

FILM STUDY GROUP

REPORT

T.O.M. REEL NO.55

Prepared by

THE ATLANTIC REFINING COMPANY

Atlantic Ref. Co.
F.S.G.

L.L. Newman

SCANNING OF REEL #55
(Orig. Ident. Reel 30)
U.S. Government Technical Oil Mission
Bag 3414 - Target 30/4.17

SECTION 14. PATENT DISCLOSURES-UERDINGEN 1941-1945
(Completed from Reel #54)

The practice begun on other reels of listing all patent disclosures on a single reel in one place, will be followed and an appendix to this report shows such a list.

Frame 2, #1279, Mar. 13, 1942. Floor and wall coverings. The mixture of filler and an aqueous solution, emulsion or dispersion of urea-aldehyde condensation product in which the organic insoluble film-former is dispersed in colloidal form, is brought upon the surfaces to be covered.

Frame 7, #1280, Mar. 16, 1942. Hydrogenation of aromatics. Employing nickel catalyst containing chromium oxide distinguished by containing aluminum oxide.

Frame 9, #1281, Mar. 24, 1942. Hydroxylamine disulfo acid alkali. The production of sodium salt from the nitrite, bisulphite or sulphurous acid is distinguished in that the solution of alkali nitrite and alkali bisulphite is first brought continuously into a reaction space in which the solution is contacted with SO₂ to a pH-value of about 4-6, and then this solution is continuously passed to a second reaction chamber with further introduction of SO₂ until a pH-value below 2.5 is attained.

Frame 11, #1282, Mar. 31, 1942. Benzylcellulose with low benzyl content. Alkali cellulose is reacted with about 3 to 4 times its weight of benzyl chloride and about 0.5 to 2 times its weight of KOH in the form of a 20-35% solution.

Frame 14, #1272, Jan. 30, 1942. Wood board.

Frame 18, #1276, Jan. 26, 1942. Preservation of organic material such as wood, etc. Employing a solution which contains lead ions and ferricyanide ions as alkali or ammonia salt of a lower fatty acid or oxygenated fatty acids.

Frame 20, #1277, Feb. 27, 1942. Oxydiphenyl methane-carboxylic acid. The chloromethyl benzoic acid is condensed with phenols, if necessary in the presence of an acid condensation agent.

Frame 24, #1275, Feb. 26, 1942. Disinfectant and preservative material. The use of azides in which the azido group is combined with an organic residue in nonionizing compound. One of the examples cites that a weakly alkaline 15% gelatine solution was protected against bacterial attack by 0.2% sodium azido thiocarbonate or 0.3% potassium azido acetic acid.

Frame 27, #1271, Jan. 26, 1942. Condensation products. Production of condensation products of the alkyl resin type characterized that a lactam is used.

Frame 30, #1263, Jan. 13, 1942. Preservative material. Consisting of a solution which contains ferricyanide ions, the ions of a heavy metal forming sparsely soluble ferricyanide former. One of the examples cites use of textile preservative consisting of a 1% aqueous solution of a mixture of 17 parts by weight silver nitrate, one hundred five parts ammonia and 11 parts potassium ferricyanide. This solution is reduced on the fibres to make the insoluble silver ferrocyanide which was an effective protection against rot.

Frame 33, #1269, Jan. 15, 1942. Removal of silicate containing chill-mold surface in which the surfaces are treated with aqueous solution which contains hydrofluoric acid and/or an acid fluoride and if necessary a metal protecting substance.

Frame 35, #1270, Jan. 22, 1942. Formed substances from synthetic linear polyamides characterized that they contain at least one free oxy group. The example cites that 60 parts hexamethylene diamine adipate and 40 parts epsilon-amino caproic acid is used to make a super polyamide. A mixture of 300 parts of this product is dissolved at 60° in 853 parts methanol and 120 parts water, and is decomposed with 150 parts hexanetriol from formaldehyde acetal. Pouring the solution upon a flat plate and drying at 70° immediately gives a clear film of good flexibility which retains this property at extreme dryness and at temperatures down to -20°.

Frame 38, #1245, Oct. 10, 1941. Production of Chromates. A mixture of the alkaline residues of chromium ores and chromium oxides or other compounds of trivalent chromium is roasted with alkali.

