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HYDROGEN PEROXIDE

ELECTRO CHEMISCHE WERKE, HOLLRIEGELSKETH

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17 p. drawings.

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SUMMARY

A large scale plant for the production of highly concentrated hydrogen peroxide and the necessary operating personnel are available at Hollriegelskreuth near Munich. The operating details of this concentration plant are given in this report. It is known that the details of this process were given to the Japanese.

In addition, a process for producing hydrogen peroxide economically through an electric discharge is outlined. Since an exceptionally pure product is produced, this method is of very great naval interest.

In the third part of this report, a review of German peroxide production potential is given.

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HYDROGEN PEROXIDE  
ELECTRO CHEMISCHE WERKE, HOLLRIEGELSKREUTH

1. Introduction.

(a) The Electro Chemische Werke München A. G. was one of the largest producers of concentrated hydrogen peroxide in Germany. Production was carried out in two (2) steps. The first, for the production of thirty-five (35) percent solutions, was by the Adolf-Pietzsch Process which is well known in the United States, and is in use by the Buffalo Electro Chemical Company. This step will not be discussed here.

(b) The step of most immediate interest is the method of concentration of the thirty-five (35) percent solutions to eighty (80) percent or higher which makes possible the use of peroxide as an efficient fuel in submarines, rockets, rocket aircraft, assisted take off units for aircraft, and torpedoes. This process is explained in Part I of this report.

(c) This process of hydrogen peroxide concentration was sold to the firm of Mitsubishi Seishi Kaisha in Japan. Documents concerning this transaction and the accompanying negotiations on the process for production of hydrazine hydrate have been sent to the Japanese Section, SHAEE. The personnel at the plant stated that they hadn't given the Japanese all the facts of the process but the examples given us of the facts which had been omitted from the peroxide report were of such a trivial character that we would seriously underestimate Japanese intelligence in assuming that it could not fill in the missing facts. In our opinion, the Japanese have all the necessary data for the production of highly concentrated peroxide.

(d) Also of interest, is the process of direct synthesis of hydrogen peroxide from hydrogen and oxygen through a silent electric discharge. This process, which has been studied at Hollriegelskreuth for the last fourteen (14) years, was in the last stage of development. Laboratory investigation had been completed and a pilot plant was built. This had been operated for a sufficient length of time for tentative production costs to be calculated. It appears from the results obtained that the method

1. Introduction (d) (Cont'd.)

has great potentialities since a product of exceptional purity can be produced. This is exceedingly important in peroxide for naval use. Economically the process has merit particularly in the United States since the labor requirements are very low. The pilot plant had been destroyed by bombing and the parts of the laboratory equipment which were available were of very simple construction and could be easily reproduced in the United States. This method of production is reviewed in Part II of this report.

(e) German peroxide production capacity is briefly outlined in Part III. This part is largely based on figures for May 1944. Great effort was being made to increase this capacity as the military demands expanded and the success of these efforts is pointed out insofar as it is known in this section. At HÖllriegelskreuth, the concentration plant capacity was built far beyond the primary production capacity of thirty-five (35) percent material and was kept in operation by shipments from other plants. This concentration plant is now in operating condition and should be used by the United States, not only to alleviate present shortages, but also to take advantage of the long German operating experience.

PART I

PRODUCTION OF HIGH TEST PEROXIDE AT HÖLLRIEGELSKREUTH.

(a) The fundamental research on the production of highly concentrated (80 to 85) percent hydrogen peroxide was done at HÖllriegelskreuth by the Electro Chemische Werke München A.G. Laboratory work was started about 1930 and since 1936 German interest in highly concentrated peroxide has been intense. The motivator appears to have been Walter of Kiel who constantly demanded a purer and more highly concentrated product, particularly for U-boat use. The chief concern of Walter was the residue upon ignition. His final demand was for a product having a residue of 5 milligrams per liter or less. This ideal had not been accomplished but plans had been drawn up for the Rhmaspringe plant including an extra distillation step which it was thought would meet this requirement. The method

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Part I. Production of High Test Peroxide at Hollriegelskreuth (a) (Cont'd.)

described here is with minor modifications the same as is used at the newer and larger installations at Bad Lauterberg.

