOSURE (B)6

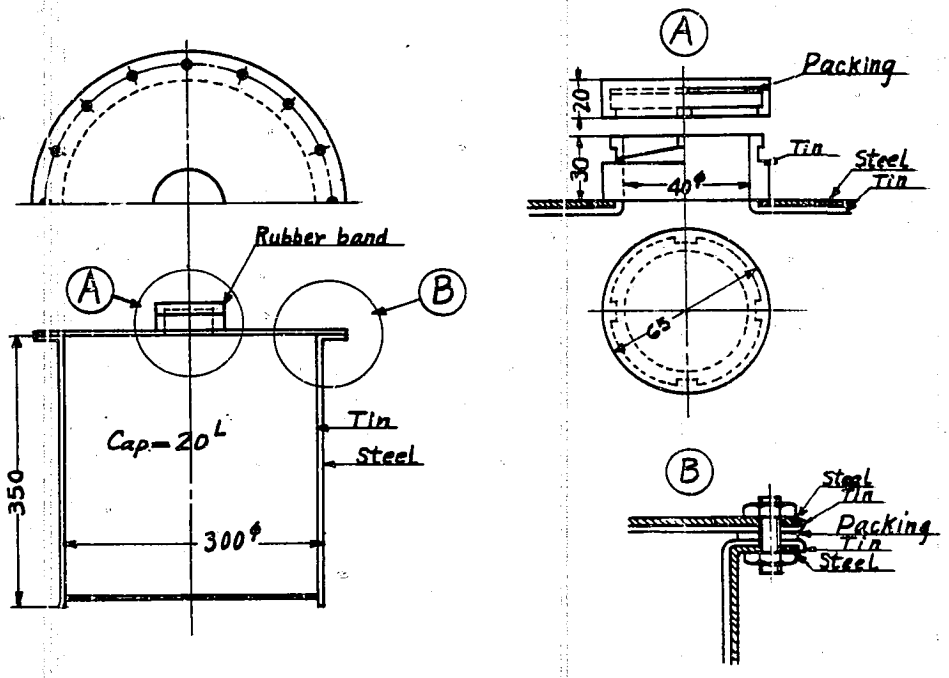

Figure 1 (B)6
H_2O_2 METAL SHIPPING CONTAINER

This vessel, produced by way of experiment, was used in the transporting test and storing test described above.

The vessel is made of steel, lined with tin, and the cover is also the same and fixed with bolts to the vessel.

The stopper is fixed with a rubber band which is at the same time a safety valve for the expansion of gas.

ENCLOSURE (B)6

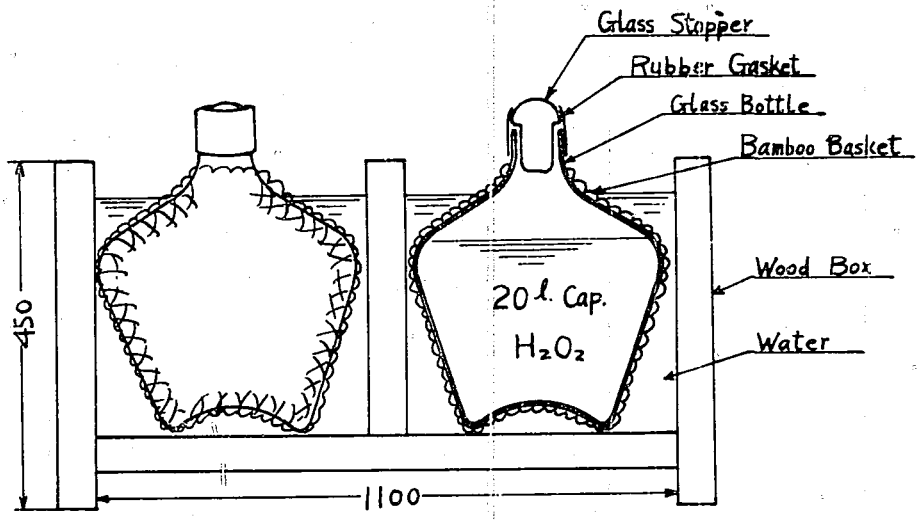

Figure 2 (B)6
H_2O_2 GLASS SHIPPING CONTAINER

Two bottles, made of glass and covered with bamboo basket, are placed in each box, separated into two parts.

The stopper, made of glass, is fixed by a rubber gasket which is at the same time a safety valve for the expansion of gas and occasional explosion.

The water in the box is used to dilute the H_2O_2, overflowing due to vibration of box or by destruction.

Figure 3 (B)6
UNDERGROUND STORAGE OF HYDROGEN PEROXIDE

ENCLOSURE (B) 7

THE DESIGN AND OPERATION OF HYDROGEN PEROXIDE CONCENTRATION PLANTS AT THE FIRST NAVAL FUEL DEPOT

by

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Research Period: 1944-1945

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December 1945

ENCLOSURE (B)7

LIST OF TABLES AND ILLUSTRATIONS

ENCLOSURE (B)7

SUMMARY

Hydrogen peroxide concentration plants were designed according to the following conditions:

Feed stock ..... 30 wt. % H_2O_2
Product ..... 82 wt. % H_2O_2

Product Output

Type 1 plant* ..... 100 tons per month design capacity.

Type 2 plant ..... 250 tons per month design capacity.

* Two units of this type were installed at the First Naval Fuel Depot.

It was planned to install this type at the Second Naval Fuel Depot and at other points, but construction was not started.

A pilot plant (TypeI) was erected at OFUNA. The product of these plants was to be used for SHUSUI, a rocket airplane. Pure 82% concentration hydrogen peroxide of sufficient quality for SHUSUI was obtained continuously.

I. INTRODUCTION

A. History of Project

The design and erection of H_2O_2 concentration plants was ordered by the Naval Supplies Bureau (Gunjukyoku) in August 1944.

A flask type concentration plant was first installed at OFUNA. A drawing of one unit of this plant is shown by Figure 3(B)7. This plant started to operate in October 1944 and was shut down in December 1944. It was equipped with 1000 5 - liter flasks and had a total capacity of 30 tons per month of 82% H_2O_2.

The first continuous plant started its operation in November 1944 and produced about 30 tons of 82% H_2O_2 per month. The design capacity of the plant was 100 tons per month, but the mist separators had not been installed and actual output was only 30 tons/month. The plant was constructed by the Hitachi Co. Ltd. (IBARAGI Prefecture). 30% H_2O_2 was shipped in from the Edogawa Co. at YAMAKITA and the Sumitomo Co. at OSAKA.

The second continuous plant, also Type I, was completed in August 1945, but it did not begin functioning.

B. Key Research Personnel Working on Project

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Nav. Chem. Eng. S. HAYASHI
Nav. Chem. Eng. S. SHINODA
Chem. Eng. Lt. Comdr. Y. YAMAMOTO

ENCLOSURE (B)7

II. DETAILED DESCRIPTION

A. The Plant

A process flow chart for Type I plant is given by Plate I(B)7. Type II plant is similar in design.

Each plant has four preliminary rectifying columns and one column for the final rectification. The columns and condensers are all inter-changeable. The preliminary rectifying step serves chiefly to remove impurities included in the feed stock to prevent possible violent decomposition of concentrated H_2O_2 in the final rectification.

A mist separator is essential to remove impurities carried from the retort with the H_2O_2 vapor, and to increase the purity of the intermediate product. If a sufficiently pure intermediate product is not obtained, the H_2O_2 in the final rectifying retort can not be concentrated to above 80%, and the yield is decreased due to decomposition.

B. Construction Materials

Construction materials used in the continous plants were as follows:

1. Retorts, mist separators, rectifying columns, Raschig rings, vacuum receivers and piping used over about 30°C ..... Porcelain.

2. Condenser tubes ..... Aluminium.

3. Heating coil in retort ..... 18-8 Cr-Ni Steel (The surface of the coil is thoroughly polished).

4. Intermediate product and product coolers, storage tanks, and tubes used under about 30°C ..... Tin.

5. Gaskets for porcelain pipes ..... Low sulphur rubber rings covered with tin plate.

6. For high temperature and large diameter parts, such as the retort covers, mist separators, and rectifying columns, smooth ground joints were adopted successfully.

C. Material and Heat Balances

The material and heat balances were calculated on the basis of the following assumptions:

Operating period per month ..... 75%, or about 23 days.
Loss of H_2O_2 by decomposition and leakage ..... zero.
Loss of heat from the surface of retorts, columns, etc. ..... zero.

1. Material Balances

a. Overall Plant. Basis: 500 kg/hr charge of 30% H_2O_2.

Input

30% H_2O_2 ..... 4 columns x 125 = 500 kg/hr

Output

83% of H_2O_2 ..... 181 kg/hr
Distilled water ..... 4 columns x 68.2 46.2 = 319 kg/hr
500 kg/hr

b. Preliminary Rectifying Column

Input

30 % of H_2O_2 ..... 4 columns x 125 = 500 kg/hr

Output

66% of H_2O_2 ..... 4 columns x 56.8 = 227.2 kg/hr
Distilled water ..... 4 columns x 68.2 = 272.8 kg/hr
500.0 kg/hr

c. Final Rectifying Column

Input

66% of H_2O_2 ..... 227.2 kg/hr

Output

83% H_2O_2 ..... 181 kg/hr
Distilled water ..... 46.2 kg/hr
227.2 kg/hr

2. Heat Balances

a. Overall Plant. (See Tables I(B)7 and II(B)7.

b. Preliminary Rectifying Columns. (See Tables III(B)7 and IV(B)7).

c. Final Rectifying Column. (See Tables V(B)7 and VI(B)7).

D. Equilibrium Data

Pressure-boiling point relations of H_2O_2 and vapor-liquid equilibrium relations of H_2O and H_2O_2 are given by Figure 2(B)7 (based on International Critical Tables) and Figure 1(B)7 (Canadian Journal of Research, 1940).

E. Product Specification and Inspections

Tentative specifications of product: (see Table VII(B)7) Stability: Decomposition must ve less than 10% when heated to 96°C for 24 hr (amount of stabilizer, 8-oxyquinoline 0.3 gm/lit, sodium pyrophosphate ($Na_4P_2O_7.10H_2O$) 0.1 gm/lit). Ignition residue: When heated to 800°C, the residue must be less than 70 mg/lit. Acidity: The H_2SO_4 content must be less than 100 mg/lit.

ENCLOSURE (B)7

Table I(B)7
INPUT

Material	kg/hr	Temp. (°C)	Kcal/hr
30% H_2O_2	4 x 125 = 500	0	
Steam to retorts Preliminary rect.	4 x 127 = 508	Only latent heat calculated	4 x 66.95 x 10^3 -207 - 3 x 10
Final rect. (1kg/cm²)	117	Only latent heat calculated	61.9 x 10^3 / 329.7 x 10^3

Table II(B)7
OUTPUT*

Material		Weight (kg/hr)	Temp. (°C)	Kcal/hr
83% H_2O_2		181	20	2.36x10^3
Distilled water	Preliminary rect. column	4x68.2=272.8	29	4x1.98x10^3 = 7.92x10^3
	Final rect. column	46.2	29	1.34x10^3
Cooling water	Partial condenser	(4x2.59+3.28)x10^3 = 13.64x10^3	16-25	(4x23.3+29.5)x10^3 =122.7x10^3
	Total condenser	(4x4.39+2.98)x10^3 = 20.54x10^3	16-25	(4x39.5+26.8)x10^3 =184.8x10^3
	Intermediate product cooler	4x0.675x10^3=2.70x10^3	16-18	4x1.35x10= 5.4x10^3
	Product cooler	2.60x10^3	16-18	5.18x10^3 / 329.70x10^3

* Note: Total Steam Consumption: 508-117 = 625kg/hr.