Frame 41, #1246, Oct. 14, 1941. Production of Chromates. A mixture of low chromium slag and chromium oxide or other compounds of trivalent chromium roasted in an alkaline condition.

Frame 44, #1259, Dec. 5, 1941. Paint binder material. Employment of aqueous solutions or emulsion of urea aldehyde condensation products which has been reacted with polyvinylacetate.

Frame 46, #1260, Dec. 5, 1941. Softening and gelatinizing material. Employment of amino-oximes or their functional derivatives for lacquers, films, etc. One of the examples cites the use of the solution of 100 parts acetyl cellulose in 400 parts acetone, 200 parts toluol and 300 parts glycol monomethyl etheracetate reacted with 50 parts of benzamide oxime.

Frame 48, #1261, Dec. 8, 1941. Preserving Process. Preservation of organic substances such as textiles, employing solutions which contain lead ions and ferricyanide ions.

Frame 50, #1262, Dec. 8, 1941. Oxidation products of saturated cyclic hydrocarbons. Employing oxygen or oxygen-containing gas mixtures at temperatures above 100° and at elevated pressure in the presence or absence of

oxidation accelerating substances, characterized that the oxidation is carried out in the presence of aqueous alkalies.

Frame 54, #1263, Dec. 9, 1941. Iron oxide pigments. A solution of an iron salt is diluted with water to a concentration below 0.1%. The precipitate resulting from ensuing hydrolysis is dried or calcined.

Frame 56, #1264, Dec. 15, 1941. Viscosimeter. Consisting in essence of a tube of non-magnetic material containing therein a ball of magnetizable material free to move.

Frame 60, #1265, Dec. 18, 1941. Polychloralkylaromatics. Aromatic hydrocarbon which contains one less methyl group than the desired polychloralkyl compound is treated in a manner to introduce a chlormethyl group and then the side chains of the condensation product are chlorinated.

Frame 63, #1266, Dec. 20, 1941. Cement and plastic material. Composed of high molecular weight condensation product made from reaction of isocyanates.

Frame 66, #1267, Dec. 20, 1941. Floor or Wall covering. High molecular weight condensation products made from isocyanate or the reaction of isocyanates with organic substances such as alkyd resins, in admixture with a filling material are placed upon the surfaces to be covered.

SECTION 15. REPORT ON OXO PROCESS 1940-1941

This section consists of several memoranda and correspondence:

