ENCLOSURE (A)

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

by

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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.