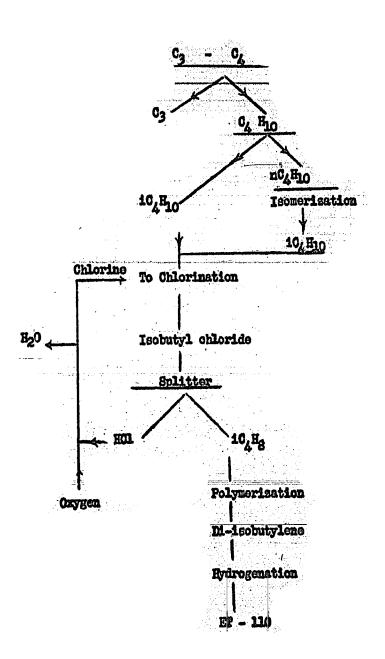
FILM STUDY GROUP

REPORT ON MICROFILM REEL NO. 30

Prepared by

THE ATLANTIC REFINING COMPANY

Scanning of Reel No. 30



SCANNING OF REEL #30

U. S. Government Technical Oil Mission

Reference, Index Page 25

1. DEHYDROGENATION OF ISOBUTANE

Frames 110 - 117 are penciled sheets summarizing utilities requirements, yields, equipment size, etc. for a dehydrogenation plant. The material is undated and the location of intended plant is not given.

2. PRODUCTION OF ET-110 AND TANOL AT HEYDEBRECK

Frames 118 to 314 cover estimates, calculations, summary sheets and correspondence relating to this plant. The original estimate dated December 17, 1940 called for an expenditure of RM 113,000,000. The production was estimated to be 50,000 tons Tanol per year and 35,000 tons motor fuel per year. In February 1942, negotiations were begun to increase the Tanol production by 60% and the gasoline output by 50%. Full production on the enlarged plant was expected by September 1, 1943.

The essence of the ET-110 plant was to fractionate raw butane for the elimination of C3, use of a column taking isobutane overhead and normal butane is bottoms, the latter being passed through an isomerization plant and returned to the C3-C4 separation column. The overhead isobutane was delydrogenated with chlorine and was then subjected to polymerization. The polymer was hydrogenated to produce ET-110, which is in effect iso-octane. The accompanying sketch made from frame 147 delineates the principal steps of the process. In July 1942 substantial agreement had been reached whereby the Oppau process was to be used in Haydebreck, receiving as charge stock a C4 fraction diverted from an alkylation plant in Blechhammer to the new ET-110 plant. Full production was expected by October, 1944. Bills of material, details of construction and utilities requirements are shown. There is one step which was not previously discussed; namely the pre-hydrogenation of the raw charge stock to convert clefin to saturated hydrocarbon.

Plan and elevation views are given for the several steps in the process from which could be gathered a very good idea of the layout of this plant.

3. PEROPTAN

Frame 316 dated July 12, 1944 begins a meagre discussion on Peroptan (Triptane) produced by coupling propylchloride and isobntene. There are no technical details.

4. THE DEHYDROGENATION OF BUTANE TO PRODUCE BUTADIENE

Discussed at great length beginning with Frame 318. The process consists of reacting chlorine with butane in suitable heat controlling, tubular type heat exchangers, followed by a series of four fractionating polymens. The first removes hydrochloric acids the second takes butane as overhead for re-cycling;

the third removed monochloralbutane which is also re-cycled, while the fourth column takes dichlorbutane overhead, leaving bottoms rejected from the process. The several towers operate at 20, 5, 0 and 0 atmospheres pressure respectively.

The second major operation is the splitting of dichlorbutane to produce butadiene and hydrochloric acid. All equipment is at atmospheric pressure. The dichlorbutane is heated in a furnace and then cooled in a spray tower where the principal overhead is a mixture of butadiene and hydrochloric acid. This mixture is subjected to an cil wash for removal of hydrocarbon, permitting hydrochloric acid to pass overhead and out of the system. There are three succeeding towers in which the butadiene is stripped from the wash oil in the first; light hydrocarbons such as methane and propylene are eliminated in the second column; butadiene is taken overhead in the third column, leaving dichlorbutane bottoms which are re-cycled to the heater splitter. The overhead butadiene is dried with caustic potash.