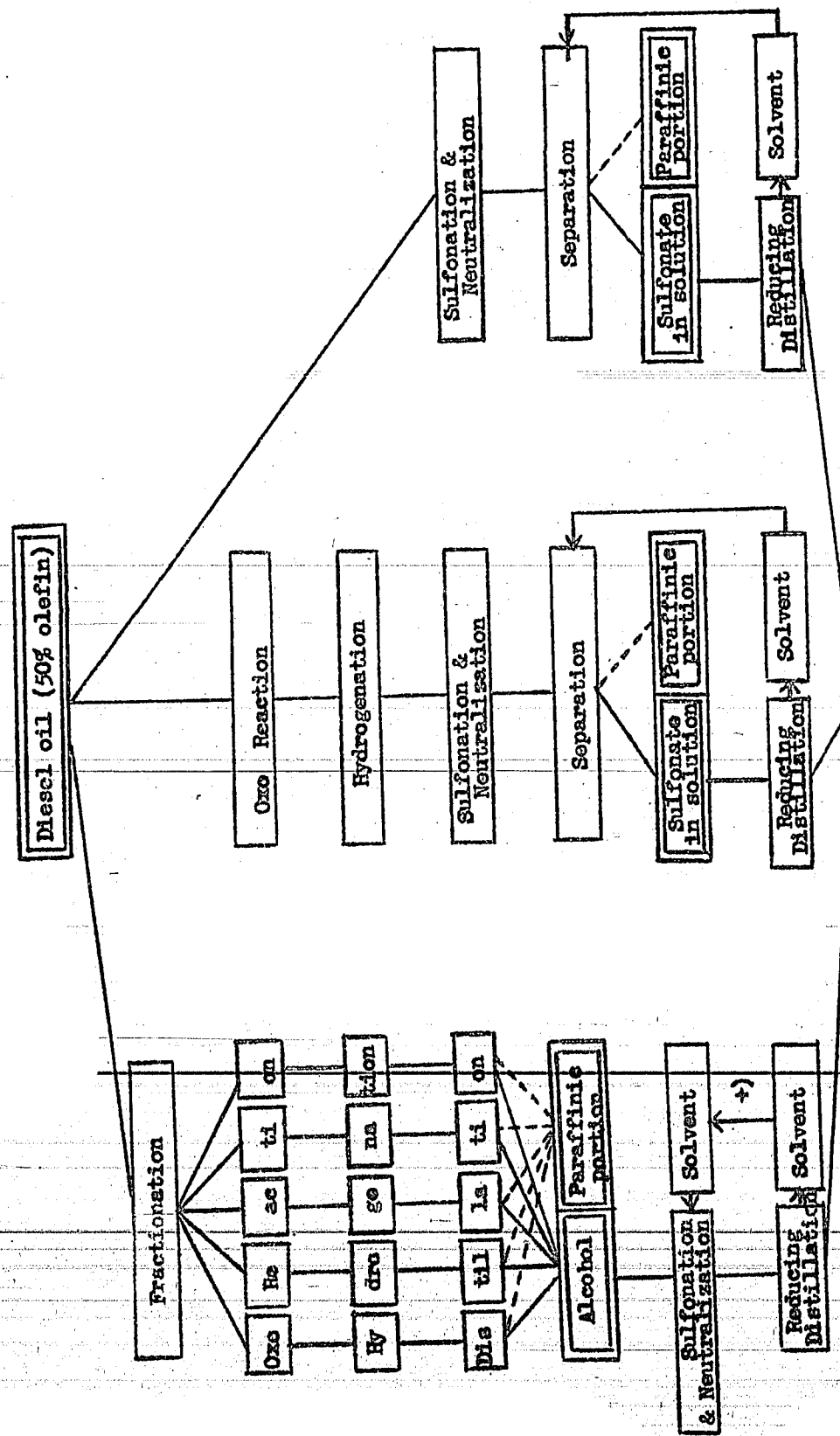
Frame 72, Oct. 8, 1941. Memorandum of conference Sept. 15, 1941 on analytical methods used in evaluating the process. It is entirely lacking in matter descriptive of the several analytical methods to determine the olefin or alcohol content of stocks, and will be of little interest.

Frame 86, letter Ambros to Martin July 11, 1941. Discusses available charge stocks and manufacture of oxo products.

Frame 91, Nov. 14, 1940. Visit of I.G. engineers to Ruhrchemie. This report is not supported by detailed data nor flow diagrams; the text is inferior in description of the process to the summaries written by members of the Technical Oil Mission. It may be presumed that substantial improvements and modifications to the process were made in the intervening four years.

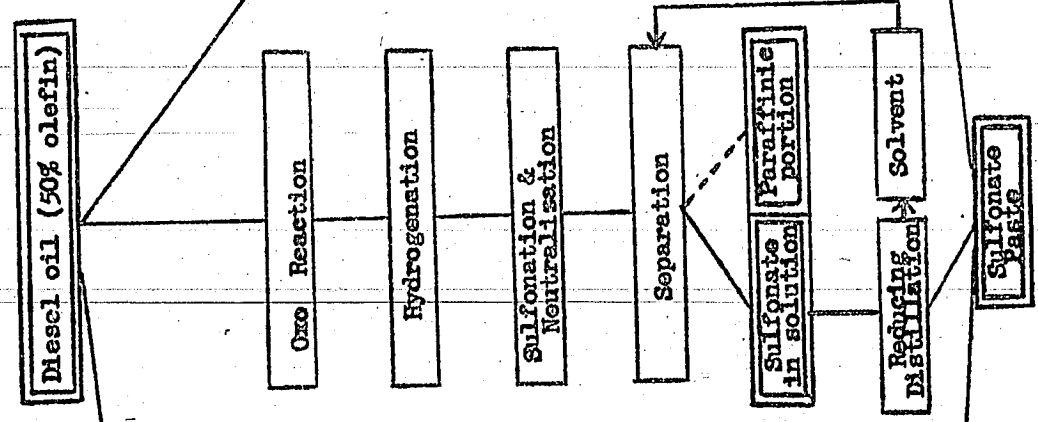
Frame 102, letter Ambros Oct. 24, 1940. States that the oxo process competes successfully with the direct sulfonation process which because of the formation of side reaction products does not appear to be cheaper. Raw materials were available from oxo plant to make 6000 - 8000 tons alcohol per year (C₁₀ - C₂₀). The products have good physical properties as washing materials.

