

**FILM STUDY GROUP**  
**REPORT ON MICROFILM REEL NO. 14**  
**Prepared by**  
**CALIFORNIA RESEARCH CORPORATION**

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ABSTRACT OF TECHNICAL

OIL MISSION MICROFILM

REEL NO. 14

(Prepared by California Research Corporation)

OIL MISSION MICROFILM REEL 14

OXO PROCESS

Frame 478

A flow diagram and material balance for the manufacture of alcohols by the synthesis of aldehydes and subsequent hydrogenation. Dated February 7, 1940..

Frames 479 to 483

A memorandum on discussions of IG with Ruhrchemie on the Oxo Process, February 19, 1940. The preparation of olefins by the Fischer synthesis at low and high pressures and with an iron catalyst were discussed with yields given. Also the preparation of olefins by thermal cracking of paraffin wax was discussed. The yield of olefins from cracking wax was 85%. The position of the double bond was at the end of the chain when using temperatures of 250°C. and in the middle of the chain at temperatures of 350°C. The catalyst for the Oxo Process is the Fischer Cobalt-Kieselgur-magnesium oxide preparation. The catalyst was suspended in either a neutral oil or the olefin stock and then treated with water gas. At 105 to 115°C. the yield of aldehyde was 90% from olefins and water gas at 100 to 200 atmospheres for a few hours. The reaction mixture without catalyst separation was then treated at 180°C. with pure hydrogen to form the alcohols. Both straight chain and  $\alpha$ -methyl alcohols are formed. A reaction mechanism by which these are obtained is shown. This reaction is said to be general and will work for any olefin. The formation of ketones has also been observed through the reaction of two molecules of olefin with one molecule of CO. Details for the preparation of approximately 40,000 tons of high molecular weight alcohols from 120,000 tons of raw synthesis product are given. By-products include a large quantity of low molecular weight alcohols and aldehydes.

Frames 484 to 488

A memorandum dated February 21, 1940, by Ruhrchemie giving detailed instructions for the preparation of aldehydes and alcohols from olefins. These instructions include examples for both low boiling and high boiling olefins. The method of reaction is similar to that described in the preceding frames.

Frames 489 to 492

A flow diagram showing the source of materials and process steps for the Oxo Process.

Frame 493

A memorandum of a meeting discussing briefly the details on the preparation of metal carbonyls and their physiological effects. Dated December 9, 1940.

Frames 494 to 499

A memorandum dated February 6, 1941, discusses the synthesis of synthetic detergents and wetting agents directly through the sulfonation of hydrocarbon and sulfonation of alcohols. A discussion is given of the possible sources of olefins for alcohol synthesis through the Oxo Process and of the sulfonation of these alcohols.

Frames 500 to 502

February 29, 1940. A memorandum discussing the Ruhrohemic experimental operation on the Oxo Process. It concludes that the process is attractive for further work but that many problems are yet to be solved.

Frames 503 to 506

A memorandum dated April 30, 1941, discussing the cost of producing synthetic wetting agents using olefin feed stocks with and without alcohols. The basis is 10,000 tons of olefins per year. A tabular summary of cost comparisons is given.

Frames 507 to 509

A memorandum dated December 4, 1941. Exchanging experimental information by the operators of several pilot plants. The merits of fixed bed versus suspended catalysts were discussed but no final recommendations made. Catalyst life was unknown. With ethylene the product consisted of 30% propionaldehyde, 30% diethyl ketone, and 40% higher boiling residues. At higher temperatures, 300°C. and 200 atmospheres, the principle product is propyl alcohol. With propylene the ratio of normal to isobutyl alcohols is 60 to 40 and figures as high as 70 to 30 have been reported. Other unsaturated products tested included butadiene and isoprene and it was concluded that only one of the double bonds reacted. Incomplete reaction was obtained with unsaturated acids and vinyl ether.

Frames 510-511

A letter dated December 23, 1941, discussing the problem of using feed stocks containing a low percentage of olefin in the Oxo Process. The two alternative methods of separating the alcohols formed are by sulfuric acid and boric acid treatment. While insufficient experimental data are available to make a firm decision, it was concluded that indications are in favor of the boric acid treatment.

Frames 512, 513

A letter dated December 2, 1941, discussing the advisability of applying the Oxo Process to feed stocks containing 25% olefins or less. The usual process of separating the alcohols by distillation was considered to be uneconomical but separation by sulfonation or formation of boric acid ester was considered possible.

Frames 514 to 517

A letter dated February 5, 1942, giving details of a pilot plant run on the Oxo Process with a particular discussion of the difficulties of temperature control.

Frames 518, 519

A letter dated February 12, 1942, discussing the use of Oxo alcohols and their sulfuric acid esters as washing agents, particularly in connection with the various possible uses they might have in the textile industry and the difficulties in preparing suitable detergents from these substances.

Frames 520 to 528

February 10, 1942. A comprehensive report on the present status of the Oxo Process including details of pilot plant operation at Merseburg. Yields of alcohol, preparation of feed stock, catalyst problems, temperature control, etc., are all discussed. All laboratory work on this and related problems including the addition of CO to diolefins, etc., is also summarized.

Frames 529 to 531

A memorandum dated February 10, 1942, giving the proceedings of a meeting to discuss the design of a commercial plant for the Oxo Process. Discussions were based on the experience of various pilot plants.

Frames 532 to 538

A report dated February 11, 1942, giving details on the design and operation of a large scale Oxo Plant at Oberhausen-Heiten. This process is to be a batch or non-continuous operation, a flow diagram is included. Starting material would be an olefinic product from Fischer synthesis containing 35-40% olefins.

Frames 539 to 556

This is a report dated February 25, 1942, of work done at Louna on the reaction products from the Oxo Process. Some pure olefins, namely, isohexylene, cyclohexene and dodecene and some commercially available products -- a  $C_{14}$  isohexene heptene copolymer, cracked olefins from paraffin wax and olefins from the Fischer Synol process were used. Theoretically, the primary products from the Oxo Process should be primary aldehydes, beta-methyl aldehydes, straight chain ketones, and beta-methyl ketones. Secondary reactions are the condensation of the aldehydes and ketones formed to produce high molecular weight aldehydes or ketones, the reaction of two aldehydes to form an acid and an alcohol as in the Cannizzaro reaction, and the esterification of the acid by the alcohol to form a high molecular weight ester. In work with the pure compounds, it was found that all these products appeared in the reaction mix although the respective quantities of the different compounds was not specified. In the case of the commercial olefins, the reaction was not stopped at the aldehyde stage but the reaction mix was hydrogenated to form alcohols. The resulting product contained essentially only alcohols rather than a large mixture of compounds found in the aldehyde stage indicating that the hydrogenation step had hydrogenated esters, acids, aldehydes, etc., formed to the alcohols. Also included is a comparison of the detergent characteristics of detergents formed from the sulfonation of Oxo Process alcohols from naturally occurring alcohols and from the direct sulfonation of olefins. Tables showing the wetting time, foam height, etc., of these various detergents are given. It was concluded that detergents formed from the sulfonation of alcohols are superior to those formed by the direct sulfonation of olefins.

Frames 557 to 561

A memorandum dated February 27, 1941, concerning a discussion of design details of the Oxo Plant at Oberhausen with particular reference to details of distillation equipment.

Frames 562-563

A memorandum dated March 17, 1942, on a meeting in which the economics of the Oxo Process using Synol reaction products as starting material are discussed, particularly with reference to the utilization of the  $C_7$  to  $C_{12}$  alcohols formed in this process. It was concluded that only small amounts could be used by the lacquer and plasticizer industries.

Frames 564 to 584

A memorandum dated March 28, 1942, covering the economics of producing alcohols from Fischer-Tropsch synthesis product by the Oxo process. For a starting material the product from the middle pressure Fischer gasoline synthesis is taken. This contains approximately 35% paraffins, 15% alcohols, and 50% olefins. The economics are calculated under four cases and from 100,000 tons of starting material it was estimated that from 14,000 to 40,000 tons of high molecular weight alcohols could be produced depending on the type of operation. There are four diagrams and ten tables giving the details of this cost analysis.

Frames 585 to 590

A memorandum dated March 30, 1942, discussing utilization of the products from the Oxo Process and possible expansions. In the discussion, it was decided that at present there was no market for the low molecular weight alcohols formed by this process.