The essence of this process was also applicable to butylenes received as such, or prepared from butyl alcohol. In such instances, however, it appeared common practice to segregate the nCLHg for the chlorination step.

Oracking of butane to butylene and hydrogen - Frame 346, October 25, 1938.

Thermodynamic calculations are shown to predict the probable thermal decomposition of butane. The memorandum discusses experiments in which butane is reacted with hydrochloric acid and chlorine, yielding considerable amounts of butylene but no butadiene. However, mixtures of butane-butylene yields up to 10% butadiene.

Frame 353 and succeeding pages, dated July 18, 1939 is the record of a conference held between representatives of Standard Oil Co. (New Jersey) and I.G. on the subject of production of butadiene from butylene. Referring to flow diagram shown on frame 332 the following was disclosed:

Chlorine is contacted with butylene, taking care not to introduce an excess. Temperatures must not exceed 25° to 30° C. The process yields 96% dichlorbutylene with 50% chlorination of the reacting butylene. It is possible to chlorinate mixtures of butylene and butane. For example, if a mixture containing 30% butylene is processed so that half the butylene is reacted, then 1% of the butane present is simultaneously chlorinated; if 3/4 of the butylene is chlorinated, then from 20% to 30% of the butane present is converted to dichlorbutane and hydrochloric acid. Both normal butylenes apparently react in a similar manner. Isobutylene gives chlorisobutylene and hydrochloric acid according to the literature.

The dichlorbutylene is split into butadiene and hydrochloric acid by heating to a temperature of 650° to 800° C, yielding 5/10 to 7/10 kilograms butadiene per hour, per liter of oven space. The heater is of alloy construction, containing chrome and perhaps molybdenum. The heated gases are cooled to 300° C

by counter-current eashing to free them of hydrochloric acid gas. The washer must, of course, be resistent to hydrochloric acid.

It is apparent that after the conference in April, 1939 between Standard Oil and I.G. representatives (Frame 353), the research and development work upon this dehydrogenation process for making butadiens was pushed very hard, and that further pressure was exerted by the entry of Germany into the war. There is a lapse between October, 1940 and June, 1942, at which latter date (Frame 370) design data calculations are found, describing a plant for the production of 18,400 tons per year normal butylene from 20,000 tons per year of normal butane, through the route of chlorination. Note should be made in this process that butylchloride (0,4901) is the intermediate reaction product. This plant is evidently designed for use in Heydebreck, and includes hydrogenation and HOl exidation for the regeneration of chlorine. The foregoing design data, beginning at Frame 370 and continuing to Frame 406, will be found particularly complete. Summary sheets showing costs of a 20,000 tons per year butadiene plant in Reydebreck are given.

5. ISOBUTYL ALCOHOL

Frames 436 to 462 deal with discussion and calculations upon rectification of crude butyl-oil, particularly for an ester-oil plant in Heydebreck. This section is not of particular interest.

6. ALKYLATION

Frames 463 - 507. A report, May 27, 1940, from the Oppau Laboratory on the production of aviation fuel by alkylation of isobutane with normal butylene.

In the discussions upon the process and results, it is difficult to determine whether the expressions of opinion are derived from German data or from conclusions reached from a survey of foreign (American) literature. It is certain that the investigator knew that a high ratio of isobutane to olefin was favorable to high product quality. A low concentration enables polymerisation of the olefin to proceed, rather than alkylation. The catalyst was 96% to 97% sulpharic acid which underwent deterioration in use. Decomposition was said to result in 50,, which for the greater part was taken overhead with the isobutane. The acid could be maintained at proper operating strength by continuously withdrawing some of the spent soid and replacing it with fresh acid or with furing sulphuric acid or 803. Yield of alkylate in batch-wise use of sulphuric acid, was about 10 to 1 by weight. Dispersion of hydrocarbon in the sold to obtain the necessary emulsion was secured by passing the hydrocarbon through an sold-resistant filter plate. The writer speaks of the alkylatlon reaction being better in the liquid phase than in the gas phase. Whather this is to be interpreted as a mint that they tried alkylation in the gas phase is problematical. Only sufficient pressure need be maintained to keep the isobutane in liquid phase. Temperatures between 0 and 20 0 gave best yield and octans number of product. Acid concentrations from 96.5 to the 100.44 were tried; but it was noted that with the stronger acid the yield of alkylate per unit of soid was low. A sketch of a small scale alkylation unit follows in principle features that of present day laboratory waite.