A.) Oxo Process

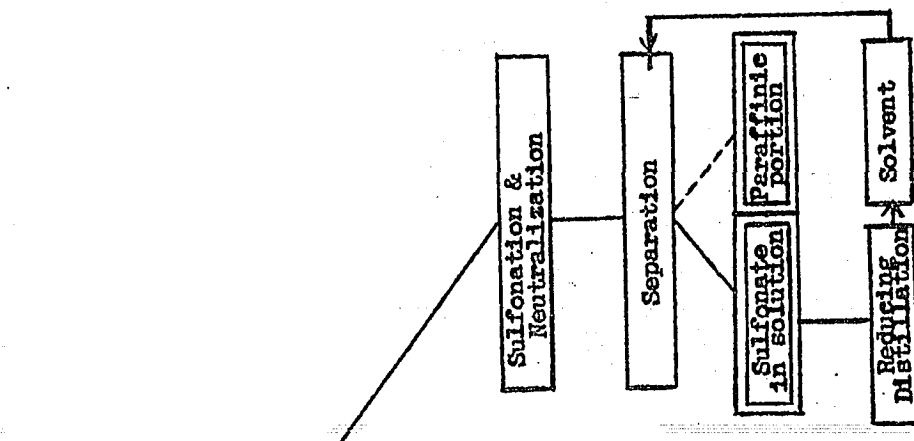


+) Optional

B.) Oxo Separation Process



C.) Olefin-H₂SO₄ Process



Frame 115, Oxo conference reported Oct. 8, 1940. These generalized discussions though less explicit than later detailed reports on individual subjects, nevertheless give a broad picture of the situation in 1940. It was highly desirable to produce textile chemicals from alcohols and fatty acids as well as individual sulphonic acids. Three methods were available:

(a) Production of individual alcohols by the oxo process of Ruhrchemie and sulfonation of these alcohols.

(b) Production of a mixture of raw alcohols by the oxo process, sulfonation of this mixture and separation of the paraffinic portion by the oxo extraction process developed at Ludwigshafen.

(c) Sulfonation of the olefin-paraffin mixture, separation of the unsulfonated portion by the olefin-sulphuric acid process.

The recovery of olefins developed by Ruhrchemie used an iron catalyst to process gas mixtures in which the CO and H₂ were in approximately equal proportions. The primary product consisted of about 60% naphtha boiling up to 200°, 30% diesel oil with a boiling range 200-320° and 10% higher boiling oil. The diesel oil contains about 40-50% olefin.

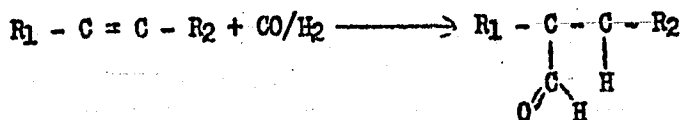
The flow diagram taken from frame 126 (facing) illustrates many of the questions which arose as to the preferred route which should be followed. This period marks the move to pool information possessed by I.G. and Ruhrchemie.

Frame 152, Memo. June 13, 1940. Examination and evaluation of oxo products. Describes the determination of acid, carbonyl and hydroxyl numbers in such detail that the various steps may be followed with reasonable accuracy.

Frame 169 and a number of preceding pages are concerned with the early work of Smith, Hawk and Golden in the United States, where there was a possibility that their work on reaction of C₂H₄ with water gas antedated the oxo process.

Frame 170, Memo. Feb. 22, 1940. Synthetic fatty alcohols as raw material for industrial and household washing materials. This memorandum answered questions as to what application there might be for synthetic alcohol in laundering and textile fields. Alcohols with chains of 12 to 18 carbon atoms were desired. Most useful was straight chain, saturated primary alcohol for making sulfonates. For laundering at high temperature, cetyl and octadecyl sulfonates are preferred. For washing at lower temperature (30-40°), the sulfonates from alcohols with chain lengths C₁₂-C₁₄ are preferred. Mixtures of sulfonates of different chain lengths so far has given no improvement over that afforded by individual components. The fatty alcohol sulfonates are considered superior for washing wools. Low concentration of long chained soap is good for cleaning cotton. The requirements of fat for the soap industry in peace time amount to 200,000 tons of fatty acids. The tenor of the report was to encourage work to develop substitutes for natural fatty material.