Frames 591 to 593

A letter dated April 20, 1942, concerning the use of water in the Oxo Process. It was stated that water addition not only had the advantage of helping with temperature control but influenced the reaction favorably. Thus with ethylene a 90% yield of propionaldehyde was obtained, the water inhibiting side reactions to form ketones, etc.

Frames 594 to 595

A letter dated April 27, 1942, concerning a proposed continuous operation of the Oxo process. It was stated that the pilot plant at Merseburg had been operated satisfactorily and it was suggested that the plant of the Oxo Company at Holten be converted to this basis since smaller catalyst losses are experienced and an increase of tenfold in the plant capacity could be achieved. No details of the proposed continuous operation are given.

Frames 596 to 597

A letter dated May 4, 1942, with further discussion of the use of a continuous process for the Oxo reaction. No technical information is given.

Frames 598 to 600

A letter dated May 5, 1942, concerning the economic problems resulting from conversion of the Oxo Process to continuous production and the consequent excessively high capacity resulting from such conversion. No technical information is given.

Frame 601

A diagram giving an estimate of yield of various products from the Oxo Process. This should be included with a memorandum of March 28, 1942, which is covered in Frames 564-584.

Frames 602-604

A memorandum dated May 12, 1942, discussing the proposed conversion of the pilot plant at Merseburg into a production plant. No technical information is given.

Frames 605 to 607

A memorandum dated May 28, 1942, discussing the design and construction costs of a 20,000 tons per year Oxo plant. While few details of actual method of operation are given, it was stated that the operation would be a continuous suspended catalyst process as developed at the pilot plant at Merseburg. The catalyst would be the Fischer catalyst (35% Co, 2% ThO<sub>2</sub>, 2% MgO on Kieselguhr). It was estimated that the catalyst could be used fifty times before regeneration and that 70 kilograms of fresh catalyst would have to be added daily. Used catalyst can be regenerated. No figures on catalyst loss are available. The feed to the plant would be an oil containing 50% olefins with an average molecular weight of 150. A table showing an estimate of plant costs and a rough flow diagram are shown.

Frames 608 to 620

A report dated June 1, 1942, giving an analysis of the cost of preparing alcohols by various methods; i.e., methanol and isobutyl oil synthesis, Oxo synthesis, Synol synthesis, etc. It was concluded that the high molecular weight alcohols from the Oxo process could be compared favorably economically and that the Synol process enters into the picture only if straight chain alcohols are necessary. No technical information was given. The cost analysis is reported in tabular form.

Frame 621

A letter dated June 17, 1942, requesting planned experimentation on the conversion of neutral oils from Fischer synthesis to alcohols.

Frame 622

A letter dated June 23, 1942, discussing the conversion of a sample of neutral oil from an ester oil plant by the Oxo process.

Frame 623

A table giving certain physical and chemical constants; i.e., hydroxyl number, carbonyl number, etc., of aldehydes, esters, olefins, ketones, alcohols, etc.



Frame 624

A note dated July 17, 1942, regarding the secrecy in connection with the use of the term "Synol laboratory."

Frame 625

A letter dated July 11, 1942, requesting cooperative analytical work.

Frame 626

A letter dated July 11, 1942, requesting an exchange of analytical information.

Frame 627

Comparative analytical data on olefins for the Oxo process.

Frame 628

A letter of transmittal dated July 9, 1942, concerning samples of Oxo Process alcohols.

Frames 629 to 630

A memorandum dated July 14, 1942, on a discussion about obtaining alcohols for ester oils from the Oxo synthesis.

Frames 631 to 634

A memorandum dated July 15, 1942, on a discussion of the continuous operation of the Oxo Process. It was pointed out that the cobalt catalyst is very sensitive to sulfur poisoning in the hydrogenation step but not so much so in the Oxo step and that perhaps a copper chromite catalyst should be substituted for the cobalt catalyst in the hydrogenation step. A continuous process developed at Ludwigshaven was described using a combination fixed bed and dissolved catalyst as follows: Cobalt salts of fatty acids are dissolved in the feed and this is passed over pumice containing small quantities of cobalt at 130-140°C. in the presence of CO + H<sub>2</sub>. The reaction product is then passed over pumice at 120-130°C. under 200 atmospheres of hydrogen and 90% of cobalt is precipitated. A second similar treat removes the balance. The reaction mix is then hydrogenated over copper chromite. Advantages of this procedure are that the filtration in the Leuna process is eliminated. However, the plant capacity is much smaller and is of the order of that for the suspended catalyst batch operation.

Frame 635

A letter dated July 25, 1942, concerning the possibility of using Oxo process alcohol for the manufacture of ester type lubricating oils.

Frames 636-650

A report dated August 21, 1942, concerning the mechanism of the Oxo reaction and description of the product. It was shown that even though pure straight chain olefins having the double bond at the end were used, a mixture of isomeric alcohols was obtained. These isomers consisted not only of  $\alpha$ -methyl but of  $\alpha$ -alkyl alcohols in general, indicating isomerization of the double bond. With this type of pure starting material only about 40% of the product was straight chain alcohol. It was shown that this isomerization occurs during the Oxo reaction and that cobalt carbonyl is the catalyst causing the isomerization of the double bond. The isomerization and the Oxo reaction are competing reactions with the Oxo reaction somewhat faster since a greater proportion of the product is straight chain than the pure isomerization experiments would have indicated. Iron carbonyl is also a mild isomerization catalyst but nickel carbonyl is not. It was concluded that since Synol alcohols are practically completely straight chain, that the mechanism of their formation could not go through an olefin intermediate but that the olefins in the Synol product probably were formed by the dehydration of Synol alcohol followed by isomerization in the presence of the iron carbonyl.

Frame 651 to 653

A letter dated September 17, 1942, concerning the proposed use of Oxo Process alcohols of seven to ten carbon atoms in plasticizers. The proposal was to convert a kerosin fraction of seven to ten carbon atoms by the Oxo Process removing the alcohol by esterification with phthalic acid, the resulting phthalic acid esters to be used as plasticizers.

Frame 654

A report dated September 28, 1942, on the water absorption of C-18 Oxo alcohols.

Frames 655 to 658

A memorandum dated October 8, 1942, concerning the hydrogenation of a large batch of methyl ester of methyl adipic acid to methyl-1,6-hexane diol. A flow diagram of the apparatus is given.

Frames 659 - 665

A letter dated October 12, 1942, concerning the evaluation of Oxo alcohol sulfates as wetting and washing agents. Three samples were taken containing, respectively, C<sub>12</sub>-C<sub>18</sub>, C<sub>13</sub>-C<sub>18</sub>, C<sub>14</sub>-C<sub>18</sub> alcohols, and they were evaluated comparatively. All these Oxo sulfates met the requirements for storage stability, wetting power and foaming properties. They were found to be good for washing both wool and cotton.

Frames 666 to 667

A letter dated October 12, 1942, containing a brief description of the preparation and properties of Oxo detergents for patent purposes.

Frames 668 to 673

A memorandum dated October 20, 1942, discussing the possibility of using the Oxo plant at Louisa for the production of C<sub>7</sub>-C<sub>10</sub> alcohols. It is of particular interest since it gives a rather complete description of proposed plant operation (batch process), including an operating description, estimates of throughput, yield, H<sub>2</sub> and CO consumption, heat of reaction, catalyst consumption, stock losses, hydrogen purification problems, etc. Some of the figures mentioned were: a throughput of 1050 l/cu. meter of reactor volume of a feed containing 35% olefins; total heat of reaction of 150 Kcal/kg of feed (including hydrogenation step), and catalyst consumption of 16 g/kg of feed processed (catalyst can be regenerated).

Frame 674

A letter dated October 27, 1942, concerning the testing of Oxo alcohol sulfates as textile agents.

Frame 675

A letter dated November 9, 1942, requesting a sample of cracked oil for use in the Oxo synthesis.

Frame 676

Correspondence dated November 25, 1942, concerning the supply of cracked oil for use in the Oxo synthesis.

Frame 677

A letter dated December 2, 1942, requesting the testing of "Lana" type Oxo products.

Frames 678 to 680

A letter dated December 9, 1942, discussing the properties of Oxo alcohols and their products. No significant technical information is given.

Frames 683 to 684

A memorandum dated December 15, 1942, giving further information about the Ludwigshaven continuous Oxo process (Combination dissolved and fixed bed catalyst) including details for preparation of catalyst, reaction conditions and recovery of catalyst. It was mentioned that by this process no ketones are formed but about 10% of the product is heavy oil.