SECTION 6. REEL #30 (Frame 477)

B₂80₄ Alkylation of Rydrocarbons (Oct. 1940 - Feb. 1941)

Feed Composition (Olefinio)	(1)	(2)	(3)	(4)	(5)
916	-87-r	-5.7 8.8	-5.7 8.8	8/	-1.6) 1.3
び飛 (1) の 暗 (2)	(7.9	80.0	80.0	1:	1)
C _k H ₃ (1so)) 2.3	4.5	4.5	1	95.6
C5BLO			, · • ,	. 	
Product Components				2 - 1 1 1 1 <u>1 1 1 1 1 1 1 1 1 1 1 1 1 1 </u>	**
2,3-dimethyl butane	2.6	· · · · <u>· ·</u> · ·		H	5
2,4- pentano	47.0	4.5	7.0	missim.	8
2,3- " " "	24.8	4.1	· · · · · · · · · · · · · · · · · · ·		2
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2,5- " hexane 2-and3-methyl heptane	-	-		enelysts	3.2
r-and-movilys impliand	1 184 97 19			-	
2,2,4-trimethyl pentane	6.5 2.6	25.5 28.4	41.5 16.5	મુ	36.5 10.2
2,3,4- " " 2,3,3- " "	4.6	28.5	25.0	khle	17.7
en e Coph e e monte e e e e e e e e e e e e e e e e e e	9.7	3.2	10.0		
Operating Temp. °C	27	0	20	0	25
Octano Number of Alkylate (ms) 87.5	96	92	93.5	91

Remarkst

Run (1) Triptene and nechezane were looked for.
Octane number above 90 not expected.

Rum (2) Lack of dimethyl herane and 2,2,3trimethyl pentane was noted.

Run (3) The adverse effect of increasing temperature on product yield and octane was noted.

Analysis of Alkylation Products, Resulting from the Use of Butylene and Propylene.

Frame 477. April 15, 1941.

About 20 pages are devoted to interpretation of the course of the alkylation reaction with different clefinic feed stocks, and from this memorandum it may be concluded that the Germans were advancing their knowledge of alkylation at about the same rate as in America. The alkylates were analysed both by fractionation in special columns and by Raman spectrograph. The author believed the Raman spectrograph was well adapted for practical examination of alkylates. The alkylates were made with 98% sulphuric acid, at a maximum temperature of 27°C. and a space rate of 100 grams olefin per liter of sulphuric acid per hour was used. Ratio of isobutane to olefin was about 10. The isobutane was 95% pure and contained traces of propane, hazane, anylene, with 4% butylene and 1% normal butane. After stabilisation of the reactor product, the fraction up to 185° C was used for analysis. (Table on facing page)

Cost Calculations for Production of Alkylate with Butylene Produced by Fixed and Moving Bed Debydrogenation Catalysis.

Frames 499 to 507. November 10, 1943.

Catalytic Dehydrogenation with Fixed Catalyst (Oppan).

In this process butane is passed through four consecutive contact ovens, whereby the temperature is raised from 560 to 575° C. In regenerating by burning off the coke from the inactivated catalyst, the oldest oven is cut out, purged and blown with hot air while the dehydrogenation is continued in two other ovens. The time on stream is about 6 hours. The regeneration itself is about 4 hours, and about 2 hours are required for purging. The ovens were so planned that the necessary monthly catalyst change (at 400 hours) can be accomplished in 6 hours. An ultimate butylene yield of 87% and a once-through yield of 31% is attained.

Catalytic Dehydrogenation with Moving Bed Catalyst (Leuna).

The process gives an ultimate yield of 85% butylene and a once-through yield of 25%. Helds up to 88% can be attained at increased cost.