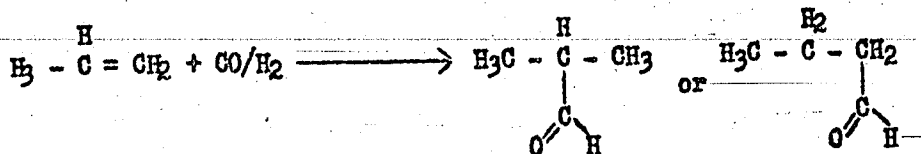
Frame 192, Memo. Feb. 14, 1940. Synthesis of aldehydes and other oxygen-containing compounds from CO and H₂. Reports discussion between Ruhrchemie and I.G. Jan. 19, 1940. The new process which proposes that the two companies shall develop commercially, outlines the following chemistry: It does not resemble the Syntrol method of Frans Fischer, but is an entirely new and important reaction for making aldehydes. Olefins react under pressure and at temperatures as low as 50-150° in the presence of alkali-free iron catalyst according to the reaction:



Ethylene reacts:-



Propylene gives either iso or normal butyraldehyde



In a similar fashion, terpene will yield the corresponding aldehyde. In each case the unsaturated material reacts with water gas under pressure to yield the aldehyde of the next highest number of carbon atoms.

Heavier oils such as are made by the Fischer synthesis below 20 atmospheres and with olefin content of 85%, can be converted to aldehydes having one more carbon atom. The Ruhrchemie staff has also experimented with C₂H₂ to make dialdehydes and to make succinic acids.

The aldehydes can be oxidized with air to the corresponding carbon acids or can be reduced to alcohols. Only primary alcohols are formed, although the hydrocarbon chain may be branched. All discussion is of a general nature rather than accurate disclosure of operating details.

SECTION 16. STATISTICS ON PARAFFIN AND COAL TAR PRODUCTS 1941-43

This section (frames 212-237) is correspondence and tabulations referring to production, allotment and application of hydrocarbon products and many of their derivatives. The reviewer does not believe that it possesses other than historical value.

SECTION 17. REVIEW OF RESEARCH GROUP 1 - WORK AND COSTS 1935

This is a highly condensed summary of research work (frames 238-320) covering the following principal subjects: fertilizers, metals, inorganic and physical chemistry, coal and oil, hydrocarbons, organic chemistry. At least as far as the portion concerning phosphate is concerned, the reviewer presumes that patentable material has already been published and has confined the review to an enumeration of subtitles given in an index:

Fertilizers

Nitrogen lime phosphate (raw phosphate was treated with a mixture of nitric and phosphoric acid)

Sintered phosphate (raw phosphate was heated to 1100° with sodium bicarbonate or soda)

Humus fertilizers (simultaneous treatment of coal and raw phosphate with nitrogen oxide or Cl₂, or Cl₂ and SO₂ to oxidize the coal substance to humic acid. The reaction product is neutralized with NH₃ and mixed with KCl)

Improvement to soda production

NaNO₃ and KNO₃

White calcium cyanamide

Submerged combustion

Boron preparation to prevent heart and dry rot of root

Work on the constitution and improvement in storage and distribution characteristics of fertilizers

Work on Lonsa salt: $5[\text{Ca}(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}] \cdot \text{NH}_4\text{NO}_3$

Work at the Limburgerhof research station

Metals

Iron carbonyls for electrical and pharmaceutical purposes

Nickel iron was produced for magnetic properties and for corrosion-resistant materials

Nickel carbonyls

Inorganic and physical chemistry

Catalysis, particularly the study of extended surfaces

Catalytic hydration of acetylene to acetaldehyde

Heavy water. Through distillation, heavy water was concentrated from proportions 1:5000 to 1:1000. The cost and rate of production was considered unfavorable when compared to a Norwegian installation.