Frames 685 to 686

A memorandum dated December 15, 1942, concerning a discussion of the supply of olefins by Ruhrchemie.

Frames 687 to 689

A memorandum dated December 16, 1942, concerning the sulfonation of Oxo alcohol. It was concluded that chlorosulfonic acid is the best sulfating agent. It was also concluded that the sulfonation of the hydrocarbon-alcohol mixed product from the Oxo reaction followed by separation of the sulfate was superior to separation of the alcohol from the hydrocarbon by boric acid extraction followed by sulfonation of the pure alcohol. Some details of the sulfonation and extraction procedure are given.

Frame 690

A letter dated December 17, 1942, offering some samples of Oxo alcohols.

Frame 691

A letter dated December 18, 1942, containing a request for the allocation of material to expand the Oxo plant. One reason given is use of Oxo alcohols in esters for special lubricants.

Frames 692 to 693

A report dated January 8, 1943, concerning the formation of fatty acids from Oxo alcohols by caustic fusion. These frames are practically illegible but it appears that details of the operation are given.

Frame 694

A supplement to the request for material for the expansion of the Oxo plant dated January 12, 1943.

Frame 695

A discussion dated January 14, 1943, on the properties of Oxo-alcohol sulfates as textile agents.

Frame 696

A memorandum dated January 15, 1943, describing the properties of textile agents made from Oxo alcohols and comparing them with other soaps. They were found to be unstable to hardness, acid and heavy metals but in alkaline soft water were superior to soap.

Frames 698 to 702

A memorandum dated January 29, 1943, concerning the inspection of the Ruhrchemie Oxo plant and a discussion of the plant operations. No technical information is given. One flow sheet of the Ludwigshaven continuous process is shown.

Frames 703 to 704

A letter dated February 9, 1943, concerning the allocation of cracked oil for experimental purposes in the Oxo process.

Frame 705

A letter dated February 10, 1943, concerning a supply of cracked olefins for experimentation in the Oxo process.

Frames 707 to 708

A memorandum dated February 17, 1943, concerning the present status of the Oxo process and necessary future development. No technical information is given.

Frame 709

A letter dated February 22, 1943, concerning the supply of cracked oil.

Frame 710

A letter dated February 22, 1943, concerning the potential supply of  $C_8, C_{12}$  alcohols by the Michael process.

Frame 711

A request dated February 27, 1943, for funds for the expansion of the Oxo plant.

Frame 712

A request dated January 28, 1942, for funds for the expansion of the Oxo plant.

Frames 713 to 717

A memorandum dated March 29, 1943, concerning the conversion of the Oxo plant to continuous operation. It was proposed to have two contactors in each step (Oxo step and hydrogenation step). In each step one reactor would have counter-current gas and liquid flow and the other parallel gas and liquid flow. A suggestion for eliminating the necessity for removing CO from the hydrogen recycle stream by a brief preliminary hydrogenation is included. Flow sheet and product balance diagrams are given.

Frame 718

A memorandum dated June 3, 1943, concerning the supply of cracked oil.

Frame 719

Letter dated July 7, 1943, and June 28 concerning the supply of cracked oil.

Frame 720

The same. Dated July 3, 1943.

Frames 721 to 722

Letter dated July 5, 1943, on the supply of cracked oil.

Frame 723

A letter dated July 16, 1943, on the supply of cracked oil.

Frames 724 to 739

A memorandum dated August 4, 1943, containing comparison of the economics of sulfonating the crude Oxo alcohol-paraffin mixture as compared with separating the alcohols and then sulfonating. The pros and cons of each method are discussed and it was concluded that sulfonation of the crude Oxo mixture is to be preferred. Several charts and tables illustrating this economic comparison are included.

Frames 740 to 772

A report dated November 3, 1943, concerning a rather detailed evaluation of various olefin products (Fischer olefins, Synol products, cracked olefins, etc.) for use in the Oxo process. Conclusions reached were that (1) all the olefins can be converted to alcohol with yields of over 95% (2) that the cobalt catalyst gives a more uniform product than an iron catalyst yielding only olefins, paraffins, and alcohols; whereas, in products from an iron catalyst considerable amount of acids, esters, and aldehydes are present. The Synol product is a satisfactory feed in the production of alcohols in general but is poor for the production of high molecular weight alcohol in as much as this fraction is a very small part of the total. A number of tables of comparative data are given in the report.

Frames 773 to 776

A report dated November 8, 1943, on the preparation of xanthates of Oxo and Synol alcohols, particularly with respect to their possible use in the manufacture of rayon. It was concluded that they were not particularly outstanding.

Frame 777

November 22, 1943. Cover letter to above report.

Frames 778 to 779

A letter dated December 7, 1943, requesting information concerning the possible harmful physiological effect (possibility of causing tuberculosis) of branched chained fatty acid from the Oxo process.

Frame 780

Dated February 9, 1944 - cover letter for the following report.

Frame 781

A report dated February 4, 1944, on the physiological effect of branched fatty acid from the Oxo process. It was concluded that these would have no harmful effect.

Frames 782 to 783

December 20, 1943. Analytical results on olefins and alcohols from the Oxo process.

Frames 784 to 786

December 20, 1943. Analytical results on comparative samples of hydrocarbons and alcohols from the Oxo process.

Frames 787 to 789

April 5, 1944. Concerning the Oxo and Synol process and the Hostapen process (sulf-oxidation).

Frame 790

Cover letter dated April 17, 1944, on three samples of aldehydes giving physical and chemical data.

Frame 791

A letter dated May 9, 1944, giving physical data on some Oxo alcohol fractions.

Frames 792 to 793

A letter dated June 6, 1944, concerning delivery of samples of Oxo products for experimental purposes and also describing the products of the Oxo reaction with isocyanlene.

Frames 794 to 797

A letter dated June 21, 1944, concerning problems at the Oxo plant at Holten. It was suggested that perhaps the concentration of alcohols in the product could be increased by methanol extraction.

Frames 798 to 801

A report dated June 29, 1944, giving the details of the preparation of plasticizers (phthalic acid esters), from Oxo alcohols. A table of the properties of these esters is given.

Frame 802

Page from a report dated July 6, 1944, on the Oxo and Synol processes. This contains the same information as Frames 788 to 789.

Frame 804

Data on Oxo alcohols made from olefins obtained from low temperature carbonization of tar. Dated October 27, 1944.

Frame 803

Memorandum dated August 9, 1944, concerning the composition of the Oxo catalyst.

ANALYTICAL METHODS FOR OXO PROCESS

Frames 805 to 812

This is a report dated August 19, 1941, concerning the methods of analysis for the charge stock and finished product of the Oxo reaction. Methods for determining the amount of active olefins (Iodine-Rhodan number), molecular size (boiling point), and character of impurities (acid number, etc.), of the charge stock and the alcohol content, molecular size, side reaction products, etc., in the product are given. All the analytical methods appear to be old established ones.

Frames 813 to 818

A memorandum dated September 4, 1941, covering a discussion of the above methods of analysis. In general they concur although some additional and alternate suggestions were made. A list of the inspections necessary on the starting material and the product is given. The details of certain determinations such as hydroxyl number and carbonyl number are given.

Frame 819

A memorandum dated September 3, 1941, giving a quick determination for hydrocarbon soluble in  $H_2SO_4 - H_3PO_4$ .



Frames 820 to 833

A memorandum dated October 8, 1941, concerning a discussion on analytical techniques. The discussion was general in character and gave no detailed methods of analysis. There was considerable discussion on the structure of the olefins and alcohols both as to the mechanism of formation and means of determining structure. Some approximate methods of determining the degree of branching as through the use of antimony pentachloride were mentioned but no analytical methods for determining definitely the structure of the olefins and alcohols was given. Certain empirical methods such as the quality of the resulting detergent were mentioned in connection with the determination of structure.

Frames 834 to 844

A letter dated July 18, 1942, giving the results of analysis (hydroxyl number, iodine number, etc.) of cooperative samples together with comments on the analytical methods used. In some cases the results of different laboratories varied considerably and some details of methods to avoid this were suggested. There are three pages of detailed description of analytical methods which are practically illegible.

Frames 845 to 853

A series of letters dated December, 1943, through January, 1944, giving results of a cooperative analysis of a C<sub>16</sub> Oxo alcohol sample.