Total Cooling Water Consumption: 13.64+20.54+2.60=39.48 ton/hr

ENCLOSURE (B)7

Table III(B)7
INPUT

Material	Kg/hr.	Temp. (°C)	Kcal/hr.
30% H_2O_2	4x125=500	0	0
Steam to retorts (1kg/cm²)	4x127=508	Only latent heat calculated	$4x66.95x10^3=267.8x10^3$ $267.8x10^3$

Table IV(B)7
OUTPUT

Material	Kg/hr	Temp. (°C)	Kcal/hr
66% H_2O_2	4x56.8=227.2	20	$4x0.82x10^3=3.28x10^3$
Distilled Water	4x68.2=272.8	29	$4x1.98x10^3=7.92x10^3$
Cooling Water			
Partial Condenser	$4x2.59x10^3=10.36x10^3$	16-25	$4x23.3x10^3=93.2x10^3$
Total Condenser	$4x4.39x10^3=17.56x10^3$	16-25	$4x39.5.10^3=158.0x10^3$
Intermediate Product cooler	$4x0.675x10^3=2.7x10^3$	16-18	$4x1.35x10^3=5.4x10^3$ $267.80x10^3$

Table V(B)7
INPUT

Material	Kg/hr	Temp. (°C)	Kcal/hr
66% H_2O_2	181	20	$3.28x10^3$
Steam to retort (1kg/cm²)	46.2	29	$61.9\ x10^3$ $65.18x10^3$

ENCLOSURE (B)7

Table VI(B)7
OUTPUT

Material	Kg/hr	Temp. (°C)	Kcal/hr
83% H_2O_2	181	20	2.36×10^3
Distilled water	46.2	29	1.34×10^3
Cooling water			
Partial condenser	3.28×10^3	16-25	29.5×10^3
Total condenser	2.98×10^3	16-25	26.8×10^3
Product cooler	2.60×10^3	16-18	5.18×10^3
			65.18×10^5

Table VII(B)7
TYPICAL PRODUCT AND FEED STOCK, INSPECTIONS

	Feed stock	Product
Conc. of H_2O_2	32%(wt)	82% (wt)
Stability	5% (Amount of decomp. at 80°C, 6 hr)	7%
Ignition residue	(Spec.:Less than 300 mg/l)	45 mg/l
Acidity	50 mg/l	90 mg/l

ENCLOSURE (B)7

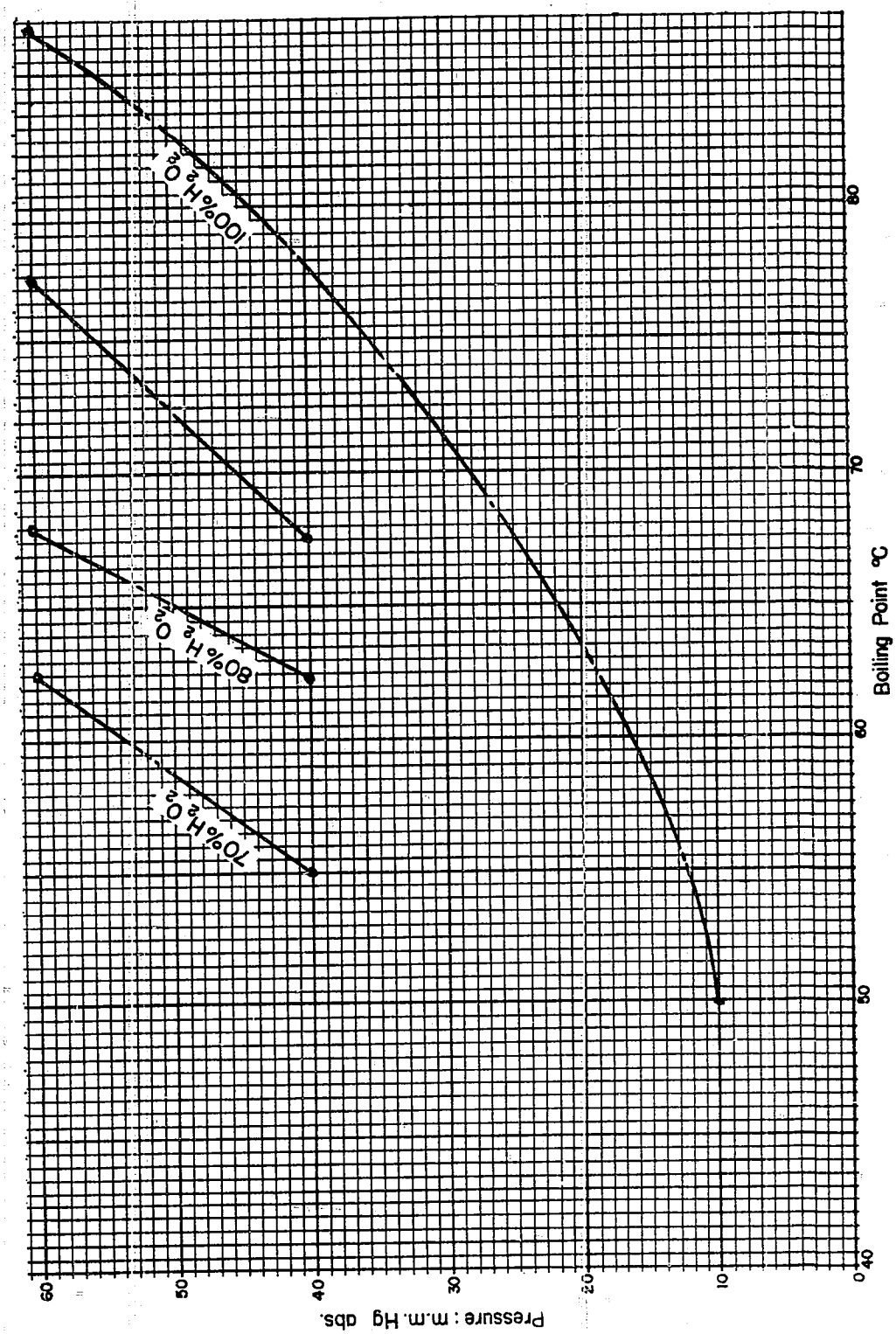


Figure 1 (B)7
PRESSURE-BOILING POINT RELATIONS
AT CONSTANT CONCENTRATIONS OF H_2O_2

ENCLOSURE (B)7

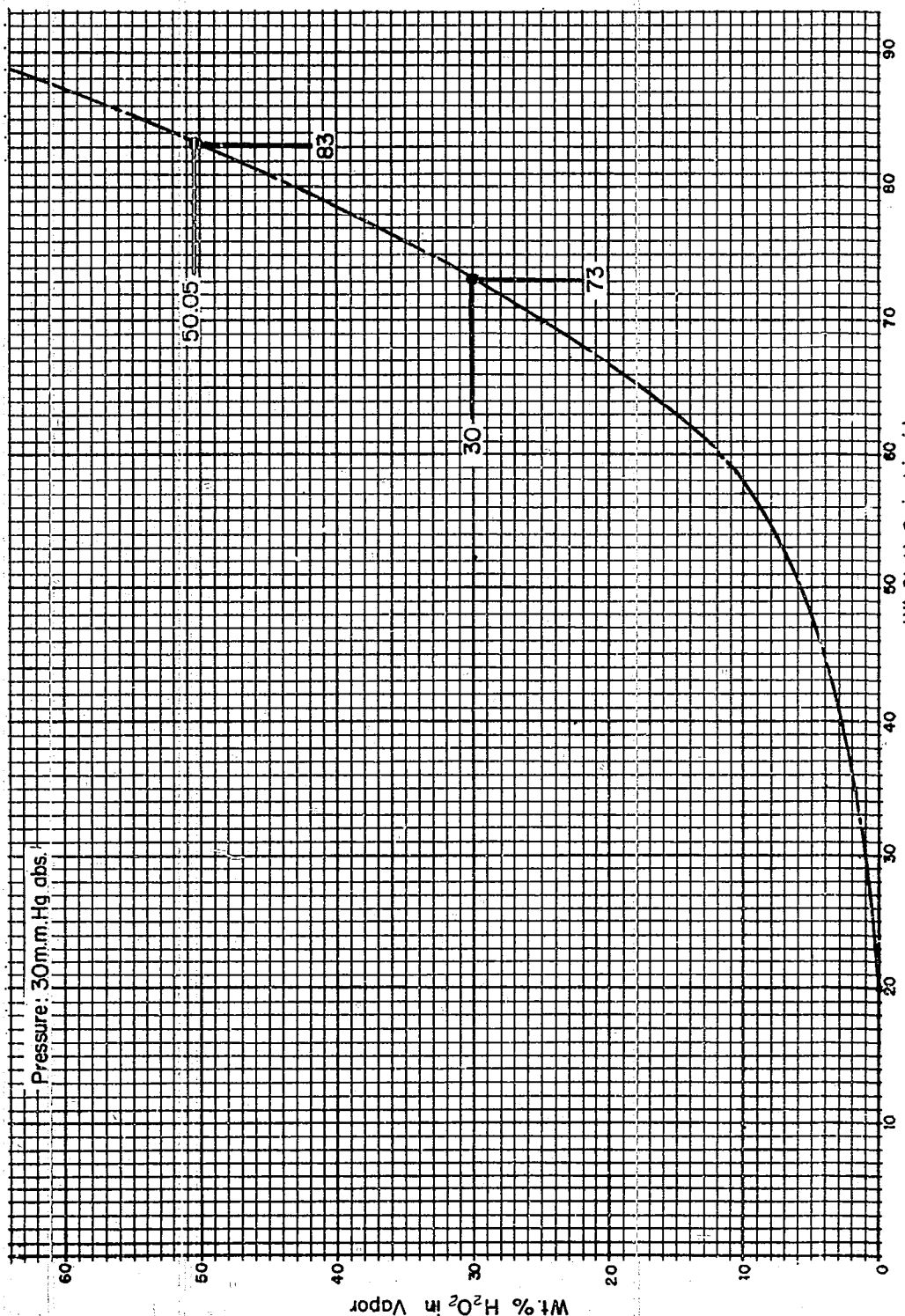
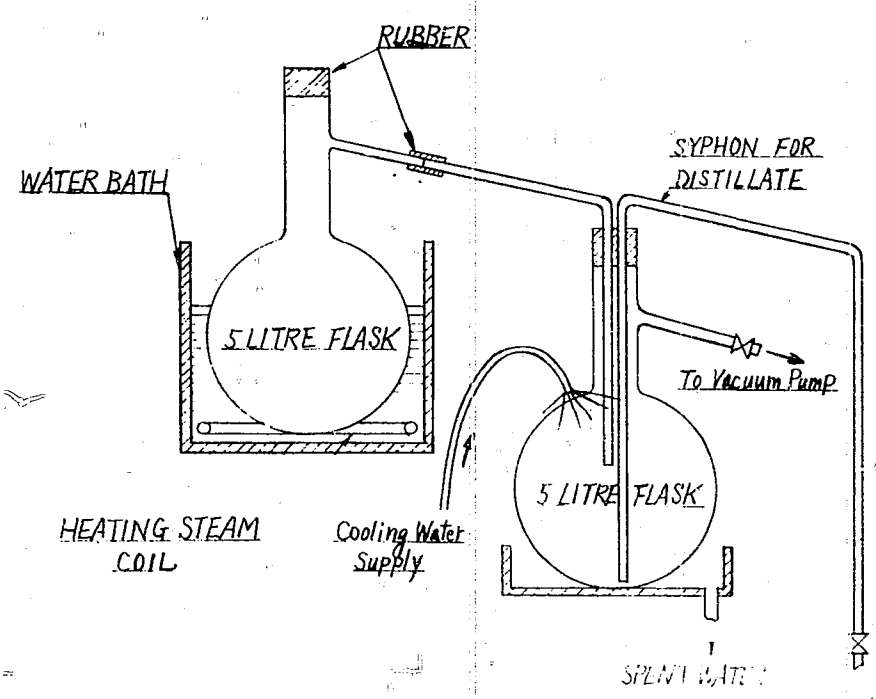


Figure 2 (B)7
VAPOR-LIQUID EQUILIBRIUM RELATIONS AT CONSTANT TOTAL PRESSURE FOR MIXTURES OF H_2O AND H_2O_2

ENCLOSURE (B)7



	Work Condition	
Charge	3 Lit.	32% H_2O_2
Product	¾ Lit.	82% H_2O_2
Distillate	2¼ Lit.	10% H_2O_2
Vacuum		80 mm Hg
Temperture		85 °C Max.