Activated hydrogen (by means of glowing tungsten wire the atomic form was produced)

Cement

Optical glass

Fluorine compounds

Clays

Coal and Oil

Activated carbon

Briquetting

Montan Wax or Pitch

Separation of phenol from water

Lubricating oil. Paraffin, by cracking or chlorination with subsequent

Coal and Oil (cont'd.)
splitting off of HCL, was converted to olefins which were then polymerized and hydrogenated

Paraflow

Oil soluble dyes

Naphtha synthesis by Fischer process

Naphtha analyses

Hydrocarbons

Gasification and gas purification. Under the latter subject was studied the alkasid process, H₂S removal by selective oxidation, removal of organic S

CH₄ was used to make HCN and H₂, as well as C₂H₂ by the arc process

Synthetic rubber

C₂H₆ was used to synthesize ethylene oxide, ethyl chloride, vinyl chloride

Propane, butane and pentane

High molecular weight polymer (100,000 - 350,000) derivatives of iC₄H₈

Organic chemistry. The principal subjects covered were:

Artificial silk

Improvement of alcohol, amine

Recovery of sugar from wood

Paraffin oxidation

Waxes

Urea-formaldehyde condensation products

Preservatives

The above listing of principal projects reported by this portion of the I.G. laboratories is cited to show the extensiveness of their research activities. The individual portions seldom reveal sufficient detail on any process and those interested in any of the subject titles will have to depend upon the further discovery of primary research reports.

SECTION 18. PRODUCTION OF KYBOL (DI-ETHYL BENZENE) AT SCHKOPAU AND LUDWIGSHAFEN, 1941

This letter of June 23, 1941 appearing on frame 322 directs I.G. to proceed with the production of kybol, and assures a supply of benzol. The reviewer presumes that the kybol was used in aviation fuel for improvement of rich rating comparable to cumene employed in the United States.

SECTION 19. SUMMARY OF I.G. PLANS AND PROCESSES FEB. 1942 HISTORY FROM 1937, PLANS THROUGH 1945, BUREAU SPARTE I

This document of about 40 pages was written Feb. 11, 1942 at Oppau. It traces the development of processes and plans from 1937 to the time of writing, and forecasts production and operation. The inspired writer did not have in mind the events of 1945 when he said, "-----the profits in the years 1942-1945 are subject to great errors in calculation and we can only point out certain tendencies and dependence upon a large number of factors which cannot be evaluated with security today as in normal times of peaceful development."

This report speaks of the past, present and projected developments at the several plants. This entire section must be regarded rather as of historical interest in interpreting German war potential rather than any exposition of technical processes.

SECTION 20. MISCELLANEOUS DOCUMENTS HUELS

The following documents appear:

July 1, 1941 - Chart tabulating estimated production of synthetic rubber, aldehyde, kybol, etc. with utility requirements for the processes.

Frame 366 - Schematic flow diagram with quantities involved for this plant during the year 1941.

Frame 372, Nov. 29, 1939 - Sketch of material flow in the polymerization of Buna-S.

Frame 373, Mar. 27, 1940 - Utilities and chemical requirements for ethyl benzene, styrol, polystyrol III, 1939.

Frame 375 - Production of catalyst for dehydrogenation of Butanol.
A process was developed to make butadiene catalyst by spraying phosphate solution on coke. Means were developed for heating the spray directly with a gas flame. This process was considered to have an advantage over the one developed at Schkopau, in that it used simpler apparatus, increased the catalyst yield, decreased the drying time and gave a better yield of butadiene. The Huels butadiene plant catalyst needs were met by the new process.

This catalyst had been developed because of the insufficient amount of graphite hitherto used as the carrier. The process is described: The trommel is filled with 100 kilos coke which contains 16% water. The water is driven out while the coal is heated in the trommel to attain a content of 23-25% P₂O₅. The following quantities of materials are involved: 84 kilos dried coke, 50 kilos NaH₂PO₄, 7 kilos H₃PO₄, 3.9 kilos butylamine; 144.9 kilos total. The material is said to have a residence time of 10 hours at about 200° and an equal time at 240°.