Frames 854 to 858

A series of letters dated from May to July, 1944, containing the results of cooperative analysis of C<sub>11</sub> - C<sub>12</sub> and C<sub>12</sub> - C<sub>13</sub> Oxo alcohols.

HYDROGENATION

Frames 861 to 890

This is a report dated May, 1938, on experimental work done in connection with the design of a hydrogenation plant at Iatzendorf. The work consisted of the hydrogenation at high pressure in both liquid and gas phases of a mixture of coal tar, Fischer middle oil and Fischer cracked residue. A variety of catalysts were used. It was found that catalysts No. 6104 and No. 6434 were the most desirable. Most of the work was done in the gas phase at pressures around 500 atmospheres with once-through yields of gasoline ranging from 30% to 45% and with octane numbers ranging from 35 to 80. A table is given summarizing the results of this work. Some experimentation was done hydrogenating the heaviest fraction liquid phase but it was not determined whether or not this liquid phase operation was necessary or desirable. Flow diagrams on the proposed plant are given.

Frames 891 to 913

A detailed report dated July 21, 1938, covering experimental work done on the filtration of sludge from brown coal hydrogenation. Considerable inconsistencies were noted and no definite conclusions were reached as to the most desirable conditions.

Frames 914 to 951

A rather complete report dated March 15, 1942, on the starting of propane dewaxing plant Me 944. A great number of operating difficulties were encountered and /complete description of operating procedure is given. No definite conclusion as to the economic suitability of the plant had as yet been reached. Flow diagrams of the plant are given.

Frames 952 to 989

A report dated April 17, 1940, concerning the control of the interphase level between gasoline and water in the hydrogenation plant at Leuna. Two methods are described in detail. One method uses the differences in electrical conductivity of the two substances; the other, differences in specific gravity. The methods have been worked out for operation at both low and high pressures. Detailed drawings of the apparatus are given.

Frames 990 to 1002

A report on the aromatization of middle oil from coal hydrogenation dated April 10, 1941. The greater part of this report is illegible so that an accurate evaluation of the contents was not possible. Operations apparently were carried out at high hydrogen pressures (450 to 600 atmospheres) and temperature of around 450°C. One catalyst mentioned was Lu No. 7978 (Waldheim catalyst). Gasolines containing from 33 to 46% aromatics were reported.

Frames 1003 to 1014

A report dated April 17, 1941, comparing hydrogenation of middle oil in the gas phase at 300 and 700 atmospheres. The advantages of 700 atmospheres operation are:

1. Cheaper catalyst can be used, hence saving molybdenum and tungsten.
2. Higher through-put can be obtained, and
3. There is a less loss to gas.

The advantages of 300 atmospheres operation are:

1. The materials required for building the plant for 700 atmospheres plant operation are scarce and expensive.
2. The plant cost at 700 atmospheres is higher than the 300 atmospheres even after considering the increased through-put.

No definite conclusion as to which pressure is the most desirable was reached since the type of operation, character of feed stock, and the final products desired, which must enter into each decision vary from case to case.

#### Frames 1015 to 1041

A report on work carried out between January 25 and April 4, 1941, on the hydrogenation of gasoline containing and gasoline free middle oils from the hydrogenation plant at Scholven and from the hydrogenation of Upper Silesian coal. Experiments were carried out at around 500 atmospheres hydrogen pressure and the catalyst was Ruhrol catalyst K413. Complete details of the results of these experiments are given. Typical conditions and results are: Pressure, 500 atmospheres; space rate, one to two V/V/Hr.; gasoline yields from 40% to 70% (including gasoline in charge); aromatic contents of gasolines 40-50%; clear octane number of gasoline 70-80; losses to gas from 16% to 20%.

#### Frames 1042 to 1050

A report dated February, 1944, on work done on the hydrogenation of lignin and brown coal for phenol production. A number of catalysts, temperatures and hydrogen partial pressures were tried and it was found that the most satisfactory conditions were 80 atmospheres pressure, 400°C. with a nickel carbonate catalyst. Under these conditions a yield of 7% phenol was obtained from lignin and 4% from brown coal.

#### Frames 1051 to 1064

A report dated February 23, 1944, giving a comparison of the economics of the Linde and Garelach units for the recovery of ethane, propane and butane from the high concentration gases from hydrogenation. Tables and flow sheets are included.

#### Frame 1065

A note dated May, 1944, concerning the plan of expansion of a plant for working up the coal slurry residue.

#### Frames 1066 to 1075

A report dated February 20, 1939, on an inspection of the rotating kiln at Scholven. A discussion of sludge processing is included with considerable attention being given to the possibility of filtration, centrifuging, pressure distillation, etc., but no conclusions were reached.

Frames 1076 to 1078

March 2, 1944. On the operation of a low temperature carbonization kiln.

Frame 1079

A brief note dated February 25, 1944, containing design data for a rotating kiln.

Frames 1080 to 1082

A report dated November 5, 1943, concerning exchange of experience with rotating kilns. The information is entirely mechanical in nature.

Frame 1083

A brief memorandum dated October 8, 1943, on the installation and operation of rotating kilns.

Frame 1084

A memorandum dated May 26, 1943, on the estimated energy requirements for the low temperature carbonization of high residuals.

Frames 1085 to 1087

Memorandum dated March 12, 1943, on the operation of a rotating kiln at Leuna. One flow sheet is included. Some information on throughput, yield, etc., is included.

Frame 1088

Memorandum dated March 3, 1943, on the use of a rotating kiln for the carbonization of heavy oil containing sand.

Frames 1089 to 1090

A note dated March 3, 1943, describing the operation of a rotating carbonization kiln. A flow sheet showing the operation is included. No technical information is given.

Frame 1091

A memorandum dated February 23, 1943, on the intended use for two new rotating carbonization kilns.

Frame 1092

A memorandum dated March 13, 1943, on the expansion of the coal drying plant.

Frames 1093 to 1095

A memorandum dated March 12, 1943, on the installation of a rotating carbonization kiln. A flow sheet is included.

Frame 1096

A memorandum dated March 13, 1943 on the installation of a new rotating kiln.

Frames 1097 to 1100

February 2, 1943. A description of the mechanical operation of the rotating carbonization kilns, (three copies). A drawing is included.

DHD - AND HF - PROCESS (HYDROFORMING)

Frame 1102

A memorandum giving the amount and composition of gases produced in the hydroforming process without adequate identification as to feed stock, operating conditions, etc.

Frames 1103 to 1106

A memorandum dated the 6th of June, 1942, relative to a discussion of April 27, 1942, on the status of the hydroforming and DHD processes at Luena and Ludwigshafen. Tabular summarization of the effect of temperatures and pressures are given as the basis for conclusions regarding plant construction as follows: avoidance of temperature swings greater than 25°C.; a great range of pressure for the operation, gas recycle rates of possibly 1.5 CBM/Kg never less than 1 CBM/Kg, and feed rates of about 0.5 Kg./L/Hr.

Frames 1107 to 1111

Continuation of discussion comparing results at Luena and Merseburg particularly with regard to adiabatic and tabular heated reactors. Familiar discussion of operating troubles in hydroforming.

Frame 1112

A laboratory memorandum dated March 15, 1944, discussing the use of the hydroformed fraction boiling above 500°C. Of no interest.

Frames 1113 and 1114

A memorandum briefly discussing yields and gas composition in hydroforming. Not of interest.

Frames 1115 and 1116

A chart illustrating the yields of products obtained in hydroforming several different type naphthas. Typical yields shown for hydroforming 126,000 tons of paraffin base oil are 100,000 tons of hydroformed naphtha, 1560 tons isobutane, 3250 tons of normal butane, 6700 tons of ethane, 7,000 tons propane and 4100 tons of methane.

CATALYTIC DEHYDROGENATION OF BUTANE

Frames 1118 and 1119

A memorandum reporting laboratory results obtained on dehydrogenation of normal butane and isobutane with two catalysts, one a 9% alumina, 5% chromic oxide composition, the other an alumina base catalyst prepared by precipitating from aluminum nitrate solution with ammonia and containing 90% aluminum oxide, 8% chromic oxide and 2% potassium oxide. The yields and conversions obtained with the latter catalyst were substantially better than those obtained with the former. Typical figures for the latter catalyst are the conversion of 25% of normal butane per pass with a 90% ultimate yield operating at 520 - 580°C. with an 8-hour reaction period and at a space rate of 1,000 volumes of gas per volume catalyst per hour.