Figure 3 (B)7
FLASK PLANT UNIT

Figure 4 (B)7
HYDROGEN PEROXIDE CONCENTRATION APPARATUS
1. GENERAL VIEW

ENCLOSURE (B)7

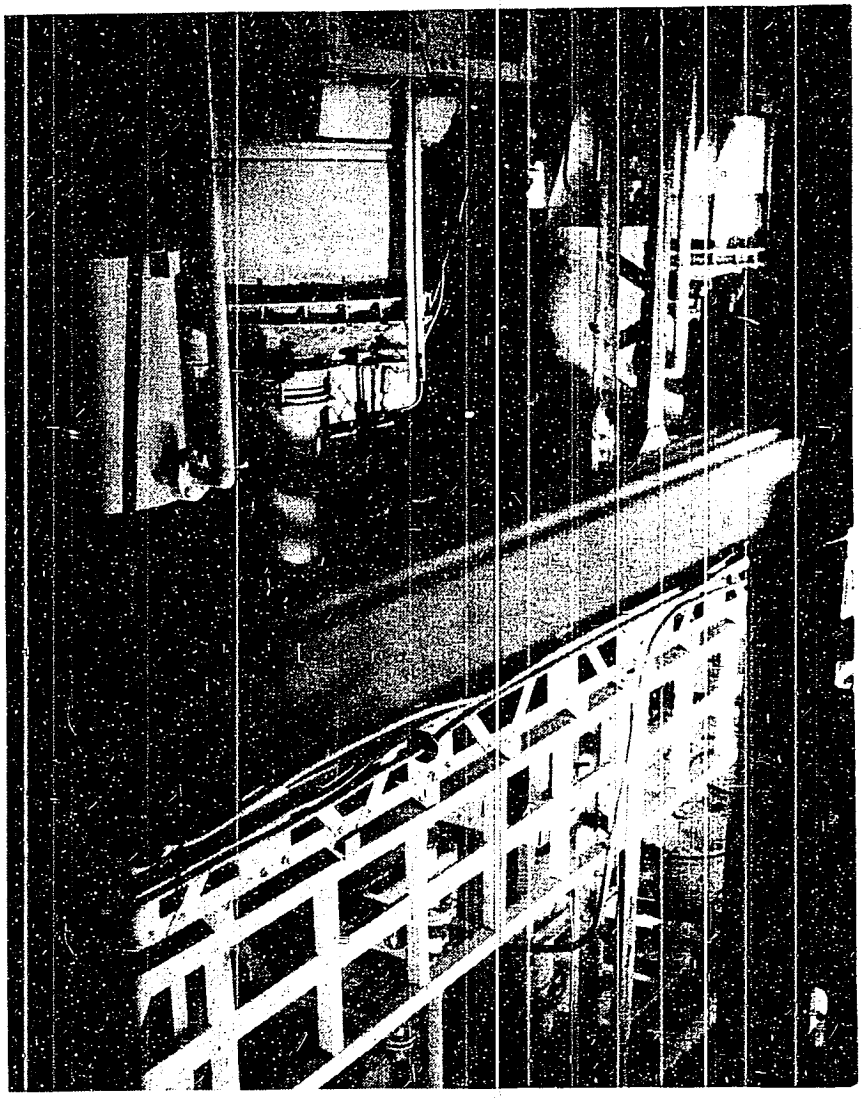
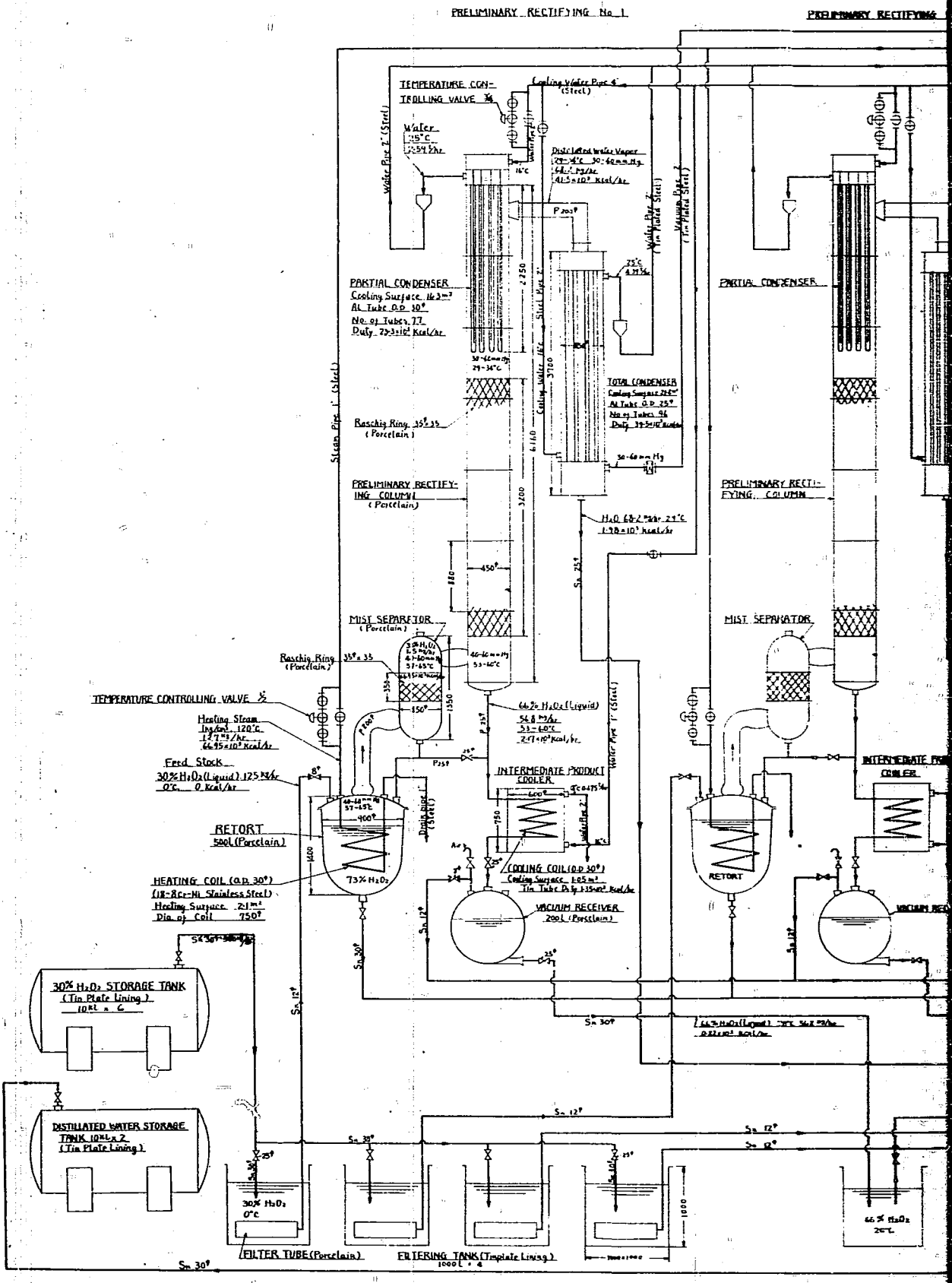
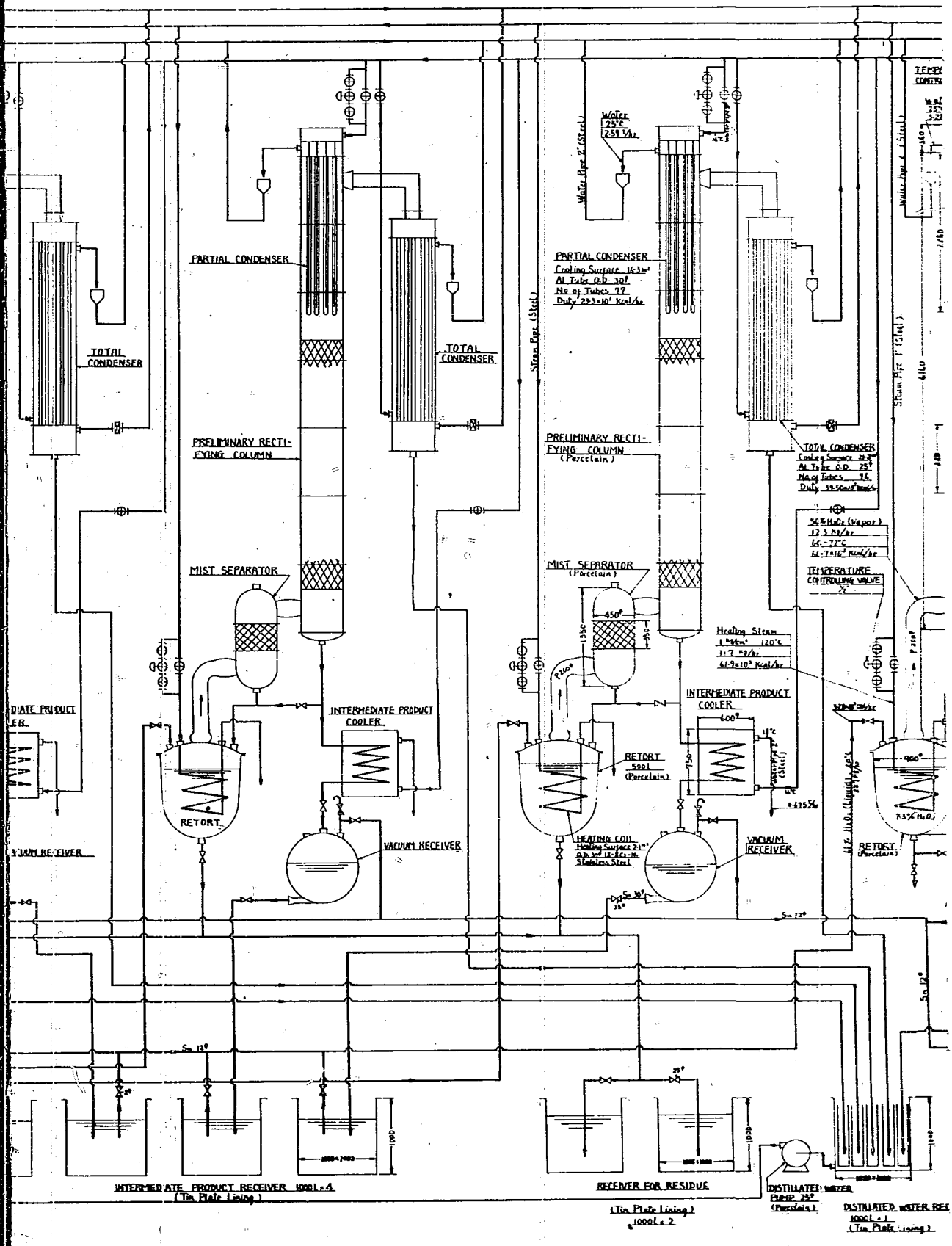
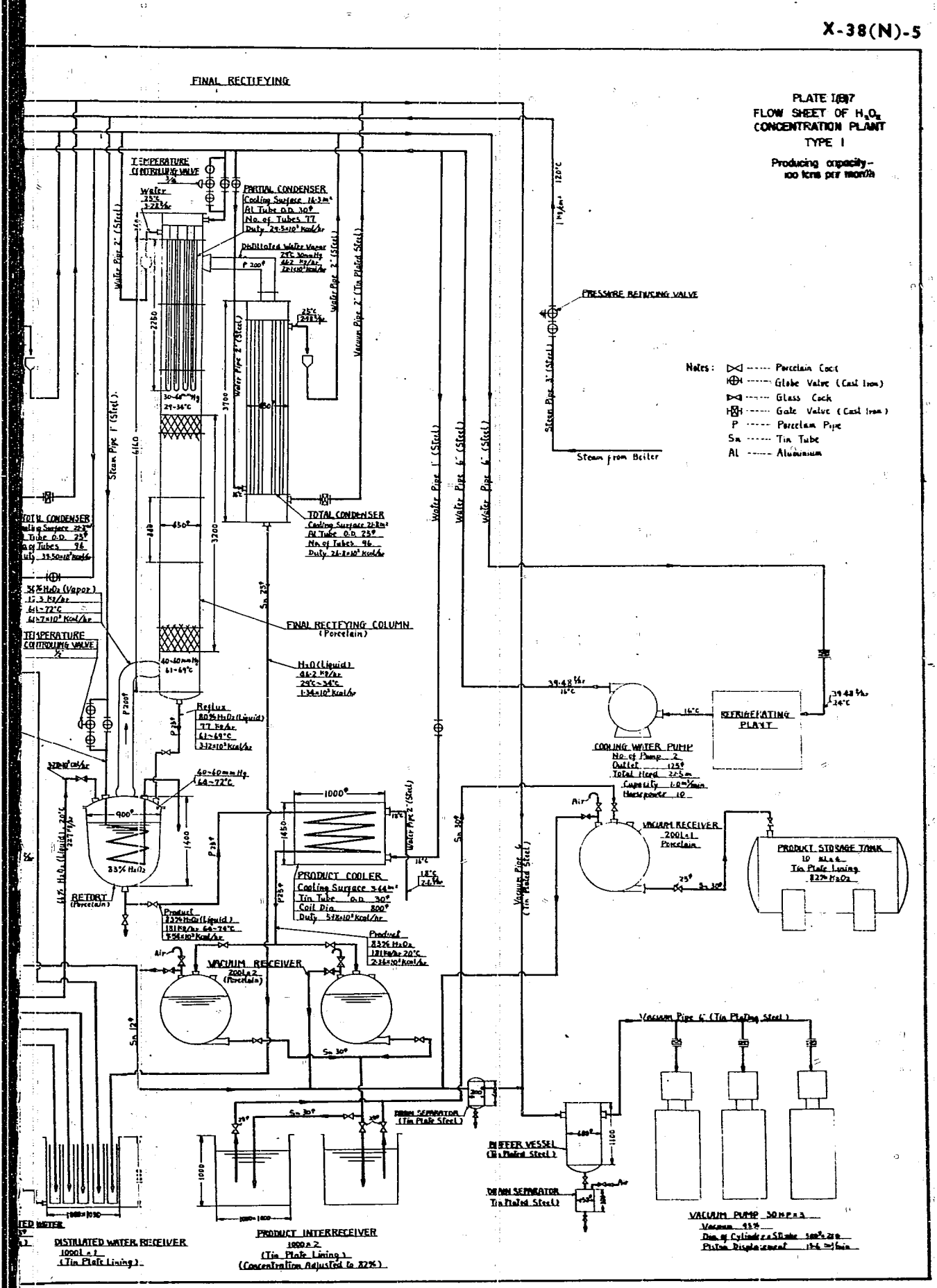