There are no technical details to disclose the nature of the catalysts, and the principal portion of the memorandum is devoted to cost calculations which seem to indicate a narrow margin in favor of the fixed bed catalytic process, both in respect to alkylate costs and steel requirements.

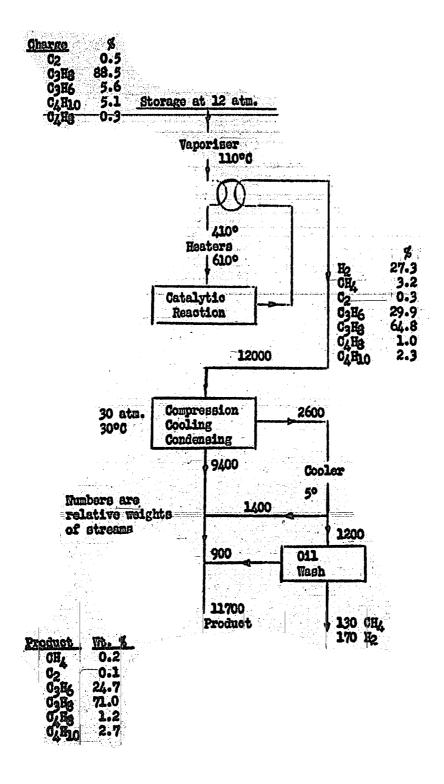
7. PRODUCTION OF DI-I OPROPIL ETHER

Frames 508 to 530.

The sequence of material in this section is apparently broken. A flow sheet indicates that propose received into the plant would contain about 1% of propylene, which was subjected to a prelydrogenation step before being giveneed to the ollowing delydrogenation process. It appears that in May, 1943

CATALYTIC DEHYDROGENATION OF PROPANE

(Frame 547)



a decision had been reached to install the process in Heydebreck, Upper Silesia. A plant was projected which would use 70,000 tons of propane annually, and would produce about 65,000 tons di-isopropyl other yearly and, as a by-product, 16,500 tons allyl chloride per year. The cost was estimated as 34.7 million RM and would require 28,000 tons of steel. The flow diagram included as a portion of this section is not in accord with the text, so that we can only surmise the exact order of processing. Since there are no detailed operating instructions, nor description of the catalyst employed, the memorandum is of minor interest.

In July, 1943 a plant for the production of di-isopropyl other was proposed for location in Romania. Reviewers should be alert to uncover detailed descriptions of this process, or supplementary information which can be pieced with that in this present section.

8. CORRESPONDENCE ON OPPANOL AND BUNA

The first five frames deal with allotment of materials in research development work. No interest.

Work on the continuous polymerization of butadiene is disclosed (Frame 539). The quantity of alkali-metal was of the order of 1.5 tons for each 3,500 tons butadiene processed. In July 1943, plans were approved for a butadiene polymerization plant with a capacity of 30 tons per month. The section ends at this point so the reviewer has no knowledge as to whether this continuous polymerization unit was constructed and operated.

9. SEPARATION OF PROPYLENE FROM CAS MIXTURES-LUDWIGSHAFES

The recovery of propylene made by the dehydrogenation of propane or secured as a by-product in the feed preparation unit of an alkylation plant, is covered at great length beginning at Frame 544. Sketch of Frame 547 shows the principal steps in the production of propylene from propane. The cost of the plant to produce 23,000 tons of propylene annually, exclusive of land and power requirements, was estimated at 6-2/3 million MM. Propane was evaluated at 32.8 MM per hundred kilograms and the overall cost of propylene in 30% solution, was estimated to be 53.3 RM per 100 kilograms, of which 2.4 marks are assigned to catalyst and wash oil use while 13.3 marks represent direct operating costs.

Frame 548+, May 13, 1943, and Oppan memorandum discusses the recovery of concentrated propylene from a catalytic dehydrogenation process. The catalytic gas contains .2% acetylene, which is hydrogenated by passing over chromium oxide nickel catalyst at about 200° C. About 18 to 22% propylene per pass is obtained in the dehydro step. The acetylene-free gas is compressed to 10 atm spheres and at this pressure is counter-currently washed with a solution of caustic copper nitrate ethanolamine solution, which serves to concentrate ole in from the mixture.