The catalyst was tested in an iron reaction tube placed in a vertical oven. A container at the lower end was heated by an electric air bath to about 240-250°. The solution of butylene glycol in water is vaporized and passed through the shortest possible path up through the catalyst. The effluent vapors are condensed for the separation of water and high boiling by-products. The next flask in series contains concentrated KOH which separates out the greatest part of aldehyde; the remainder is absorbed in two drying towers provided with solid KOH. The C₄H₆ with a boiling point of -5° is recovered in a condenser cooled by CO₂.

SECTION 1. PREPARATION OF DICARBOXYLIC ACIDS BY ELECTROLYSIS

Report Oct. 1, 1942, Frame 392 - The electrosynthesis of sebacic acid from the monomethyl ester of adipic acid for production of resinous material was developed. The alkali salt of monomethyl ester of adipic acid in methyl alcohol water-free solution is electrolyzed by a current density of about 0.02-0.1 amp./sq.cm. of anode surface and the spent half ester is recycled. The half ester salt in methanol solution is dissociated and the acid radical which migrates to the anode is subjected to the above process. The alkali metal separates on the cathode and reacts either with methanol or free half ester with evolution of H₂ and regeneration of the half ester salt or alkali alcoholate.

SECTION 2. ELECTROSYNTHESIS OF SEBACIC ACID DIMETHYL ESTERS

Other reports which are concerned with the same topic as Section 1, are given for Oct. 1943 (frame 397); Aug. 1943 (frame 399); Apr. 1943 (frame 401); Feb. 1943 (frame 404). There is no indication in the text that the work was discontinued after the issuance of the report of Oct. 1943.