Figure 5 (B)7
HYDROGEN PEROXIDE CONCENTRATION APPARATUS
2. DETAIL OF THE CONCENTRATION TOWER


PRELIMINARY RECTIFYING No. 1
PRELIMINARY RECTIFYING
TEMPERATURE CONTROLLING VALVE
Cooling Water Pipe 4" (Steel)
Water 15°C 0.54 M³/hr
Distillated Water Vapor 25~45°C 30~60 mm Hg 64.7 M³/hr 41.5×10³ Kcal/hr
Water Pipe 2" (Steel)
Water Pipe 4" (Tin Plated Steel)
Vacuum Pipe 2" (Tin Plated Steel)
PARTIAL CONDENSER
Cooling Surface 16.3 m²
Al Tube O.D 30°
No. of Tubes 77
Duty 29.3×10³ Kcal/hr
Steam Pipe 1" (Steel)
Cooling Water 16"
Raschig Ring 35°×35 (Porcelain)
PRELIMINARY RECTIFYING COLUMN (Porcelain)
TOTAL CONDENSER
Cooling Surface 28.5 m²
Al Tube O.D 25°
No. of Tubes 96
Duty 39.5×10³ Kcal/hr
H₂O 68.2 M³/hr 29°C 1.98×10³ Kcal/hr
MIST SEPARETOR (Porcelain)
Raschig Ring 35°×35 (Porcelain)
TEMPERATURE CONTROLLING VALVE
Heating Steam 1 kg/cm² 120°C 127 M³/hr 64.95×10³ Kcal/hr
Feed Stock 30% H₂O₂ (Liquid) 125 M³/hr 0°C 0 Kcal/hr
66% H₂O₂ (Liquid) 54.8 M³/hr 53~60°C 2.7×10³ Kcal/hr
Water Pipe 1" (Steel)
INTERMEDIATE PRODUCT COOLER
RETORT 500l (Porcelain)
Drain Pipe 1" (Steel)
HEATING COIL (O.D 30°) (18-8 Cr-Ni Stainless Steel) Heating Surface 2.1 m² Dia. of Coil 750°
73% H₂O₂
COOLING COIL (O.D 30°) Cooling Surface 1.05 m² Tin Tube 0.5 t 1.15 m² Kcal/hr
VACUUM RECEIVER 200l (Porcelain)
30% H₂O₂ STORAGE TANK (Tin Plate Lining) 10KL × 6
DISTILLATED WATER STORAGE TANK 10KL × 2 (Tin Plate Lining)
30% H₂O₂ 0°C
FILTER TUBE (Porcelain)
FILTERING TANK (Tinplate Lining) 1000l × 4
66% H₂O₂ 20°C
PRELIMINARY RECTIFYING COLUMN
MIST SEPARATOR
RETORT
INTERMEDIATE PRODUCT COOLER
VACUUM RECEIVER


TIFYING No. 2
PRELIMINARY RECTIFYING No.3
PRELIMINARY RECTIFYING No.4
PARTIAL CONDENSER
TOTAL CONDENSER
TOTAL CONDENSER
PRELIMINARY RECTI-FYING COLUMN
MIST SEPARATOR
INTERMEDIATE PRODUCT COOLER
RETORT
VACUUM RECEIVER
Steam Pipe (Steel)
Water 25°C 259 T/hr
Water Pipe 2" (Steel)
PARTIAL CONDENSER
Cooling Surface 16.3m²
Al Tube O.D 30φ
No of Tubes 77
Duty 23.3×10³ Kcal/hr
PRELIMINARY RECTI-FYING COLUMN (Porcelain)
MIST SEPARATOR (Porcelain)
TOTAL CONDENSER
Cooling Surface 23.3
Al Tube O.D 25φ
No of Tubes 96
Duty 39.5×10³ Kcal/hr
50% H₂O₂ (Vapor)
12.3 M³/hr
66.-72°C
66.7×10³ Kcal/hr
TEMPERATURE CONTROLLING VALVE
Heating Steam
1.8 Kg/cm² 120°C
1.7 T/hr
61.9×10³ Kcal/hr
INTERMEDIATE PRODUCT COOLER
RETORT 500l (Porcelain)
HEATING COIL
Heating Surface 2.1m²
O.D 30φ 18-8 Cr-Ni Stainless Steel
VACUUM RECEIVER
RETORT (Porcelain)
INTERMEDIATE PRODUCT RECEIVER 1000l×4 (Tin Plate Lining)
RECEIVER FOR RESIDUE (Tin Plate Lining) 1000l×2
DISTILLATED WATER PUMP 25φ (Porcelain)
DISTILLATED WATER REC 1000l (Tin Plate Lining)


FINAL RECTIFYING
PLATE 1(8)7
FLOW SHEET OF H_2O_2 CONCENTRATION PLANT
TYPE I
Producing capacity – 100 tons per month
TEMPERATURE CONTROLLING VALVE
Water 25°C 2.22 M³/hr
PARTIAL CONDENSER
Cooling Surface 16.3m²
Al Tube O.D. 30φ
No. of Tubes 77
Duty 29.5×10³ Kcal/hr
Distilled Water Vapor 24% 30mm Hg 462 Kg/hr 221×10³ Kcal/hr
P 200φ
25°C 2.22 M³/hr
Water Pipe 2" (Steel)
Vacuum Pipe 2" (Tin Plated Steel)
Steam Pipe 1" (Steel)
2260
3700
450
6110
30~60 mm Hg 29~34°C
PRESSURE REDUCING VALVE
Steam Pipe 3" (Steel)
Steam from Boiler
1 Kg/cm² 120°C
Water Pipe 1" (Steel)
Water Pipe 6" (Steel)
Notes:
Porcelain Cock
Globe Valve (Cast Iron)
Glass Cock
Gate Valve (Cast Iron)
P ----- Porcelain Pipe
Sn ----- Tin Tube
Al ----- Aluminium
TOTAL CONDENSER
Cooling Surface 22.8m²
Al Tube O.D. 25φ
No. of Tubes 96
Duty 24.8×10³ Kcal/hr
450φ
400
3200
Sn 25φ
FINAL RECTIFYING COLUMN (Porcelain)
35% H_2O_2 (Vapor) 17.3 Kg/hr 61~72°C 41.7×10³ Kcal/hr
TEMPERATURE CONTROLLING VALVE
40~60 mm Hg 61~69°C
H_2O (Liquid) 46.2 Kg/hr 29°C~34°C 1.34×10³ Kcal/hr
Reflux 80% H_2O_2 (Liquid) 77 Kg/hr 61~69°C 3.12×10³ Kcal/hr
P 200φ
P 25φ
32.8×10³ Kcal/hr
40~60 mm Hg 64~72°C
900φ
1400
33% H_2O_2
61% H_2O (Liquid) 20°C 221 Kg/hr
RETORT (Porcelain)
P 25φ
Product 83% H_2O_2 (Liquid) 181 Kg/hr 64~72°C 9.54×10³ Kcal/hr
1000φ
1850
PRODUCT COOLER
Cooling Surface 3.44m²
Tin Tube O.D. 30φ
Coil Dia. 800φ
Duty 5.42×10³ Kcal/hr
18°C 2.6 M³/hr
Water Pipe 2" (Steel)
Product 83% H_2O_2 181 Kg/hr 20°C 2.34×10³ Kcal/hr
Sn 30φ
Vacuum Pipe 4" (Tin Plated Steel)
Air
VACUUM RECEIVER 200l×1 Porcelain
PRODUCT STORAGE TANK 10 m³×4 Tin Plate Lining 82% H_2O_2
25°
Sn 30φ
39.48 M³/hr 15°C
39.48 M³/hr 24°C
16°C
REFRIGERATING PLANT
COOLING WATER PUMP
No. of Pump 2
Outlet 125φ
Total Head 22.5m
Capacity 1.0 m³/min
Horsepower 10
Air
VACUUM RECEIVER 200l×2 (Porcelain)
Sn 12φ
Sn 30φ
Vacuum Pipe 6" (Tin Plated Steel)
DRAIN SEPARATOR (Tin Plate Steel)
Sn 30φ
RECEIVER VESSEL (Tin Plated Steel)
400
1100
DRAIN SEPARATOR Tin Plated Steel
VACUUM PUMP 30 H.P.×3
Vacuum 95%
Dia. of Cylinder × Stroke 180φ × 210
Piston Displacement 13.6 m³/min
DISTILLATED WATER RECEIVER 1000l×1 (Tin Plate Lining)
PRODUCT INTERRECEIVER 1000l×2 (Tin Plate Lining) (Concentration Adjusted to 82%)

ENCLOSURE (B) 8

SYNTHESIS OF HYDRAZINE

by

ENG. LIEUT. COMDR. Y. MOMOTARI

ENG. LIEUT. COMDR. T. YAMAMOTO

ENG. LIEUT. S. ENDO

Research Period: 1944

Prepared for and Reviewed with Authors
by U. S. Naval Technical Mission to Japan

December 1945

ENCLOSURE (B)8

LIST OF TABLES AND ILLUSTRATIONS

ENCLOSURE (B)8

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.