(b) The concentration plant at Hollriegelskreuth has a capacity of approximately 400 tons per month of 80 percent material. The original capacity of the primary production plant for 35 percent peroxide was about 180 tons per month calculated as 80 percent. This plant was bombed out in June 1944 but the concentration plant was left intact. Since then a new plant, capable of producing 50 tons per month of 35 percent peroxide calculated as 80 percent has been built but was never put into operation. ~~It was estimated that about one month's work would be required to get this part of the plant producing.~~ The concentration plant is still in excellent condition, ready for immediate operation.

(c) Drawing No. 1 is a schematic diagram of the concentration plant. It consists essentially of five (5) ceramic columns; each fitted with a dephlegmator and condenser, at the top and a still and separator at the bottom. All five columns are physically the same; however, in operation, four (4) of the columns act in parallel for concentrating to 72 percent and the fifth does the final concentration to 33 to 35 percent.

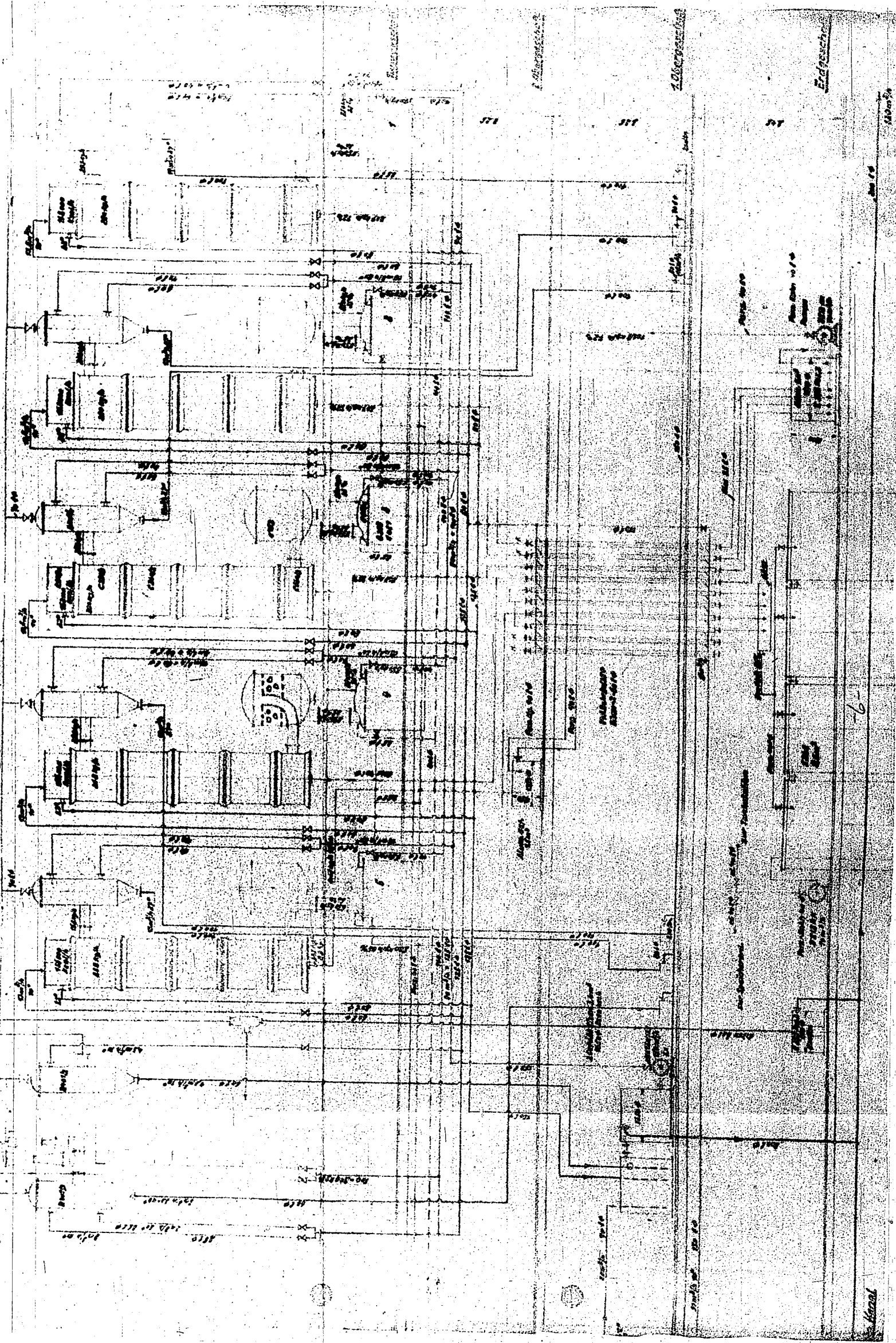
(d) The raw 35 percent material is obtained from the primary production plant through temporary storage tanks. It is stabilized with 0.1 grams 8-oxyquinoline and 0.1 - 0.3 grams tetra sodium pyrophosphate per liter; and is .01 N acid.  $AlPO_4$ ,  $(NH_4)_2SO_4$ ,  $KHSO_4$ ,  $H_2SO_4$ ,  $Na_4P_2O_7$  are present as impurities. Entering the four (4) ceramic stills it is mass heated through V14A stainless steel heating coils. Supervision is very particular that these coils be made of V14A steel which is a very hard, high molybdenum stainless made by Krupp for this purpose. A mirror finish is required. The steam in the coils is at 3 to 4 atmospheres gage pressure and the pressure inside the still above the liquid is 45 millimeters mercury. The temperature of the liquor is 67 degree centigrade.