Frames 1120 and 1121

A memorandum dated December 17, 1941, giving equilibrium figures in the dehydrogenation of butane calculated from the literature.

Frame 1122

A memorandum giving results obtained in a 5-liter pilot reactor on normal butane dehydrogenation. No data of interest.

Frame 1123

Another memorandum dated February 7, 1942, referring to butane dehydrogenation and containing no technical information of interest.

Frames 1124 to 1127

A memorandum discussing the development of a preferred catalyst for butane dehydrogenation. It is concluded that a peptized alumina base material is most desirable from the standpoint of catalyst activity and life, that the optimum chromic oxide content is within the range 7 to 15%, that the catalyst should contain potassium as the alkali metal and that its concentration should be 2% expressed as potassium oxide. A description of the peptizing procedure for the alumina base material used is given.

Frames 1128 to 1129

Description of experimental catalyst tubes used at Leuna and Oppau for experimental tests of dehydrogenation catalyst. Standardization of testing methods discussed.

Frames 1130 to 1132

Historical outline of the development of butane dehydrogenation for iso-octane production starting in 1934. Production started in 1940. Isomerization began in 1936 in a preliminary fashion. Polymerization

proven in 1939. Became aware of foreign work on alkylation by literature and patent publications in 1936 and 1937. Started work at Luena in 1938. Pilot plant work started December 1939. First large scale results in March 1944.

Frame 1133

Not of interest.

Frames 1134 to 1135

Draft of report on butane dehydrogenation showing results similar to those given before for the two catalysts. Status of alkylation discussed. Status of butylene concentration with silver nitrate wash. Status of isomerization in Luena.

Frame 1136 to 1143

October 15, 1942. Cost estimation for alkylate fuel by several processes. Discussion of economics of the several processes leads to conclusions that the process involving butene from butane by catalytic dehydrogenation is most economical and that other processes; such as, dehydrochlorination are more expensive.

Frames 1144 and 1145

Summary of the estimated investment and operating costs for butylene production and alkylate production by the several processes.

Frames 1146 to 1149

Summary of costs of production of iso-octane.

Frame 1150

A block flow diagram for an alkylate plant incorporating catalytic dehydrogenation and isomerization.

Frame 1151

Flow diagram of similar processes.

Frame 1152

Alkylate plant flow diagram with butenes production by dehydrochlorination and without isomerization.

Frame 1153

Similar flow diagram with isomerization.

Frame 1154

Flow diagram of alkylate plant with dehydrochlorination and isomerization using slightly different process.

Frame 1155

Flow diagram for production of ET-100, isooctane, by dehydrochlorination to isobutane, polymerization and hydrogenation. Normal butane is isomerized to isobutane.

Frame 1156

ET-100 production by very slightly different process.

Frame 1157

Stock balance flow diagram for dehydrochlorination by the Bahr process with increased butadiene production.

Frames 1158 to 1159

Description of step-wise dehydrogenation of butane in four adiabatic steps with reheating between each step. Advantage taken of heat exchange. Small possibility that commercial application would be carried out soon. Dated December 3, 1942.

Frames 1160 to 1162

February 10, 1943. Cost comparison of the fixed bed and moving catalyst bed for butane dehydrogenation. On the basis of investment cost and steel requirements, the fixed bed process is preferred. With a catalyst life of 1,000 hours the fixed bed process has definite economic advantages.

Frames 1163 to 1166

Summary tables for cost comparison on fixed and moving catalyst bed for butane dehydrogenation.

Frames 1167 to 1168

Weight balance flow diagrams for catalytic dehydrogenation of butane for alkylate production.

Frame 1169

Flow diagram of the step-wise catalytic dehydrogenation of butane described above.

Frames 1170

July 28, 1943. Regarding a large scale test on butane dehydrogenation at Leuna. Mentions high pressure drop on regeneration and the



necessity for large compressors. Present equipment limitations would give long regeneration periods and plant would have to be built differently for low pressure drop.

Frame 1171

September 14, 1943. Discussions of fixed bed dehydrogenation tests and particularly the difficulties in setting up a suitable cycle.

Frame 1172

Cycle diagrams for Frame 1171.

Frames 1173, 1174

March 26, 1944. It was concluded from American literature that propylene could be used in alkylation but that the acid consumption would be high, of the order of 1/2 pound per pound of alkylate and that higher temperatures would have to be used. Propylene would be derived by fixed bed catalytic dehydrogenation of propane in heated tubular reactors giving 20% conversion and 88% yield. The alkylation of propylene would have meant extensive changes and a large investment in alkylation plants. The acid consumption would be too high for practical value. No product quality data were available.

ALKYLATION

Frame 1176

This gives a brief statement of the status of sulfuric acid alkylation at the Leuna Works January 28, 1941. Alkylate qualities and yields are related to isobutane concentration, operating temperature and acid concentration. The highest octane number shown is 97 obtained at 0°C. and 80% isobutane concentration. None of the data shown are new or of particular interest.

Frames 1177, 1178 and 1179

These show flow diagrams together with a brief discussion of a large scale alkylate test run at the Leuna Works April 7, 1941, using a reactor of about 100 gallons capacity. Isobutene was the olefin charged in order to increase the sensitivity of alkylate quality relative to the operating conditions used. The operating temperature was 0°C. and the alkylate concentration, 20%. The octane number of the alkylate produced was 95 to 95.5 by the motor method. No features of particular interest were noted.

Frames 1180 to 1192

A discussion of the status of normal butane dehydrogenation and of alkylation at the Leuna Works as of June 9, 1942, is reported. Experimental results obtained with two dehydrogenation catalysts are briefly described. Typical figures for a catalyst comprising alumina clay containing 10% chromic oxide and 2% potassium oxide are 30% conversion to unsaturates per pass and 88 to 90% ultimate yield of butene. With the second catalyst comprising peptized alumina clay, again containing chromic oxide and potassium oxide, both the conversion and ultimate yields are slightly higher, 33% and 92 - 94%, respectively. The peptized alumina base catalyst also exhibited greater stability in runs lasting up to 400 hours. No particularly new features on normal butane dehydrogenation were noted.

The status of butene alkylation, normal butane isomerization, and of butylene extraction from a  $C_4$  cut with silver nitrate solution are briefly described and illustrated with charts and tables. The charts show typical effects of well established operating conditions on alkylate quality, acid consumption, etc. In connection with the discussion of butane isomerization an aluminum chloride catalyst containing iron is referred to as being much more active than pure aluminum chloride.

Frame 1193

A brief letter discussing sulfuric acid requirements in alkylation dated July 22, 1942. Refers to certain improvements made but gives no quantitative figures.

Frames 1194 to 1216

A report of the first commission of mineral oil discussing the status of alkylation as of April 9, 1941, is presented. The report emphasizes the importance of maintaining a high concentration of isobutane for best alkylate quality. A typical acid consumption reported is 10% by weight of the alkylate at 45% isobutane concentration. The acid requirement is stated to increase with decreasing isobutane concentration. A brief discussion of the separation of butene from the  $C_4$  cut by washing with 50% silver nitrate solution is presented. The relative advantages and disadvantages of silver nitrate wash versus straight distillation for eliminating normal butane in the reaction mixture and maintaining a high isobutane concentration are reviewed. In reference to the production of butene by catalytic dehydrogenation of normal butane the statement is made that the product contains a predominance of alpha butene.

A discussion of sulfuric acid recovery indicates that the method used was dilutions to about 50% concentration, separation of the oil layer and reconcentration to 96% acid. The yield of acid in the recovery step was 80-85%, corresponding to a net fresh acid requirement of 2% by weight of the alkylate.

The report refers to a number of charts giving quantitative relations on effects of operating conditions in alkylation, solubility of butene in silver nitrate, etc. These charts are missing.

Frames 1217 to 1226

A general exchange of information by operators of butane dehydrogenation plants using the T-52 process is presented. No items of interest were noted.

Frames 1227 to 1243

A discussion of the comparative costs of alkylate manufactured by the catalytic dehydrogenation route and by the chlorination-dehydrochlorination sequence starting with normal butane. In both cases tables and flow diagrams including specific cost figures and material balances are included. The report was dated November 2, 1942.