B. Key Research Personnel Working on Project

Chem. Eng. Lieut. Comdr. Y. MOMOTARI
Chem. Eng. Lieut. Comdr. T. YAMAMOTO
Chem. Eng. Lieut. S. ENDO

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.

ENCLOSURE (B)8

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 50°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

ENCLOSURE (B)8

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.

ENCLOSURE (B)8

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
Glue 10% 2.8cc
NH_3/NaOCl = 20

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

ENCLOSURE (B)8

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	10°C	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

ENCLOSURE (B)8

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

ENCLOSURE (B)8

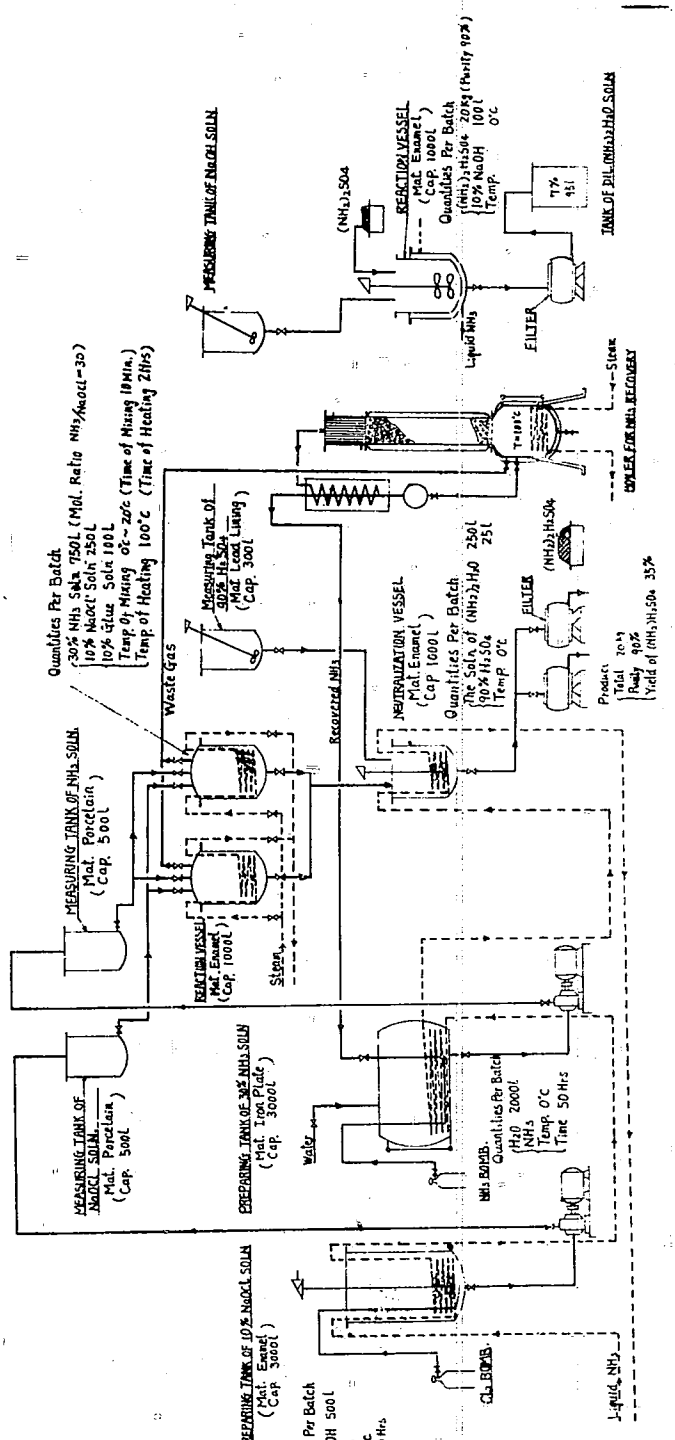


Figure 1 (B)8

FLOW SHEET OF PILOT PLANT FOR HYDRAZINE SYNTHESIS

ENCLOSURE (B) 9

SYNTHESIS OF HYDRAZINE FROM UREA

by

CHEM. ENG. LIEUT. COMDR. T. YAMAMOTO

CHEM. ENG. LIEUT. H. NAKAO

Research Period: 1944

Prepared for and Reviewed with Authors
by U. S. Naval Technical Mission to Japan

December 1945

ENCLOSURE (B)9

LIST OF TABLES AND ILLUSTRATIONS

ENCLOSURE (B)9

SUMMARY

The synthesis of hydrazine from urea and sodium hypochlorite was studied. Solutions of urea and sodium hypochlorite were mixed and heated. After cooling, the hydrazine formed was precipitated by sulfuric acid, and hydrazine sulphate was separated and weighed. The necessary conditions to obtain high yields of hydrazine were as follows:

1. The mol ratio of urea to sodium hypochlorite was 1 : 1 or 1 : 0.8.

2. The concentration of the sodium hypochlorite was 1-1.25N.

3. Urea should be dissolved in a small amount of water prior to the addition of hypochlorite.

4. The temperature of mixing the raw materials must be below 5°C.

5. The temperature required to complete the reaction was 90°C.

6. In this reaction 3 mols of caustic soda to 1 mol of urea were required.

7. When 0.5 grams of glue per mol of sodium hypochlorite was added in the solution, the yield of hydrazine increased considerably.

8. The presence of rusty iron in the reaction vessel must be avoided.

I. INTRODUCTION

Hydrazine mixed with hydrogen peroxide was used for the energy source of the rocket. Although hydrazine is generally synthesized from ammonia and sodium hypochlorite, a large quantity of ammonia must be treated because of the small yield of hydrazine to ammonia used. The method using urea as the raw material was previously known, but since the exact conditions to obtain the maximum yield was not obvious, this method was studied. The experiments were begun in July 1944 and were finished in September 1944 by Chem. Eng. Lieut. Comdr. T. YAMAMOTO, Chem. Eng. Lieut. H. NAKAO, and Chem. Eng. Lieut. Comdr. Y. MOMOTARI.

II. DESCRIPTION OF APPARATUS AND PROCEDURE

A. A 3-necked flask with a glass stirrer was used as the reaction vessel.

B. Material Used

1. Sodium hypochlorite solution. 500 grams of bleaching powder were dissolved in 2.5 liters of water, and was added to 500 grams of sodium sulphate. After the calcium sulphate settled, the solution was filtered and the concentration of sodium hypochlorite was measured by iodometry. The concentration of sodium hypochlorite was adjusted to 1 N.

3. Glue Solution. A 1% solution of glue was made and 75cc per mol of sodium hypochlorite was used.

C. Details of Test Procedure and Conditions

Each solution was cooled to 5°C and mixed. The glue solution was added to the mixture of sodium hypochlorite and urea. The mixture was heated to 95°C and, after cooling, concentrated sulphuric acid was added until the concentration of sulphuric acid in the solution was 20%. The precipitated hydrazine sulphate was filtered, washed with alcohol, and dried at 100°C. The weight and purity were measured, and the percent yield was calculated.

III. EXPERIMENTAL RESULTS

A. The Effect of the Mol Ratio of Urea and Sodium Hypochlorite upon the Yield of Hydrazine

The results are tabulated in Table I(B)9, showing the ratio of urea to sodium hypochlorite should be 1 : 1-0.8.

B. The Effect of the Concentration of Sodium Hypochlorite upon the Yield of Hydrazine

The reaction was carried out using volumes of one mol sodium hypochlorite solution ranging from 600 - 2250cc and mol ratios of urea to sodium hypochlorite ranging from 1:0.8 to 1:1.35. The experimental results are tabulated in Table II(B)9, and show that the best conditions are a mol ratio of urea to hypochlorite of 1:0.8-0.9; and that the best volume for one mol of hypochlorite at this ratio is 1000-800cc. This corresponds to a 1.0 - 1.25 N solution of hypochlorite.

C. The Effect of Temperature on Mixing of the Raw Materials upon the Yield of Hydrazine

Using a mol ratio of urea to sodium hypochlorite of 1:0.8, and a concentration of 1 N sodium hypochlorite, yields were compared at various mixing temperatures.

The results are shown in Table III(B)9.

It is obvious that the temperature of mixing should be below 5°C.

D. The Effect of the Heating Temperature upon the Yield of Hydrazine

The mixture was heated to various temperatures and was maintained at that temperature for 20 minutes before treating as mentioned above. The experimental conditions were one mol of urea to 0.8 mols of hydrogen, the concentration of sodium hypochlorite was 1 mol of NaOCl per 800cc and the mixing temperature was 5°C. The results are shown in Table IV(B)9, and show that the temperature of heating must be higher than 90oC; but when the temperature is too high, hydrazine will be lost by evaporation.

E. The Effect of the Amount of Caustic Soda upon the Yield of Hydrazine

The effect of the amount of caustic soda on the yield of hydrazine was tested and it was found that the use of 3 mols of caustic soda to one mol of urea was sufficient as shown in Table V(B)9.

ENCLOSURE (B)9

F. The Effect of Glue on the Yield of Hydrazine

The results are tabulated in Table VI(B)9. The experimental conditions were as follows:

The mol ratio of urea to sodium hypochlorite was 1:0.8; the concentration of sodium hypochlorite was one mol of sodium hypochlorite in 800cc; the mol ratio of urea to caustic soda was 1:2.5; and the concentration of the glue was varied from 0 to 2.4 grams per mol of sodium hypochlorite.

From these data it appeared that the addition of 0.5 grams of glue per mol of sodium hypochlorite was sufficient to obtain a high yield of hydrazine.

G. The Effect of the Materials of the Reaction Vessel on the Yield of Hydrazine.

In order to clarify the effect of several materials on the reaction, various test pieces were put in the glass reaction vessel and the yield of hydrazine was measured. The results are shown in Table VII(B) 9. As indicated in Table VII(B)9, no yield was obtained when rusty steal was present in the reaction mixture.

This might be caused by the oxidation of hydrazine by Fe_2O_3 and the fact that glue is of no value in controlling this oxidation reaction.