(e) After equilibrium is established, the liquid phase contains 75 percent peroxide and the vapor phase passing to the separator contains 35 percent peroxide. The liquor is now 0.05-0.10 N in acid.

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Part I. Production of High Test Peroxide at Hollriegelskreuth (Cont'd.)

(f) The vapors enter the separator which is a ceramic or aluminum vessel divided near the center by about  $\frac{1}{2}$  meter of Raschig rings. The vapors enter below this division, pass through the rings and exit from the top of the separator to the bottom of the rectifying column. The separator thus acts to remove entrained liquid and also as a very short distillation column. The bottom of the separator drains back into the still.

(g) From the separator, the vapors pass to the bottom of the rectifying column. This is ceramic of 1,050 millimeters diameter packed with 4 meters of 25 x 25 millimeter ceramic Raschig rings. The vapors pass up the column, are concentrated and the effluent gases are cooled by a double walled water-cooled aluminum dephlegmator. From this, they flow to a water condenser. These vapors still contain some peroxide and approximately 0.5 percent of the total peroxide distilled is lost in the condenser cooling water. The concentrated 70 percent peroxide flows down the column to the final concentration still. It will be noted that no reflux water is added to the column.

(h) The 70 percent peroxide enters the final concentration still; and, after equilibrium is established, the liquid phase peroxide concentration is 83 percent and the vapor phase 56 percent. The temperature in the liquid phase in the still is 70 degrees centigrade, and the vapor phase pressure is 45 millimeters mercury. The vapor enters the separator in the same manner as in the original distillation and from there enters the bottom of the rectifying column, travels up the column and is condensed. The higher concentration flows from the bottom of the column and re-enters the still. The finished product flows continuously from the still to coolers and then to storage. By varying the conditions in this final concentration step slightly, different grades of peroxide can be produced. For example, for torpedo grade peroxide stabilizer of 8-oxyquinoline and sodium pyrophosphate is added. Also it is possible to draw from the bottom of the column directly thus making this step a distillation. The general product made at Hollriegelskreuth went for aircraft use. The chemical characteristics of these various grades are summarized in Table I.