Frame 1244

A request for a sample of butene prepared by acetylene hydrogenation and to be used in alkylation experiments is made. Of no interest.

Frame 1245

A letter commenting on the increase in sulfuric acid consumption caused by the butadiene in the butene resulting from synthesis by acetylene hydrogenation. A 25% increase in sulfuric acid consumption due to the butadiene content is mentioned.

Frame 1246

A letter reporting the composition of the olefins obtained by acetylene hydrogenation. Typical figures in the C<sub>4</sub> fraction are 8% butadiene and traces of isobutene, 40% of alpha butene and 40% beta butylene.

Frame 1247

A letter dated April 16, 1943, reporting a 25% increase in sulfuric acid consumption due to use of butene containing 7% of butadiene.

Frame 1248

A tabulation of productions of C<sub>3</sub> and C<sub>4</sub> hydrocarbons from several Fischer plants. Of no interest.

Frames 1249 to 1250

Minutes of a meeting July 16, 1943, on sulfuric acid consumption giving typical figures of 20 - 25% by weight of alkylate produced. This consumption is considered excessive and several experiments are programmed for reducing the sulfuric acid consumption. The type of experiments planned indicates that the cause of the high acid consumption is diolefins.

Frames 1251 to 1265

An exchange of information on butane catalytic dehydrogenation and sulfuric acid alkylation dated August 27, 1943. In the sulfuric acid alkylation step difficulty due to high acid consumption, corresponding to 30% by weight of the alkylate, was mentioned. This high consumption was due to the presence of diolefins in the butene feed resulting from the catalytic dehydrogenation step. Plans were being made to reduce the diolefins by a selective catalytic hydrogenation step. It was expected that this would reduce the acid consumption to 10% by weight of the alkylate. Frame 1258 mentions a 96 octane number alkylate obtained from isobutene in the plant scale as compared to a 94 octane product expected from small scale experiments. In connection with the high acid consumption in the alkylation step, the operating temperature in the catalytic dehydrogenation step for normal butane was reduced to 720°C. as compared to the usual 800°C. in isobutene dehydrogenation.

Frame 1266

A letter commenting on difficulties in obtaining a sufficient supply of alkylate due to the small supplies of isobutane and olefins. Of no interest.

Frames 1267 to 1268

A letter dated May 26, 1944, referring to plans for propylene alkylation, the propylene to be derived by dehydrogenation of propane. The catalyst to be used in the dehydrogenation is not identified. Typical operating conditions planned are a reaction period of 6 hours, regeneration period of 4 hours with regeneration by gas containing 1-1/2% of oxygen. The conversion of propane per pass was to be 20% and the yield of propylene expected was 88% with a coke formation of 3%.

Frames 1269 to 1271

A letter dated June 15, 1944, referring to use of butene derived from Fischer plants in sulfuric acid alkylation. Of no interest.

Frame 1272

A memorandum dated July 25, 1944, referring to planned work on alkylation of propylene with isobutane using HF and other fluorine compounds as catalyst with the specific object of yielding triptane. No data are given.

BUTANE ISOMERIZATION

Frames 1273 to 1276

A memorandum referring to a process for n-butane isomerization using as catalyst alumina and other porous materials such as activated carbon, pumice and clay impregnated with aluminum chloride. A brief discussion of the merits of various concentrations of aluminum chloride in the porous support is given. No features of interest were noted.

Frames 1277 to 1278

A memorandum dated April 24, 1942, referring to the operation of the butane isomerization plant at the Leuna Works. An aluminum chloride consumption corresponding to 1% by weight of the isobutane produced is mentioned comparing with a consumption of 5/10 to 6/10% by weight predicted from pilot operations.

Frames 1279 to 1282

A memorandum commenting on the operation of the Rumanian Plant for isomerization of normal butane. Of no interest.

Frames 1283 to 1287

Minutes of a meeting dated October 16, 1942, on butane isomerization referring largely to various mechanical problems. Not of interest.

Frame 1288

A letter dated February 16, 1943, requesting details of experimental results for reducing the formation of propane and pentane during isomerization of butane. No technical information is given in this letter.

Frame 1289

A letter dated February 23, 1943, referring to butane isomerization but including no technical information of interest.

Frame 1290

A letter dated September 13, 1943, referring to butane isomerization and again containing no technical information.

METHYLATED BUTADIENE (Verbatim translation of this section is appended)

Frames 1291 to 1293

A memorandum referring to the splitting of dimethyl dioxane to yield isoprene, formaldehyde and water and similar conversion of 1,3 butylene glycol to yield butadiene. The catalyst used is a graphite base containing 5-10% sodium pyrophosphate, 3% free phosphoric acid and 30% dimeric sodium metaphosphate. In the conversion of dimethyl dioxane an alternative route involving pressure hydrogenation to yield methanol and 1,3 amylene glycol followed by dehydration of the latter to yield isoprene is mentioned as a possibility.

Frame 1294

A letter dated February 8, 1943, again referring to conversion of 1,3 dimethyl dioxane to isoprene by the two alternative routes, one involving direct splitting and the second involving hydrogenation to amylene glycol followed by dehydration. The letter states that the previous difficulty from gum formation and attendant high catalyst consumption in the direct splitting route has now been overcome and the more complicated two step process is therefore no longer necessary. The catalyst consumption mentioned is 1.3 to 2% of the isoprene made.

Frame 1295

A letter dated February 23, 1943, again commenting on the conversion of 1,3 dimethyl dioxane to isoprene and agreeing that the direct splitting route is the most desirable inasmuch as some difficulty had been encountered in the two step route involving intermediate conversion to glycol.

Frame 1296 and 1301

A memorandum dated January 5, 1942, briefly describing polymerization experiments conducted with 2,5-dimethyl hexadiene-1,5 and tetra methyl butadiene. Both compounds were obtained from isobutene. With a sodium catalyst, no polymerization of the dimethyl hexadiene was obtained. In an emulsion polymerization experiment using dimethyl hexadiene along with butadiene in a 1-1 ratio at 50°C. and for 48 hours complete conversion of the butadiene was obtained but no polymerization of the dimethyl hexadiene.

Frames 1297 to 1300

A memorandum dated October 25, 1942, referring to large scale experiments on the manufacture of methylated butadienes for manufacture of adhesive rubbers. The process described is the addition of two moles of formaldehyde to an olefin to yield a cyclic ether of alkylated 1,3 propane diol (formation of the so called 1,3 dioxanes), the cyclic ethers then being catalytically split to yield formaldehyde, water and the desired diolefin. The typed material in Frames 1297, 1298 and 1299 is very obscure. Frame 1300 is a clear chart giving the yields apparently obtained in the large scale experiments described. This chart shows that in conversion of isobutene to the desired cyclic ether, the yield was 85-90% based on the isobutene and 80% based on the formaldehyde. In the splitting step, the conversion of the methylated dioxane to the desired olefin was 40% per pass with 60% remaining unreacted. Of the 40%

~~Restricted~~

dioxane converted 95% went to isoprene, formaldehyde and water and the remaining 5% to isobutene and formaldehyde.

### TOLUENE FROM XYLENE

#### Frames 1302 to 1306

A memorandum dated January 14, 1943, describing the potential production of toluene by demethylation of xylenes and heavier aromatics. The process proposed involves contacting a fraction boiling from 115 to 250°C. with an aluminum silicate cracking catalyst at 460-480°C. along with a hydrogen gas pressure of 200 atmospheres to yield a product containing 50% toluene plus benzene and 50% of higher boiling materials. The total charge to the reactor comprises a 50-50 mixture of the 115 to 250°C. boiling range net feed and recycle stock boiling higher than toluene. A flow diagram on Frame 1306 shows a production of 675 tons of pure toluene and 340 tons of benzene from 1500 tons of net feed. A complete translation is appended.

#### Frame 1307

A letter dated January 29, 1943, briefly discussing general economic problems and feed stock availability in the conversion of xylene and heavier aromatics to toluene. One of the feed stocks considered was one containing 10% toluene, 50% xylene and 40% heavier fractions.