III. CONCLUSIONS

From the experimental results described, it was ascertained that the best procedure for obtaining high yields of hydrazine from urea is as follows: one mol of urea and three mols of caustic soda are dissolved in a small amount of water. Separately, one litre of 1 N sodium hypochlorite solution and 50cc of 1% glue solution are prepared. These solutions are cooled to 5°C, mixed, and then heated to 95°C.

When cooled, an excess of sulphuric acid is added.

The precipitate of hydrazine sulphate produced is filtered and washed. The yield of the hydrazine will be higher than 50% based on the consumed urea.

No commercial application of this process has been made.

ENCLOSURE (B)9

Table I(B)9
EFFECT OF MOL RATIO OF UREA TO HYPOCHLORITE
ON YIELD OF HYDRAZINE

Raw Material (gm-mol.)*	Yield (%)	
NaOCl	to Urea	to NaOCl
1.35	41.0	30.0
1.00	50.0	50.0
0.90	49.5	55.0
0.80	48.5	60.0
0.75	47.5	63.5
0.50	35.5	72.0

*In each NaOCl mixture were 1.0 gm-mol urea plus 2.5 gm-mols of NaOH.

Table II(B)9
THE EFFECT OF THE CONCENTRATION OF SODIUM HYPOCHLORITE
UPON THE YIELD OF HYDRAZINE

Raw Materials (gm-mol)* NaOCl	Vol. of Sol. Containing of NaOCl(cc)	Yield (%)	
		to Urea	to NaOCl
0.8	600	49.0	61.3
0.8	800	52.5	65.6
0.8	1150	48.0	60.0
0.8	1800	40.6	50.7
0.9	800	45.7	50.8
0.9	1000	51.8	57.6
0.9	1150	49.1	54.6
0.9	1800	45.7	50.8
1.0	800	44.4	44.4
1.0	1150	50.0	50.0
1.0	1800	38.5	38.5
1.0	2250	26.8	26.8
1.35	800	25.5	18.7
1.35	1150	41.4	30.7
1.35	1640	34.5	26.4
1.35	2140	9.5	7.4

*In each NaOCl mixture was 1.0 gm-mol urea.

ENCLOSURE (B)9

Table III(B)9
THE EFFECT OF THE TEMPERATURE OF MIXING OF THE RAW MATERIALS

Temp. of Mixing (°C)	Yield (%) to Urea
28	0
15	41
5	52
3	54
0	54
-5	53

Table IV(B)9
THE EFFECT OF THE HEATING TEMPERATURE UPON
THE YIELD OF HYDRAZINE

Heating Temp. (°C)	Heating Time (min)	Yield (%) to Urea
40	20	0
50	20	22
85	20	39
90	10	52
95	20	40

Table V(B)9
THE EFFECT OF THE AMOUNT OF CAUSTIC SODA
UPON THE YIELD OF HYDRAZINE

Raw Materials (gm-mol)*		Yield (%)	
Sodium hypochlorite	Caustic Soda	To Urea	to Sodium hypochlorite
0.8	2.0	31.4	39.3
0.8	2.5	54.0	67.5
0.8	3.0	58.8	73.5
0.8	5.0	58.4	73.0

*In each NaOCl was 1.0 gm-mol urea.

ENCLOSURE (B)9

Table VI(B)9
THE EFFECT OF GLUE ON THE YIELD OF HYDRAZINE

Glue used gm/mol. of NaOCl	Yield %	
	to Urea	to NaOCl
0	12.0	15.0
0.17	51.0	63.8
0.75	53.3	66.6
1.30	53.9	67.8
2.40	54.0	67.5

Table VII(B)9
THE EFFECT OF THE MATERIALS OF THE REACTION VESSEL

Test pieces	Yield of hydrazine %	Remark
none	52.0	
13-Cr-Steel	51.0	Polished before the test
18-8-Cr. Ni. Steel	41.0	
Rubber plate	49.0	
Lead	50.0	
Mild Steel	0	Rusty

ENCLOSURE (B) 10

STUDIES ON THE COMBUSTION OF HYDROGEN PEROXIDE AND HYDRAZINE HYDRATE

by

CHEM. ENG. LIEUT.
M. SHIMO

Research Period: 1944-1945

Prepared for and Reviewed with Authors
by U. S. Naval Technical Mission to Japan

December 1945

ENCLOSURE (B)10

LIST OF TABLES AND ILLUSTRATIONS

ENCLOSURE (B)10

SUMMARY

The thrust and internal pressure in a specially designed rocket type combustion chamber decreases in accordance with lowering of the concentration of hydrogen peroxide, although 60% hydrogen peroxide is still combustible.

The combustion does not greatly depend upon the amount of potassium-cuprocyanide added.

The combustion pulsates when the type of injection nozzle is inadequate.

I. INTRODUCTION

A. History of Project

These studies on a fuel which was to be used for SHUSUI, a jet airplane, were started in December 1944. An apparatus was designed in January 1945 to test ignition and combustion quality of the fuel. The apparatus was constructed during February and March; experiments were begun in April.

B. Key Research Personnel Working on Project

Chem. Eng. Lieut. M. SHIMO

II. DETAILED DESCRIPTION

A. Description of Test Apparatus

1. Two types of injection nozzles are shown in Figure 1(B)10.

2. Flow sheet of the test apparatus is shown in Figure 2(B)10.

B. Test Procedure

1. The quantity of injection liquid is controlled by putting an orifice in the pipe of each liquid.

The following compositions were used for the injection liquids:

Solution A.....80 wt.% H_2O_2

Solution B.....
- 30 wt.% $NH_2.NH_2.H_2O$
- 57 wt.% CH_3OH
- 13 wt.% H_2O
- 2.7 gm/lit $K_3[Cu(CN)_4]$

A : B = 10 : 3 (by weight)

Six liters of solution A and three liters of solution B were used in experiments. The rates of injection for both solutions were selected as follows:

Solution A 600 gm/sec; i.e., 435cc/sec. (d=1.38 gm/cc at room Temp.)
Solution B 180 gm/sec; i.e., 200cc/sec. (d=0.91 gm/cc at room Temp.)

2. After filling up tank A (See Figure 2(B)10) with solution A and tank B with solution B(C is a spare tank) and opening valve G, valve D is opened slowly.

In starting, after the internal pressures of both tanks A and B reach 3 kg/cm^2, valves E & F are opened to let both solutions flow into the combustion chamber. After starting, valve D is opened so that the internal pressure of both tanks reach 25 kg/cm^2 for a running condition of continuous combustion.

The internal pressures of both tanks are always adjusted by controlling valve D to maintain the above pressure of 25 kg/cm^2. If the internal pressures of both tanks are 25 kg/cm^2, instead of 3 kg/cm^2, from the beginning of the test, excess solution accumulates in the combustion chamber during the latent period, and a sharp explosion occurs which usually damages the thrust unit, gas analyzer connection, and internal pressure indicator.

3. Measurement. During combustion the following data are measured.

a. Internal pressures of combustion chamber with a pressure gauge and a piston and spring type indicator. (Maihak type)

b. Thrust with a thrustmeter of the magnetic striction type. (See Figure 3(B)10.)

c. Gas analysis by Orsat method (See Figure 4(B)10.) Gas analysis was planned, but not actually performed.

4. After the experiment is over, valve G is shut. Valves H and I are opened to send wash-water from tanks J and K to the combustion chamber through tanks A and B and the connecting pipe lines.

C. Summary of Data

1. Results of experiments on the combustion of hydrogen peroxide of different concentration using Nozzle No. 2 are shown in Table I(B)10. The results are plotted in Figure 5(B)10.

These experiments were made in summer, and therefore, the temperatures of the solutions were comparatively high. Experiments in colder weather are necessary.

2. Results of experiments on the influence of the amount of added catalyst (Potassium-cuprocyanide) using nozzle No. 2 are shown in Table II(B)10.

3. Experiments on pulsating combustion due to different types of injection nozzles.

No pulsating combustion occurred when injection nozzle No. 2 (in Figure 1(B)10)was used, but pulsating combustion occurred with nozzle No. 1. The indicator curves (Figure 6(B)10)show distinct differences between the two types of combustion.

III. CONCLUSIONS

The testing procedure seemed to be satisfactory.

The small amount of test data available, as shown in the summary, is due to the short period of time that this research work was in progress.

ENCLOSURE (B)10

Table I(B)10
COMBUSTION OF VARYING CONCENTRATIONS OF H_2O_2*

Conc. of H_2O_2	Internal Pressure of Combustion Chamber	Thrust	Note
80 wt.%	10 kg/cm^2	80 kg	Standard
75 wt.%	9 kg/cm^2	75 kg	Nearly same as that of 80% conc. of H_2O_2.
70 wt.%	8 kg/cm^2	73 kg	Somewhat reduced combustion.
60 wt.%	6 kg/cm^2	40 kg	Can be ignited but combustion is very mild.

*Nozzle No. 2.

Table II(B)10
EFFECT OF CATALYST CONCENTRATION ON COMBUSTION OF H_2O_2*

Catalyst added (gram/liter)	Internal Pressure of Combustion Chamber (kg/cm^2)	Thrust (kg)	Note
0	9.5	78	Sound of combustion is low but inter. press. and thrust are normal.
1	10.0	78	Results about equal
2	9.5	80	
3**	10.0	80	
6	10.0	78	
9	9.5	80	

*Nozzle No. 2.
**Standard amount of catalyst.