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Part I. Production of High Test Peroxide at Höllriegelskreuth. (Cont'd.)

(i) After about five (5) days of operation, the impurities of the raw product enumerated above, build up in the original distillation stills until a solid content of about 80 grams per liter is reached. This approaches the dangerous concentration and flashes of light can be seen in the still. The still is shut down, drained, and flushed out. The residues are recovered.

(j) The residues containing 72 percent peroxide flow to a Raschig ring packed distillation unit not shown in the diagram where they are heated by direct injection of steam and also by heating coils. The vapors leaving the top of this unit containing 9 percent peroxide pass through a separator and enter the bottom of a rectifying column. This column is similar in construction to the others used in the distillation apparatus. From the bottom of the rectifying column, 30 percent peroxide is obtained and is recycled to the raw product feed. The residue from the bottom of the distillation pot contains 10 percent peroxide and a very high concentration of salts. It was stated that this concentration was over 50 percent solids. This is discarded. The peroxide loss in this is 1 percent of the total peroxide distilled. The overall efficiency of this process in the conversion of 35 percent peroxide to 80 to 85 percent is 98 percent. This recovery is excellent. Compared to the rather cumbersome system of I.G. Farbenindustrie as explained in U.S. Naval Technical Mission in Europe Technical Report No. 92-45, the system here is very simple and efficient. Microfilms of plant drawings will be forwarded as soon as they are copied.

(k) No special treatment was given the containers at Höllriegelskreuth. It was stated that all containers were treated by the manufactures. When a new tank car arrived at Höllriegelskreuth, it was allowed to stand overnight with 30 percent peroxide. No other treatment was needed. Instructions for shipment included spraying the containers with water if the temperature rose. If this didn't work, one liter of 8 percent phosphoric acid was to be added per cubic meter of peroxide. This method was proved effective on at least one occasion.

(l) In this connection, the treatment of peroxide containers inside the torpedo may be cited. This method was not used at



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Part I. Production of High Test Peroxide at Höllriegelskreuth (Cont'd.)

Höllriegelskreuth but was used by Walter at Kiel, where very high passivity was required.

(m) The anodized aluminum container is treated in the normal way with caustic soda and nitric acid. Then after washing with water it is treated for 24 hours at room temperature in a bath made as follows:

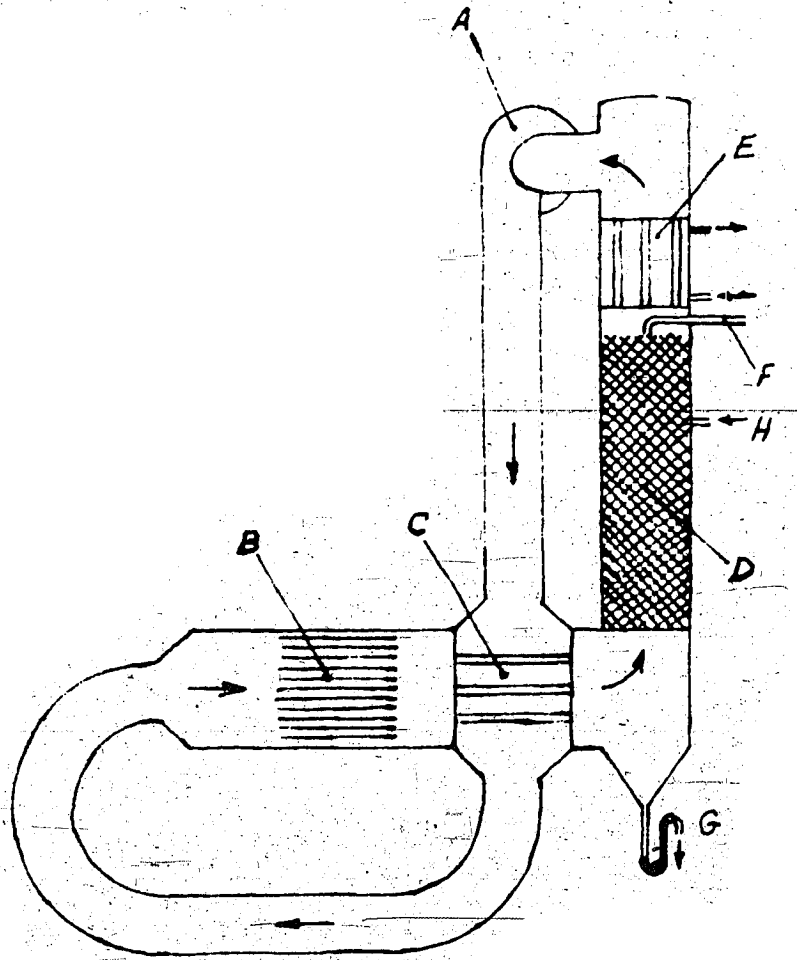
(n) In one liter of water dissolve 2 grams 8-oxy quinoline, 1.43 grams caustic soda and add 5 cubic centimeters of 30 percent peroxide. Adjust the pH of this solution to 9.6 to 10.5 with 10 percent caustic soda. After treatment wash well with water.