### HF PROCESS AND CRACKING AT MOOSBIERBAUM

#### Frame 1310

Catalytic cracking at Moosbierbaum. State of the catalytic cracking knowledge and report of development in 1941. Three possible processes were being investigated, fixed bed, moving catalyst with beads or pellets, and dust-form catalyst in gas phase cracking. The first process had been given thorough pilot plant study, and a charge rate of 0.6 V/V/Hr. gave a 30% yield of aviation gasoline from Rumanian gas oil. The satisfactory strength of the new catalysts made the moving bed process seem more desirable. The pilot plant was to begin operation in January 1942. Many methods of using the dust catalyst were developed. The most promising was the "Weltube" process which seemed to be better than the American process. The experimental state of fluid cracking was really just beginning. All three processes of cracking were to be studied at Leuna in 1942.

#### Frame 1311

Status of DED hydroforming processes in pilot plant scale at Leuna and Moosbierbaum. Adiabatic vessels with three chambers of graduated activity were used to give a yield of hydroformate of 75-76% containing 50% aromatics. With tubular reactors many experiments were made to make available design data for construction of a plant. The

data showed about the same yields in the pilot plant as in the laboratory scale equipment. The work was to be continued.

Frame 1312

Production of higher olefins. It was pointed out that the olefins in the range of C<sub>12</sub> to C<sub>20</sub> were desirable as raw materials for various synthetic processes, for example, the Grc process. By dehydrogenation or cracking of paraffinic raffinates, it was believed that a sound process for carrying out olefin production was possible. The experimental work was yet exploratory.

Frame 1313

Experiments on preparation of specification fuels from primary products of Synol. The fractions of Synol product boiling in the gasoline and Diesel oil ranges were not normal fuels in several respects. By retreating the gasoline boiling up to 200°C. with clay and dehydrating the higher alcohols present, a product can be obtained that is oxygen free and rich in olefins. This treatment raises the octane number, increases storage stability and improves odor. After the addition of inhibitor, the gasoline is satisfactory. Without such catalytic treatment, the gasoline boiling up to 160°C. has satisfactory octane number. The corrosive and gum constituents can be removed by hot caustic treatment. The addition of inhibitor, tricresol, prevents their further formation and the product is usable. Also, the storage stability of the original material can be improved by a sodium bisulfite wash. By removal of the fatty acids and esters from a suitable boiling range fraction with caustic, a suitable Diesel oil can be obtained. The yield of gasoline and Diesel oil from Synol amounts to about 44% and 31%, respectively. The work on this project was concluded.

Frames 1314 to 1318

February 1 to June 15, 1941. Preparation of high octane fuels from hydrogenation gas fractions. A statement of the practicability of normal and isobutane dehydrogenation. An indication that butene dehydrogenation to butadiene would be practical, statements on the status of the formation of isoprene from dimethyl dioxane which is in turn derived from butene and formaldehyde, the isomerization of n-butane, the sulfuric acid alkylation of isobutane with butylenes, (giving operating conditions and properties of alkylate), the concentration of butylenes by silver nitrate solution, the drying of butene for sulfuric acid alkylation with several drying agents, the most practical being calcium chloride solution. All of these processes were in the experimental stage.

Frames 1320 to 1330

September 22, 1941. An instruction from the supreme commander of the Luftwaffe to the Leuna Works ordering 42,000 to 66,000 tons of hydroformate gasoline per year to be produced from Rumanian straight-run naphtha. A second plant was to be built within a year for an additional yearly production of 75,000 to 125,000 tons of hydroformate gasoline. Gives specifications for the straight-run and the hydroformate gasolines including yield. Gives methods of testing and price to be paid (30.88 marks per kilogram of hydroformate) charging instructions, conditions of payment, and secrecy order.



Frames 1331 to 1339

September 4, 1941, at Leuna. Discussing the hydrogenation of residual oils. A plan for Moosbierbaum hydrogenation was outlined. It included treatment of Rumanian crudes. The possibilities for hydrogenation were to (1) hydrogenate the residuum in liquid phase and crack the resulting gas oil to gasoline in the gas phase (2) to crack the residue in liquid phase to gas oil and gasoline, catalytically crack the gas oil and convert the resulting Diesel oil into gasoline with catalyst 6434 and use the gasoline as raw material for hydroforming, (3) the residue is cracked by pressure distillation at about 30 atmospheres over catalyst 7846 which is aluminum oxide plus 7% molybdenum oxide and 3% nickel oxide into gasoline and gas oil. The gas oil is to be further treated in the gas phase. For the processing of residue, two extremes cases were considered, one for a paraffinic oil, the other for a naphthenic oil. For case one above, the treatment would be carried out in the liquid phase at 700 atmospheres with 2-1/2 per cent iron catalyst based on charge with a rate of 0.5 to 0.55 V/V/Hr. Stabilizer product containing 50% oil up to 350°C. and 12% gas yield. For the paraffinic raw material, 215 kg. of gasoline and 653 kg. gas oil would be obtained for each ton of charge. Similarly, for the naphthenic oil 213 kg. gasoline and 651 kg. gas oil would be obtained per ton. The resulting gas oil would be treated at 300 atmospheres after washing with sulfuric acid to remove nitrogen compounds. Catalyst 6434 was to be used with the same yield as shown above. Gas compositions and product inspections are given. The second case of liquid phase plus catalytic cracking in gas phase conversion were similarly treated for the two possible charging stocks. Weight balance and utility requirements are listed. Plant cost estimates are given. Heat and weight balance diagrams are shown.

Frames 1340 to 1342

June 26, 1942. Answer from Leuna to Luftwaffe on aviation gasoline, suggesting changes that should be made in the specifications of the gasoline to be produced.

Frames 1343 to 1350

Leuna, October 11, 1942. Review of the start up of the hydroformer at Moosbierbaum. Covers a period from July 15, 1942, to August 6, 1942. The usual difficulties with leaks, heat exchanger plugging, temperatures, compressor operations, etc., are described. The properties of the product made during this preliminary operation are listed.

Frame 1351

Moosbierbaum, September 26, 1942. A discussion of the changes desired in the plant as a result of the experience obtained in starting up the hydroformer.

Frames 1352 to 1356

More of same, illegible.

Frames 1357 to 1359

September 17, 1942. Chronological review on the construction of the hydroformer at Moosbierbaum. A detailed history of the construction and experimental work leading to the final hydroformer at Moosbierbaum. Gives the basis for design, selection of plant sites and ends with the start of operations and plant repairs after preliminary operation. It was concluded that hydroforming was a good process and that the difficulties were mechanical rather than process. Statement was made that the hydrogenated naphthas are better than paraffinic oils because of higher naphthene content.

Frame 1360 to 1361

October 1942 at Moosbierbaum. A statement of the conditions for reaction with a Rumanian naphtha of 48 to 50°C. aniline point and with 20-25% boiling up to 100°C. and a statement of the regeneration conditions. The temperatures are given in terms of millivolt readings on thermocouples.

Frames 1362 to 1369

Leuna, October 9, 1942. Starting operations of the hydroformer at Moosbierbaum from September 13 to October 2, 1942. A review of the equipment operation and conditions of process with a Rumanian charge of naphtha. Charge rate was 0.4 kg. light naphtha per liter of reaction space per-hour, 15 atmospheres pressure, 9,300 cubic meters recycle gas, recycle gas density of 0.53 to 0.56. Aniline point of unstabilized product -10°C., aromatic content of product about 60% by volume for temperatures 510 to 530°C. Transfer line temperature drop 8°C. maximum. Temperature drop varied from 5° to 30°C. in the central thermowells and from 10° to 60°C. in the outer wells near the wall. The average cycle used comprised 12.5 to 15 on-stream hours, 1-1/2 hours purge of recycle gas, 1 hour inert gas purge, 7 to 8 hours regeneration, 1 hour inert gas purge, 1 to 1-1/2 hours for repressure with recycle gas, 2 ovens in parallel operation on-stream for 1-1/2 to 2 hours. Quantities of coke were calculated by reaction heat during regeneration from thermocouple readings and amounted to about 0.6 to 0.8% from the inner couples and from 0.35 to 0.40% on the thermocouples in the outer catalyst layers. The coke distribution was very uneven, 15 to 20% in the first reactor, 25 to 35% in the second reactor, and 45 to 60% in the third reactor. Temperature rise on regeneration averaged 80 to 100°C. with a maximum of 125°C. The regeneration air amounted to about 400 to 800 cubic meters per hour with the average value in the neighborhood of 600 to 700. The oxygen content of the regeneration gas varied from 0.75 to 1.6 volume per cent. The inspections on charge and products are given.

Frames 1370 to 1375

Stock balance flow diagrams involving catalytic cracking and hydroforming. Includes some thermal cracking, distillation, solvent extraction.