ENCLOSURE (B)10

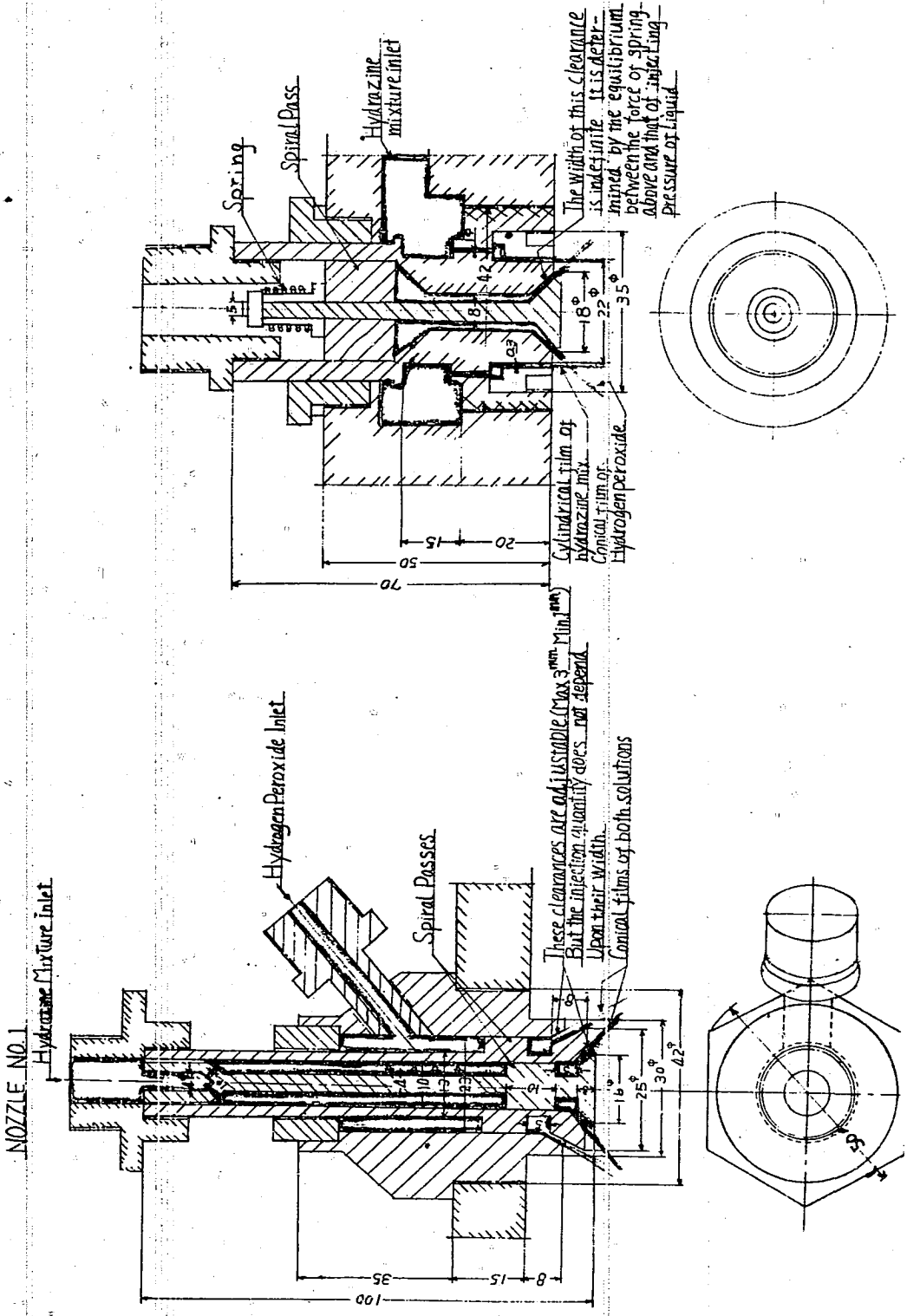


Figure 1 (B)10
SKETCH OF INJECTION NOZZLE

ENCLOSURE (B)10

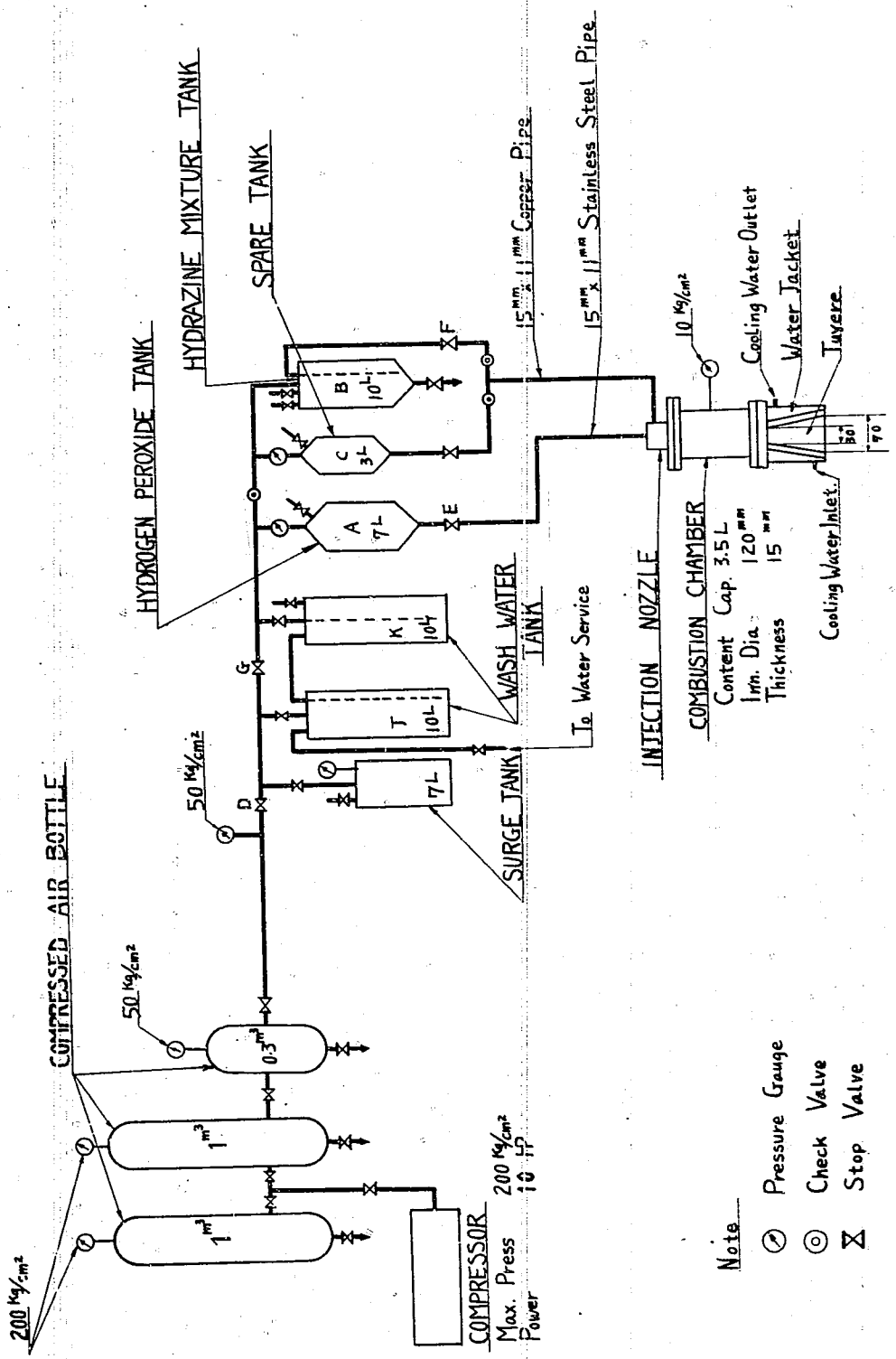


Figure 2 (B)10
FLOW SHEET OF TEST APPARATUS

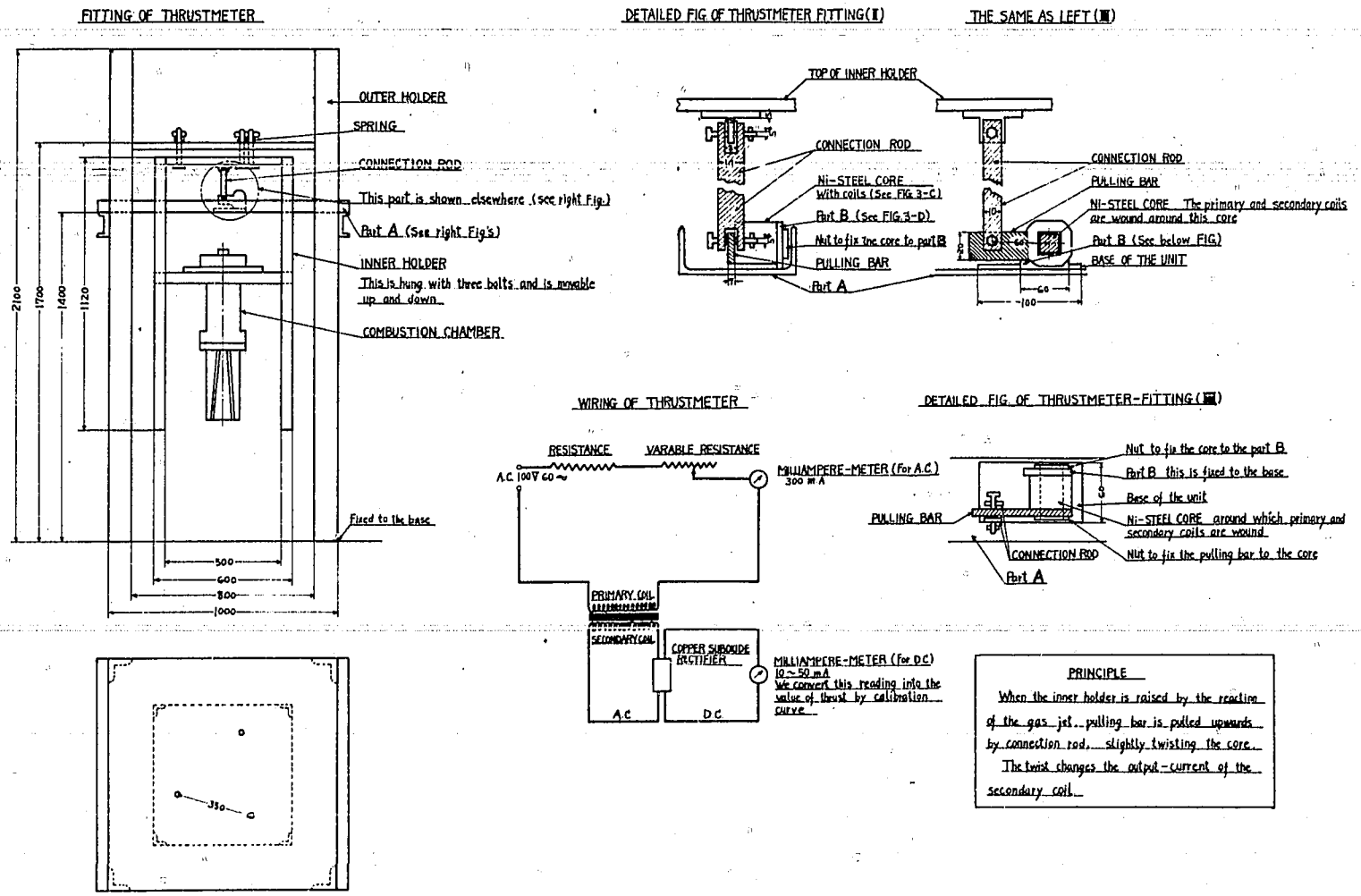
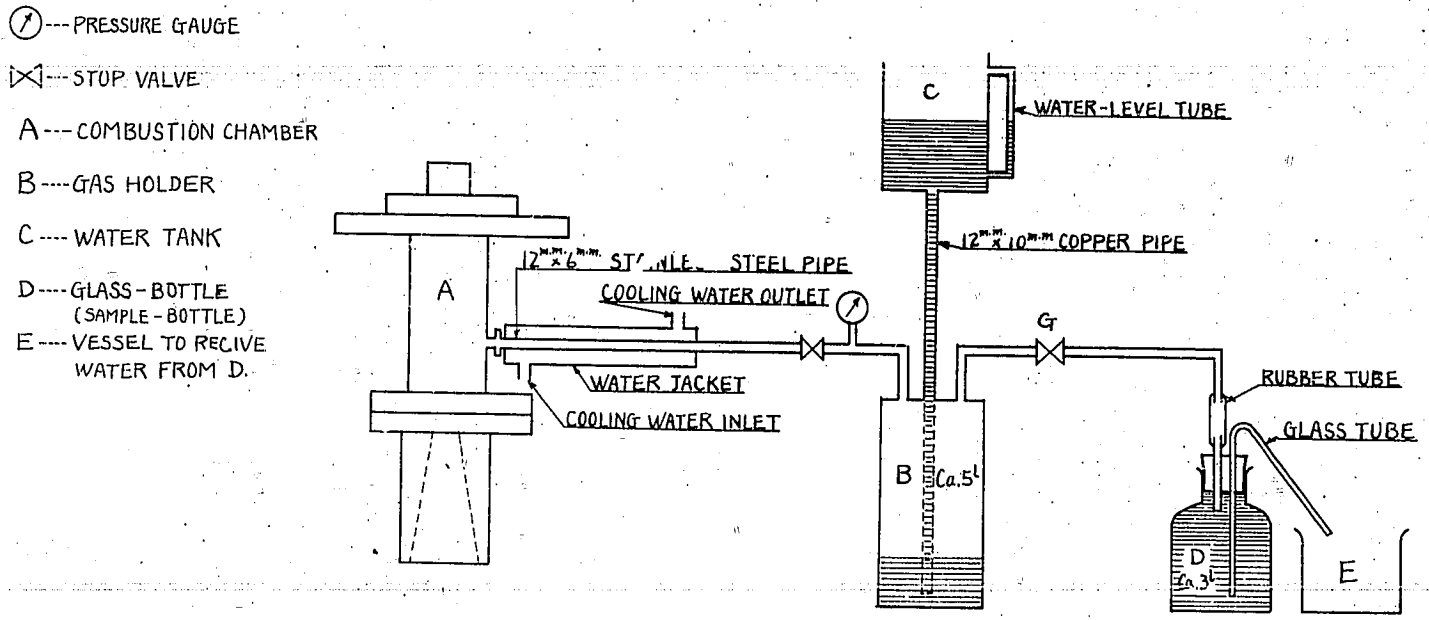


Figure 3 (B)10
FITTING OF THRUSTMETER



Gas-sampling is made as follows:

B and D are filled with water before-hand, and valves F and G are shut.