The above proposal was analyzed in a memorandum of August 10, 1943, in which two available processes, namely separation by washing with metallic salt solution and by distillation, were compared and the results applied to the calculation of cost for a plant producing 24,000 tons 03H6 per year. This memorandum of about 12 frames will be found to contain construction and operating costs for the two types of plants. The conclusion was that separation of propylene by distillation is feasible and slightly the cheaper of the two processes. There is no indication to show which process was adopted, nor the location of the plant. However, in Frame 565, June, 1944, a memorandum on operation at Heydebreck where fractionation of a propylene-ethylene mixture was carried out, mentions that a fourth of the clefinic charge stock-came from thermal cracking and recovery of the clefin by a caustic copper washing.

Frames 568 to 571 cover correspondence relating to a column proposed for propylene-containing mixtures. Prints of the column and bubble tray are given, but the conclusion reached was that the column was not satisfactory for the service intended.

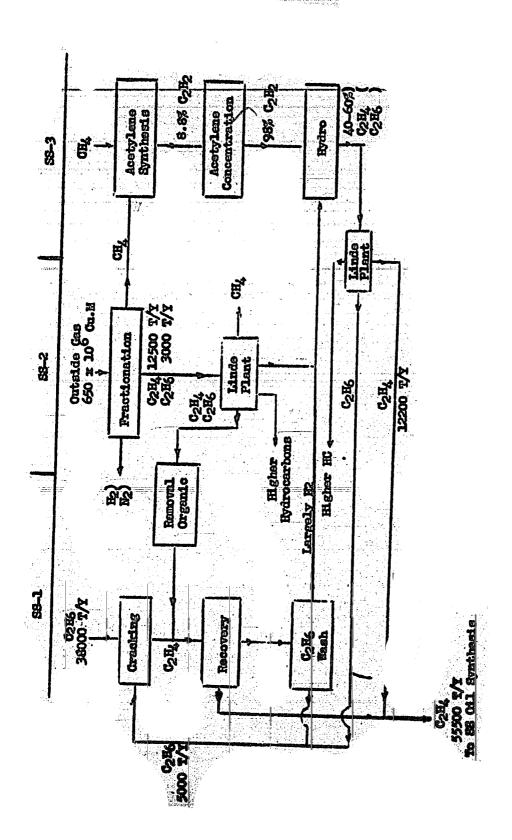
Frames 572 to 657 constitute a comprehensive report entitled "Recovery of Volatile Olefine from Mixtures with Caseous Paraffinic Hydrocarbons by Means of Selective Solvents, with Particular Reference to Normal Butylene in Admixture with Butane". The report itself is undated but supplementary sheets indicate that the work was done in the early part of 1939. The study was undertaken to overcome some of the disadvantages of separation processes such as distillation in a conventional manner, or by assotropic distillation. Aqueous inorganic solutions and organic chemicals were tried in these research studies. The project had three objectives: determination of the effectiveness of solvent in absorbing olefin from a hydrocarbon mixture; development of a practical continuous process for removal of clefin from a mixture of hydrocarbons; and thirdly the recovery of the dissolved olefin from the solvent material. It is not known how widely the information was used in Germany, but the subject matter is considered of sufficient interest so that an abstract of the report has been made.

10. COST OF PREPARATION OF PURE ETHYLENE AT HEYDERRECK

Frames 658 to 663.

Investment and operating costs are given for a plant to produce 27,500 tons of ethylene annually from 44,000 tons of ethane obtained from Bleshhamser. The ethane was to be treated for removal of carbon monoxide and organic sulphur, after which it was to be dehydrogenated in an unnamed manner. The investment was approximately 13 million marks and the cost of ethylens was estimated at 11.1 marks per kilogram, of which about 5/6 was ascribed to the purchase cost of ethane. While these sheets give a clear breakdown of cost calculations of the more formal type, there are no technical details nor flow diagram to be found in this section. The reviewer presumes that technical descriptions of the plant are available elsewhere, and an effort should be made to consolidate such information with this present report.