Part I. Production of High Test Peroxide at Höllriegelskreuth (Cont'd.)

TABLE I

MATERIAL	TN	TS	TSS
USE	AIRCRAFT & ATO UNITS	U-BOATS	TORPEDO
Concentration (Weight percent)	80	82	85
Evaporation Residue (g/l max)	5.5	0.05	0.8
Ignition Residue (g/l max)	3.0	0.02	0.3
Acid Content (milliequivalents/l)	8 - 10	1	1.5 - 2.0
Free Phosphates (g $H_3PO_4$ /l)	---	0.02	0.15
Sulfuric Acid (g. $H_2SO_4$ /l)	free: 0.5 comb: 0.7	0.005	0.005
Oxyquinoline (g/l)	0.5	---	0.3
Sodium Pyrophosphate (g/l)	0.3 - 0.4	---	0.2
Cl - ion (g/l)	---	---	---
$NH_4$ / ion (g/l)	0.2 - 0.25	---	---
Al		Trace	
ZZ max	5	5	2

SKETCH OF SYSTEM FOR PRODUCTION OF  $H_2O_2$  THROUGH ELECTRICAL DISCHARGE



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Part I. Production of High Test Peroxide at Hölleriegelskreuth (Cont'd.)

On the TS stuff a sample of 4 liters is taken. For the concentration tests, the average of two liters which must not differ from each other and from 82 percent by more than 0.2 percent is taken. The acid content test has a limit of error of 0.1 millequivalents. The limit of error on the ignition test is 3 milligrams per liter

For the TSS stuff, a sample of 2 liters is taken. Although the ZZ number for the TSS stuff is here given as 2, it was later set at a maximum of 1. This ZZ number is the percentage decomposition of a sample held at 96 degrees centigrade for 24 hours.

PART II

THE SYNTHESIS OF H<sub>2</sub>O<sub>2</sub> THROUGH AN ELECTRIC DISCHARGE

(a) The development of a process for the direct synthesis of hydrogen peroxide from hydrogen and oxygen has been carried out at the Electro-Chemische Werke since 1931. The basic facts of the process are disclosed in the American Patent No. 2,015,040. Studies had proceeded through 10 and 20 watt and 10 kilowatt units to calculations for a 2000 kilowatt unit.

(b) It is possible by this method to make peroxide of an exceptional purity; and since the controls of the apparatus are automatic, labor can be reduced to a minimum. The information on the process given here was obtained from Dr. Pietzsch. It is believed that it is accurate since he is most anxious to protect affiliated companies in the United States. Included here as Drawing No. 2, is a rough schematic sketch of the system.