Soon after the combustion begins, the valve F is opened and combustion gas is pressed into B on account of high pressure of A.

After the combustion is over the valve F is shut and G is opened, the gas is transferred to D by means of water head.

Disconnecting the rubber tube from copper pipe and closing it by pinch-cock, the bottle D is taken off.

Figure 4 (B)10
FLOW SHEET OF GAS-SAMPLING

(Thus sampled combustion gas is analyzed with gas analyzer of the Orsat type.)

ENCLOSURE (B)10

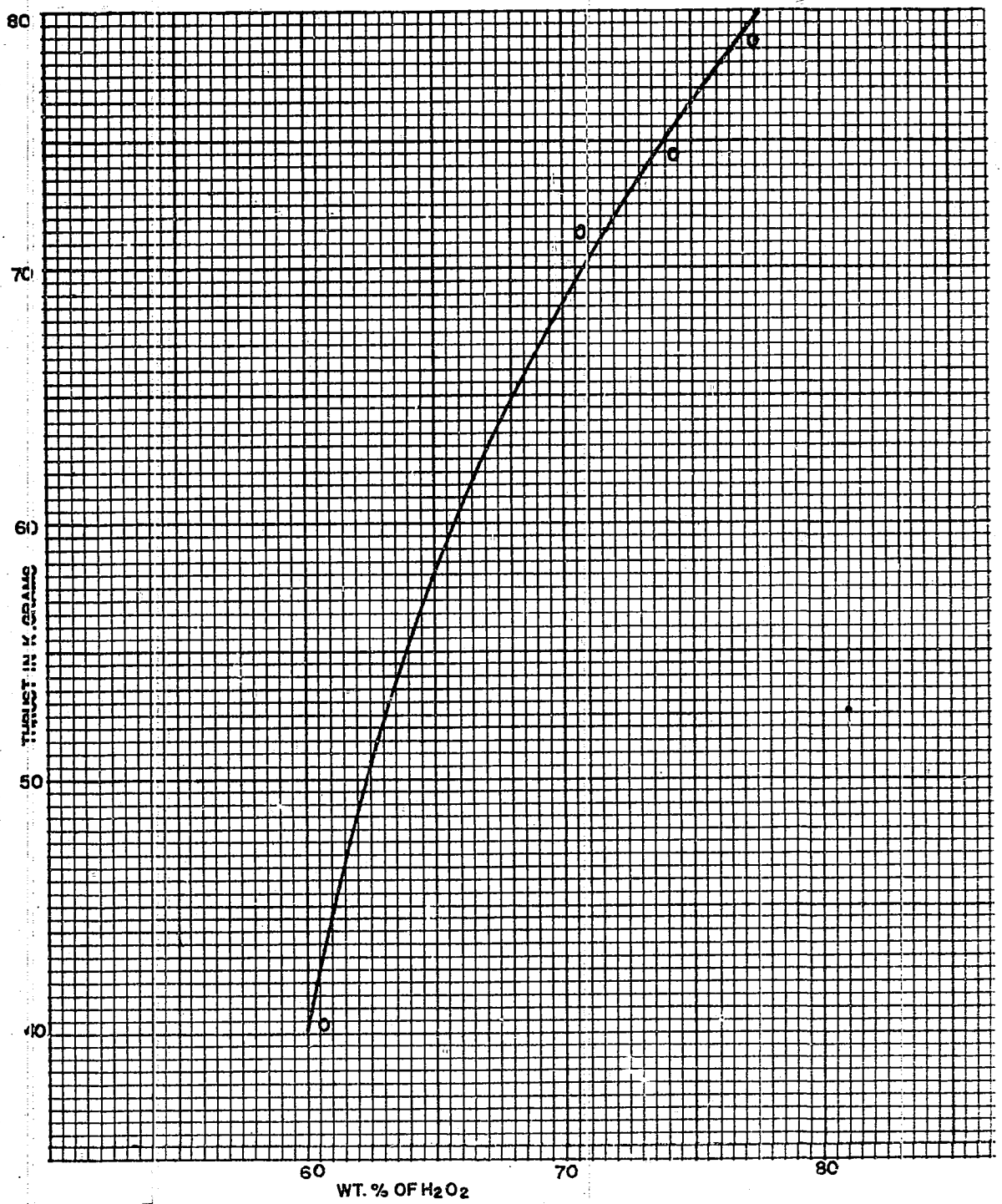


Figure 5 (B)10

THRUSTS AND CONCENTRATIONS OF H_2O_2

ENCLOSURE (B)10

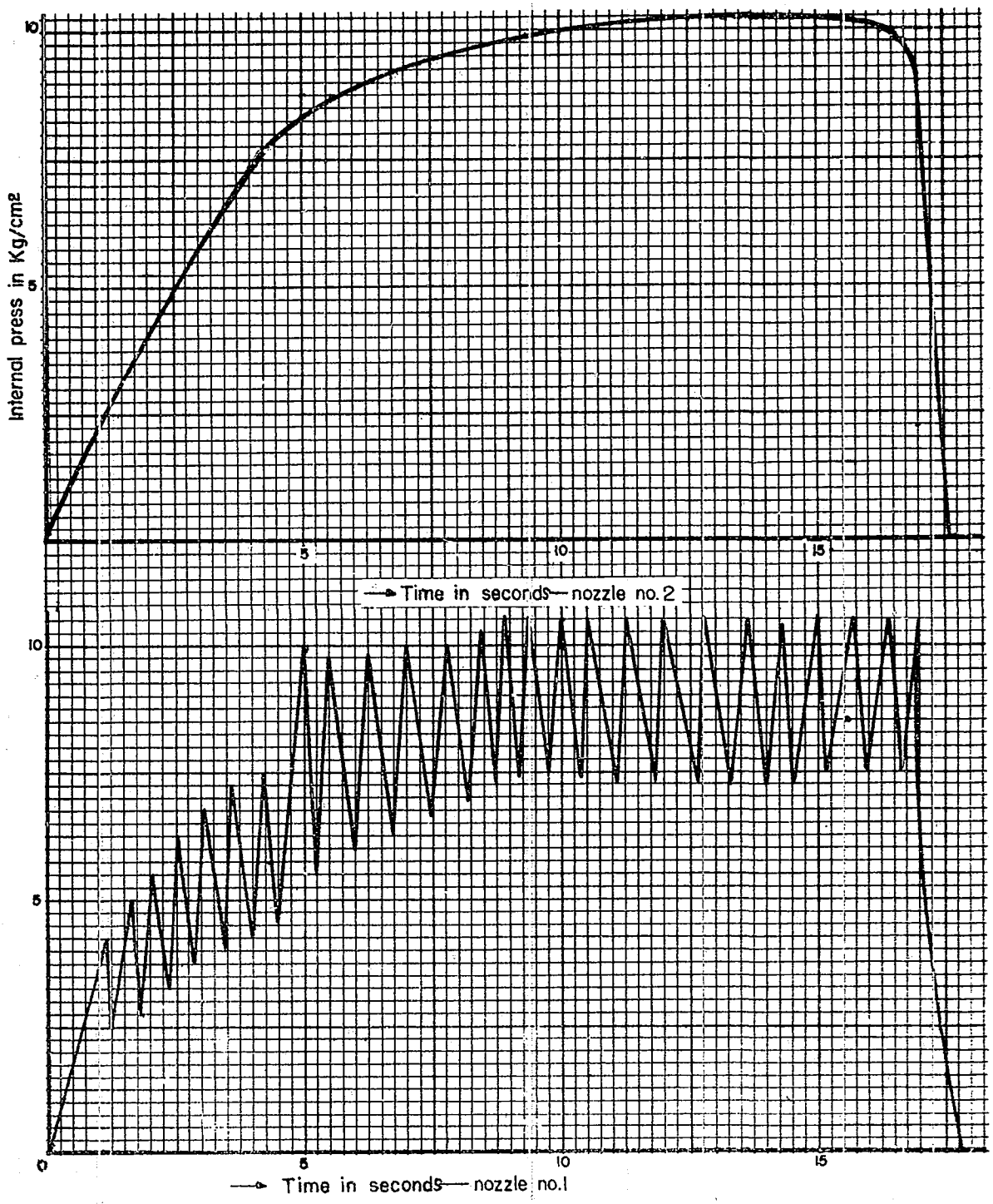


Figure 6 (B)10
INDICATOR CURVES

ENCLOSURE (B)10

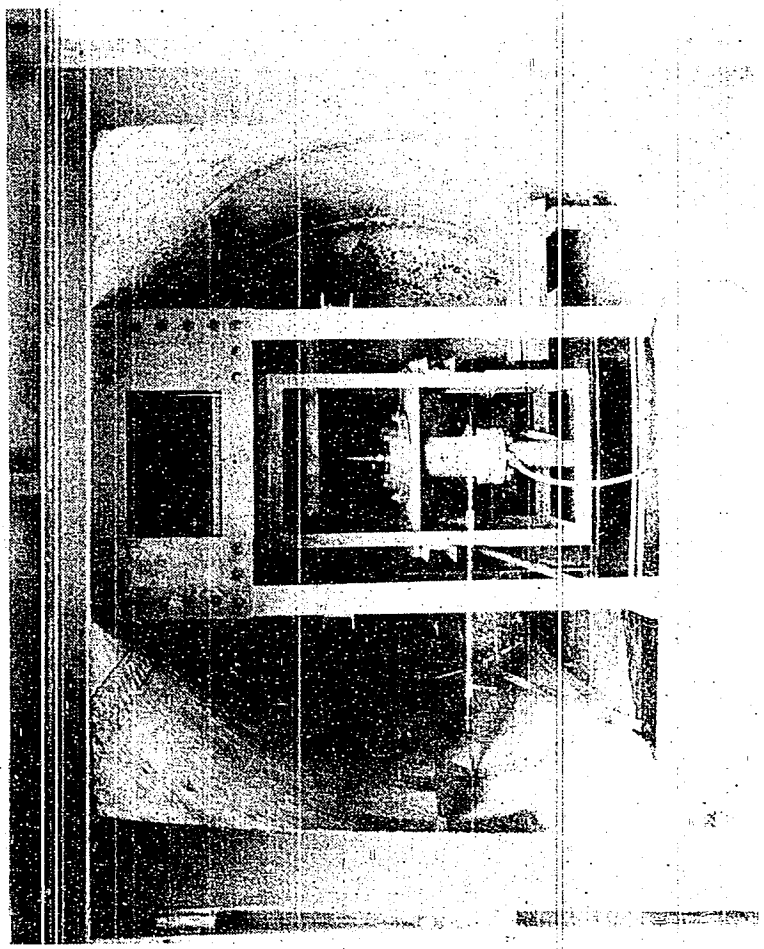


Figure 7 (B)10
TEST APPARATUS FOR ROCKET