SECTION 11. REEL #30 Frams 764



11. DEVELOPMENT OF SS-OTL PROJECT AT HEYDERRECK

Frames 664 to 878.

This material is devoted to correspondence relating to economics, i.e., cost calculations, contract details, summaries of process equipment, etc., for a plant to produce lubricating oil from ethylene. From the initial record of a conference in July, 1941 until April, 1944 this project underwent many changes on paper with reference to capacity and its integration with other SS-Oil-projects-planned or installed in Heydebreck. There are no flow diagrams nor specific operating details. The principal steps, at least for the initial design of the plant, included ethylene recovery by the use of alkaline copper solution, polymerization of the ethylene, and refining of the synthetic oil. The following running description of the process details which do enter into the correspondence will reflect the changing viewpoints of those concerned.

Ethane was to be thermally cracked at reduced pressure, and the cracked gas was to be compressed to 25 atmospheres and passed through a caustic coppersolution treater and oil absorption at 16 to 18 atmospheres to separate out others. Polymerisation was to be effected at 100 atmospheres.

On Frame 724 it is intimated that the ethylene is derived by the hydrogenation of acetylene which in turn was produced from methane by cracking. (arc?) The product-gas of acetylene synthesis after hydrogenation was 60% ethylene, 30% hydrogen, up to 4% ethane, up to 2% higher olefins, the remainder nitrogen. The hydrogenation catalyst was active for three months, after which the mass had to be regenerated with steam or air. The presence of poisons might reduce the activity to as low as two to three weeks. In June, 1942 steps were taken to increase the production from 10,000 tons to 20,000 tons annually by supplementing the ethylene derived from cracking ethane with ethylene made by the methane-acetylene process. A flow diagram has been constructed by the correspondents and is a part of this abstract at Frame 764.

This section by itself casts very little light upon the process for producing lube oils from ethylene. Reviewers should be alert to note subject matter in other reels which can be correlated with this.

12. REPORTS ON KYBOL PLANT AT HEYDEBREOK

Frames 879 to 890.

The term "Rybol" was applied to the product of the union of benzol with ethylene or propylene to produce di-ethylenzol or propylenzol, a yield about 90% of theoretical being attained. The alkylation step is carried out in this namer; propylene and ethylene are admixed with benzol and caused to react under the influence of aluminum chloride at about 80°C. The aluminum chloride forms a viscous liquid which is withdrawn from the bottom of the reactor and is circulated. The synthesized hydrocarbon is freed of catalyst, washed with vater and caustic sods, and then is distilled. The overhead from the first column is a low boiling product; from the second column, di-ethylbensene and propylbensene are takenoverhead. The bottoms of the second column are mixed with the overhead of the first column and recycled to the alkylation step. A flow diagram of the process is shown as France 884. It is uncertain whether the process was ever placed in production for the available ethylene.

13. SS OTL PROJECT AT OPPAR

Frames 891 to 916.

According to information dated October, 1941 this plant known as "SS 900" located at Oppau and built for I.G. was to have a capacity of 1,920 tons per year SS Oil produced by the polymerization of ethylene. Production was expected by June, 1943. It was estimated to cost 1,400,00 RM and required 1,300 tons of steel. Delivery of 200 tons ethylene per month derived from Saar gas was required. The process consumed the following quantities of chemical stated as tons per years.

Aluminum Chloride 135 Methanol 75 Lime 42 Lead Chloride 15

There is no statement as to the properties of the product.

14. AGREEMENTS BETWEEN HEYDEBRECK AND BLECHHAMMER
ON UTILIZATION OF METHANE AND BUTANE

Frames 917 to 972.

These are detailed memoranda and correspondence relating to or leading up to contractual agreements in which I.G., the Upper Silesia Hydrogenation Works and the Central German government were involved. Great stress was placed upon financial arrangements to insure a supply of butane for aviation fuel, and little account is given of the processes which will employ the hydrocarbon.

Such technical matters as are discussed will have greater significance if reviewed in conjunction with process details for this plant which may be found in other reels.