(c) The synthesis of hydrogen peroxide through an electric discharge depends upon the fact that free hydrogen atoms combine with molecular oxygen. The process is cyclic. 5 percent oxygen and steam is mixed with ordinary hydrogen at a little over one atmosphere pressure by means of the blower (A). The gases then go through a heat exchanger to ionizing chamber (B). In the ionizing chamber, a part of the hydrogen is atomized and ionized through an electric discharge.

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Part II. The Synthesis of  $H_2O_2$  Through An Electric Discharge (Cont'd.)

(d) The ionizing chamber (B) is made up of a large number of parallel quartz plates. One side of these has an electrically connected aluminum coating and the other side is etched with hydrofluoric acid. The plates are 5 millimeters thick and 500 x 500 millimeters in dimensions. They are placed separated 5 millimeters from each other with the uncoated sides facing. The plates are connected in parallel electrically. In operation, 12,000 volt 9,500 cycle alternating current is used. A working density of 0.96 kilowatts per pair of plates is used. For a 2,000 kilowatt current input unit, 4,420 plates are required. The average gas temperature in the ionizing chamber is 160 degrees centigrade. The gases have a water vapor content corresponding to saturation at 60 degrees centigrade.

(e) The peroxide is formed as a vapor in the ionizing chamber and is swept out with the other gases through a heat exchanger to the rectifying column. The rectifying column contains 3 meters of 35 x 35 millimeters Raschig rings. In the 2,000 kilowatt input unit five (5) such columns in parallel of 1.7 meters diameter are required. At the top of the column a condenser (E) is mounted whose cooling water enters at 25 degrees centigrade and leaves at 50 degrees. At the point (F) distilled water is admitted. At 2000 kilowatts ionization input, 538 liters distilled water per hour are necessary. From the trap (G) a 10 percent solution of hydrogen peroxide flows. This is very pure and can easily be stored as such. At the point (H) the hydrogen and oxygen used in the process are replaced from gas containers. At 2,000 kilowatt input, 46.3 cubic meters of oxygen is used. Hydrogen is added in excess so that a minimum pressure of 100 millimeters of water is maintained in the apparatus. The condenser (E) cools the gases to 60 degrees centigrade.

(f) The peroxide-free gases next flow through the blower (A) at 2,000 kilowatt input a total volume of 107,000 cubic meters of gas is used. The pressure of the blower is 200 millimeters of water. The gases next flow through the heat exchanger (C) where they are heated from 60 degrees centigrade to the temperature required in the ionization chamber. At 2000 kilowatt input 600 square meters of pure aluminum heat exchanging surface is necessary.

(g) Automatic controls are used so that the oxygen

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Part II. The Synthesis of  $H_2O_2$  Through An Electric Discharge (c) (Cont'd)

percentage remains at 5 percent and very little labor is required.

(h) The energy efficiency is in the approximate ratio of 25 grams  $H_2O_2$  per kilowatt hour. The peroxide here is calculated as 100 percent material. In the 2,000 kilowatt input apparatus, 50 kilograms  $H_2O_2$  per hour and 400 tons  $H_2O_2$  could be made in 8,000 operating hours. Only electrical energy and water at 25 degrees centigrade are used.

(i) By taking into consideration the efficiency of obtaining 9,500 cycle current by means of a rotary converter the following energy ratios were determined for the 2,000 kilowatt unit:

Electrical Energy

For Ionization	- 2560 kw.
For Electrolysis	- 469 kw.
For Blowers	- 97 kw.
For Auxiliary Apparatus	- 5 kw.
Total	- 3,131 kw.

therefore the ratio is 62.6 kilowatt hour/kilogram  $H_2 O_2$ .

(j) The major consideration in the profitability of the process is the current cost. Assuming one pfennig per kilowatt hour for electrical current and one pfennig per cubic meter for cooling water these costs are:

Electric current	62.6 pfennig
Water	1.7
Depreciation	24.3
Salaries and wages	<u>12.5</u>
Total -	101.1 pfennig/Kg. $H_2 O_2$

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Part II. The Synthesis of  $H_2O_2$  Through An Electric Discharge (Cont'd.)