Frames 1376 to 1380

November 6, 1942. A monthly report on the operations of the Moosbierbaum hydroformer for October 1942. Gives the charge quantities, yields, and analytical data for the month's operation. Average utility requirements are given. The experimental conditions for tests run with Rumanian and Hungarian naphthas are outlined. Part of operations hampered by lack of raw materials.

Frames 1381 to 1384

Monthly report for November 1942, December 6, 1942. Plant ran at a low charge rate averaging 0.275 kg. per liter per hour. Again Hungarian and Rumanian naphthas were charged and product inspections given. The conditions of the operations were tabulated.

Frames 1385 to 1386

November 27, 1942, at Leuna. Suggestions for treatment of Deurag crude at Moosbierbaum. Describes four cases for the process design of equipment to treat the Deurag crude. Includes hydrogenation, distillation, thermal cracking, catalytic cracking; gives stock balances and investment costs.

Frames 1387 to 1391

November 30, 1942. A cost estimate for the Austrian project.

Frame 1392

December 7, 1942. Memorandum regarding the Austrian project. Of no interest.

Frames 1393 to 1394

A statement of the experimental work in 1942 on fuels by (1) catalytic cracking with fixed bed, moving bed and with fluid catalyst, (2) hydroforming in adiabatic reactors or tubular reactors and (3) the preparation of anti-knock fuels from hydrogenation gas by isomerization of butane, the separation of paraffin-olefin mixtures, by azeotropic distillation, dehydrogenation of butane and propane, and by alkylation. Further product and catalyst studies will be carried out in order to have a basis for the design of the hydroforming plant and for the planning of a 100,000 yearly ton plant for catalytic cracking at Moosbierbaum. A statement that new processes will be studied.

Frames 1395 to 1396

January 7, 1943. Discussing the hydroforming of gasoline obtained from Zeitz. Two samples of low boiling hydro gasoline of relatively high bromine number and low naphthene content caused some difficulties in hydroforming. The two gasolines had 35 volume per cent and 30.5 volume per cent boiling up to 100°C. The high bromine number, 6.6 and 3.0, respectively, were described as the cause of the difficulties of increased coke formation. Apparently, short on-stream periods only were possible. The yield and aromatic content of the products were given. A tabular summary is included.

Frame 1397

February 13, 1943. (An appendix to something apparently misplaced) Discusses the change of gasoline specifications, particularly, the effect of higher end point on yield of aviation gasoline from hydrogenated gasoline or hydroformate gasoline.

Frames 1398 to 1405

June 15, 1943. A report for the month of May on operations of the Moosbierbaum hydroformer. Charge and product rates are given in addition to product inspections, operating conditions and operating difficulties. The operation of the predistillation, stabilizing, redistillation equipment is shown. A change in the distribution of catalyst in the chambers was planned.

Frame 1406

August 25, 1943. A letter from the Moosbierbaum plant to the Reich minister for aviation reviewing some of the conditions of the gasoline specifications contract.

Frames 1407 to 1409

July, 1943. Shipping instructions and specifications for VT401 gasoline, aviation gasoline for inland use.

Frame 1410

Missing

Frame 1411

October, 1943. Instructions to the Moosbierbaum plant to designate their product as VT371.

Frames 1412 to 1413

December 9, 1943. A report on fuel research in 1943. In catalytic cracking, the conclusion was reached that the moving bed process was superior to the fixed bed process. Many difficulties were experienced with the fluid catalyst in the counter-current operation. The hydroforming process was subjected to further investigation in connection with the Mocoelberbaum plant.

Gas Phase Hydrogenation

Through the use of synthetic catalysts, aluminum silicate with the addition of about 1% molybdic acid, oxygen and nitrogen-free aromatic gas oils of 70 volume per cent aromatics can be obtained with a yield of 87% at 200 atmospheres and 400 to 420°C. with a space rate of 0.4 kg./l./hr. Somewhat similar results could be obtained with the DED residue with a catalyst containing more molybdic acid, about 5%. This latter is called the Arebin process. For processing phenol and pyridine containing gas oils, a two step process was developed. The first step consisting of prehydrogenation with the hydroforming catalyst at 500°C. and the second step corresponding to the Arebin process. From coal tar, a yield of 80% of high power fuel containing 55 to 60 volume per cent of aromatic was obtained.

Dealkylation of the toluene rerun bottoms from Waldenburg in the presence of hydrogen at 100 to 200 atmospheres and 500°C. produced nitration grade toluene. Suitable catalysts include alumina-molybdic oxide at a charge rate of 0.2 kg./l./hr., giving a toluene yield of 50 to 55%, and two aluminum silicate-chromic oxide catalysts at a charge rate of 0.15 kg./l./hr. with a yield of 45 to 50 weight per cent toluene and giving much smaller amounts of methane than the molybdenum catalyst.

Work was being done on recovery of valuable oxygen compounds such as raw phenols from coal.

Preparation of Anti-Knock Fuels  
from Hydrogenation Gas Fractions

Many technical problems on AT 244 including alkylation, isomerization, and olefin-paraffin separation were worked on. For a long time the high sulfuric acid consumption in alkylation was caused by high butadiene content of the feed. This resulted from unfavorable dehydrogenation conditions, but better temperature conditions in the dehydrogenation oven and drying of the regenerated catalyst resulted in a decreased acid consumption.

Dehydrogenation of Butane and Propane

Better results were obtained for butane by using a fixed bed process in tubular vessels than in the moving bed process. It is expected that good results will be obtained for propane dehydrogenation. Work is being continued on the improvement of dehydrogenation catalysts.

Preparation of Isoprene and Methyl Isoprene from  
Formaldehyde and Isobutylene or Tri Methyl Ethylene

The dimethyl dioxane preparation gave, at 50°C., complete aldehyde utilization with yields of 80 to 85%. Trimethyl ethylene with formaldehyde gives trimethyl dioxane and preparation of methyl isoprene can be carried out with the same results as for isoprene preparation. The trimethyl ethylene could be made by partial hydrogenation of isoprene, by dehydration of C<sub>5</sub> alcohols, and by the isomerization of other branched amylenes over catalyst 163. Decomposition of trimethyl dioxane is carried out over the phosphoric acid-Kieselguhr catalyst with a catalyst consumption of about 1%, based on product, and with conversions of 40 to 50% and yields of 85 to 90%.

Work for 1944

Pilot plant cracking with the moving catalyst bed will be continued for conclusive study. Pilot plant studies will be carried out on hydroforming, Arobin and toluol processes. The recently found butane and propane dehydrogenation conditions will, if necessary, be translated to large scale plants. A half ton per day isoprene plant will be operated for both process steps.

Frames 1414 to 1429

April 18, 1944, Leuna. The partial description, stock balance calculations and process design for a moving bed catalytic cracker for three possibilities of charge rate: 130,000 yearly tons, 100,000 yearly tons, and 100,000 yearly tons with smaller regeneration capacity. After setting the basis for the calculations, the reaction vessels sizes and regeneration vessel sizes were calculated. Detailed calculations follow for two regeneration conditions giving air quantities and inlet temperatures. The control of the humidity of the spent regeneration air appears to be of some concern but without any stated reasons. Air blower requirements, including power, are included. The increased weight of metals used in the second case, a 60 square meter regenerator instead of the usual 36 square meter, are given with the estimate of additional cost. Sizes and costs of heat exchangers, blowers, and piping are included. One chart and two drawings of the regenerators are included.

Frames 1430 to 1435

June 20, 1944. A monthly report on the Moosbierbaum hydroformer operation for May. Gives the typical operating conditions, yields, and product quality inspections. Mentions the decrease in supply of Rumanian naphtha charge.

Frames 1436 to 1439

October 17, 1944. Monthly report for the August 1944, operations at Moosbierbaum. The plant was shut down June 26, 1944, because of air raid damage but was again producing August 5. Another raid occurred August 28 for a total of six alarms during the month. Operation was continued as much as possible but extensive damage to the distillation equipment control house and the redistillation section, the heavy gasoline stabilizer, the recycle gas absorber and surge tankage hampered operation. Piping and wharves were damaged. Because of the loss of predistillation

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equipment, the raw naphtha was fed directly to the plant and difficulties were experienced with the heat exchangers. Plans were made to repair damage as quickly as possible, to obtain high production rates and to provide better protection for personnel and the plants against air raids.