15. HYDROGENATION REPORTS: RESIDUE FOR ERIQUETING: PASTE PRE-HEATING: CORRESPONDENCE ON SULFIGRAN

Frames 973 to 1016.

The first section deals with the production of a briquetting material made from hydrogenation residues. The residual slurry from the hydrogenation of coal is thirmed with retort oil and centrifuged; the centrifuge bottoms are retorted in ovens. The bottoms may be used to agglomerate small size-coal or if admixed with a non-coking coal and retorted, a desirable solid fuel will be produced.

Information on briquetting material appears on a page #11, undated, but presumably part of an extensive report. One of the pages bears the imprint of Dr. Baeir and a flow diagram is dated 1942 (Ludwigs hafen).

The production of coke from retort briquettes was considered of importance

from the standpoint of making high quality coke for the manufacture of water gas and for blast furnace use. The mild hydrogenation of brown coal or low grade coal produces a pitch-like product which has good briquetting properties. The coal is slurried with middle oil and hydrogenated under mild conditions, i.e., with high thruput or low temperature. The oil is distilled from the hydrogenated product and recycled, while the residue, the so-called hydrogenated coal, becomes material for briquetting or the coal may be slurried with the retort tar and in a similar manner passed through the hydrogenation step-whereby the tar is cracked to middle oil and heating oil, and the hydrogenated coal becomes briquetting material.

While this process obviously has no American application today, the information is considered worth reviewing by those interested in establishing coal hydrogenation industries in view of the possibility of utilizing the features of the process in the production of smokeless fuel from non-coking coal or fines which otherwise would have less value than when briquetted. This item extends from Frames 974 to 980.

On Frame 981, dated Ludwigshafen October, 1940 is a record of work upon the heating of paste by the hot oil method for a 700 atmosphere chamber.

Contrasted to the method of middle oil with bismuth, the method using hot oil apparently gives much higher paste thruput. Four procedures were offered. First, (used in Scholven and Nordstern) the paste which has been brought from a temperature of 100 to 425°C in a preheater is treated with the working gas in a regenerator, after which three hairpin heaters in series raise the temperature to 470°. The pressure in the hairpin heaters is 48 atmospheres and that of the oven following is 12 atmospheres. The second method consists in separating the paste into two streams of different concentration (at higher viscosity). The third method treats at the same concentration but at lower viscosity.

Frames 999 to 1016. Correspondence on Sulfigran.

The production of Sulfigran (sodium sulphide, Na28) of which there was potential capacity in Germany of about 2,000 tons per month had been diminished by about one-third, and steps were taken to enlarge the output of this cherical. A hint is given that the Sulfigran when dried is used as catalyst in Steinkohle hydrogenation. It may also be inferred that the sodium sulphide was made either by the route of reacting sulphir with sodium carbonate or by hydrogenation of sodium sulphite or sodium sulphate. The final piece of correspondence on this subject indicates that Hey obreck would be the site for a new or enlarged Sulfigran plant.

16. DETAILS OF PREPARATION OF VARIOUS CATALYSTS

(Note that this subject is erroneously placed in the index as part of Reel 31).

The subject matter in this section is neither complete nor comprehensive, but nevertheless may be of use when correlated with similar information. The following items are discussed:

Catalyst #2041 (BZ-Kontakt)

/1729 A1(OH)3 + 88102

#1747_Aluminum_and_Silicon_in_proportions_1:20

W-Kontakt

Brown Oxide Catalyst (derived from iron sulphate, chromium oxide and saltpeter)

Gatalvat #2021 - Production of BZ-Kontakt mass dropped because or unavailability of certain clays. Evidently some of the catalyst or its equivalent was subject to poisoning by sulphur and there is mention of a purification process employing sine oxide, as well as iron oxide mass. No details on this purification have been found in this section.

W-Kontakt - The directions for making, analyzing, and determining the activity of this catalyst which was used to promote the reaction CO2+N2O are given in great detail. (Frames 1023-1043, June 1939).

The Brown Oxide Catalyst appears to have been developed in Oppau and was also used to promote the reaction for the conversion of CO to CO₂.

(7 frames, April 1940):