Note: This is a very brief outline. An immense amount of experimental data is available. This is being reviewed by Dr. Clapp of OSRD and a complete report will be issued. Micro-films of the most important data will be forwarded as soon as copied.

PART III

GERMAN PEROXIDE PRODUCTION POTENTIAL

(a) In Germany the use of hydrogen peroxide for military purposes had expanded tremendously in the last year. It was used for:

(1) Assisted Take-Off Units - both with a hydrazine hydrate fuel and by direct decomposition with permanganate.

(2) Torpedoes - with hydrazine hydrate decomposition and fuel.

(3) Ms 163 - with a hydrazine hydrate fuel for the main propulsion and with a solid decomposition catalyst for auxiliary pumping.

(4) Rockets (e.g. HS293) - with permanganate decomposition.

(5) U-Boats - with solid catalyst in conjunction with fuel oil.

(6) Launching V-1 - with permanganate decomposition.

(7) Auxiliary Pumping V-2 - with permanganate decomposition.

(b) Of these the Ms 163 and the U-Boat were the largest potential users. For U-Boat purposes an exceptionally pure product was required and therefore electro chemical methods of

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Part III. German Peroxide Production Potential (Cont'd.) (b)

production were favored. For aircraft, purity was not so important and, since platinum was very scarce, the I. G. Farbenindustrie method through 2-ethyl anthroquinone was contemplated. Table II below gives the monthly production potential of 80% peroxide as of March 1944. All of these plants are electro chemical with the exception of Kali chemie which uses  $BaO_2$ .

TABLE II

PRODUCTION POTENTIAL OF 80 PERCENT HYDROGEN PEROXIDE AS OF MARCH 1944.

<u>Company</u>	<u>Tons (80 percent) Peroxide per Month</u>
1. Electro Chemische Werke München A.G. at Höllriegelskreuth.	188
2. Otto Schickert und Co. K.G. at Bad Lauterberg.	900
3. Henkel & Cie at Düsseldorf.	65
4. Deutsche gold-w. Silberscheideanstalt at Rheinfelden.	210
5. Österreich Chemische Werke at Weissenstein.	62
6. El Chemie at Kufstein.	75
7. Kali chemie at Berlin.	65
Total -	<u>1565</u>

(c) Only the first two of these companies could concentrate peroxide to 80 percent. The others all produced 35 percent material; however, the Electro Chemische Werke had concentrating capacity not shown in the table in excess of its own requirements.



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Part III. German Peroxide Production Potential (Cont'd.) (c)

which was used to concentrate the material from the other plants.

(d) Since this list was compiled, the production capacity of several of the plants has been increased. The Bad Lauterberg capacity has been increased to approximately 1,200 tons; and a plant at Rhumspringe with a planned capacity of 1,800 tons was about one-third (1/3) completed. At Heydebrecke and at Waldenburg contemplated production by the I.G. Farbenindustrie method was for 2,000 tons at each, of which about one-third (1/3) was completed. A fair idea of total German planned production can be obtained by adding 25 percent to the production of the companies given above with the exception of the Schickert Company and adding known planned production. This is done in Table III below.

TABLE III

<u>Company</u>	<u>Planned Production Tons</u> <u>30 Percent Peroxide/Month</u>
1. Otto Schickert und Co. K.G.	
at Bad Lauterberg	1200
at Rhumspringe	1800
2. I.G. Farbenindustrie	
at Heydebrecke	2000*
at Waldenburg	2000*
3. Estimated other plants	<u>832</u>
Total -	7,832

This figure covers, therefore, the total expected demands and would have been the production disregarding bombing damage within six months. The production actually reached is estimated at approximately 2,000 tons per month. Most of this production is still intact.

\*Planned production was 2,000 tons of 100 percent material. Since this is a new process, a more conservative figure is used here.

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