SECTION 3. EXTRACTION OF LETTLAND SAPROPEL

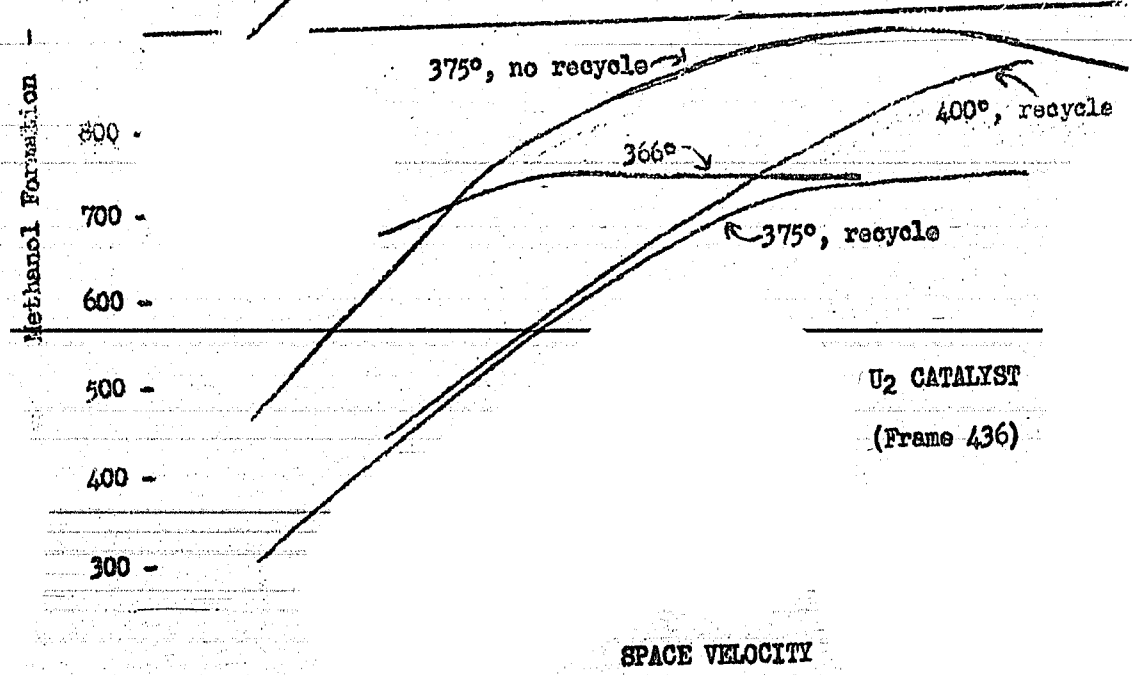
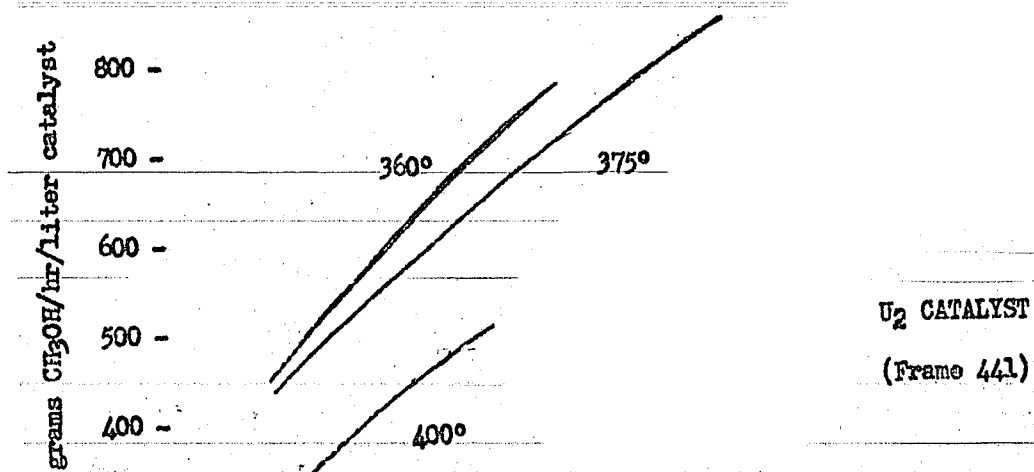
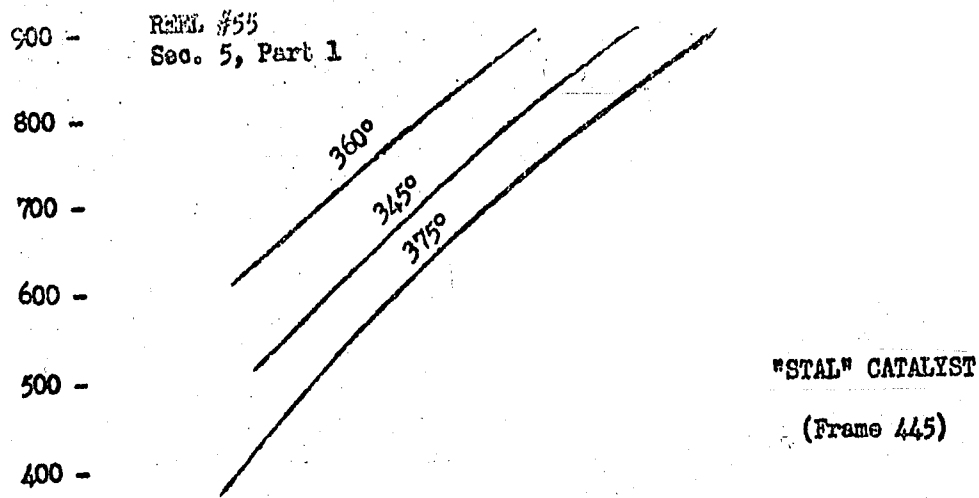
Frame 408, Apr. 1944. Samples taken from a large deposit of unspecified location were examined. The moisture content was 20% and the ash 39%. The dried, pulverized sapropel was extracted with a number of solvents. Tetralin, decalin and benzol-alcohol mixture (3:1) at about 200° yielded about 20% extract.

SECTION 4. SYNTHESIS OF HIGHER ALCOHOLS FROM WATER GAS BY ADDITION OF METHYL AND ETHYL ALCOHOLS

A report by Bayer Dec. 4, 1941, frame 410. Addition of methyl alcohol to the water gas did not appreciably increase the percentage of higher alcohol in the reaction process over that when no methanol was used. In contrast, the addition of ethyl alcohol appreciably increased the yield of higher alcohol. The catalyst "kal" made from zinc oxide and chromium hydroxide with KOH gives principally isobutyl alcohol and higher alcohols. A similar catalyst (Stal plus RB) which contains iron also, yielded considerable quantities of normal propyl alcohol.

The general conditions for addition of methanol were: 80 cc "kal" catalyst, temperature 425°, pressure 250 atmosphere, space velocity 10,000 or thruput of 800-liters charge gas per hour, methanol addition approximately 125 cc/hr.

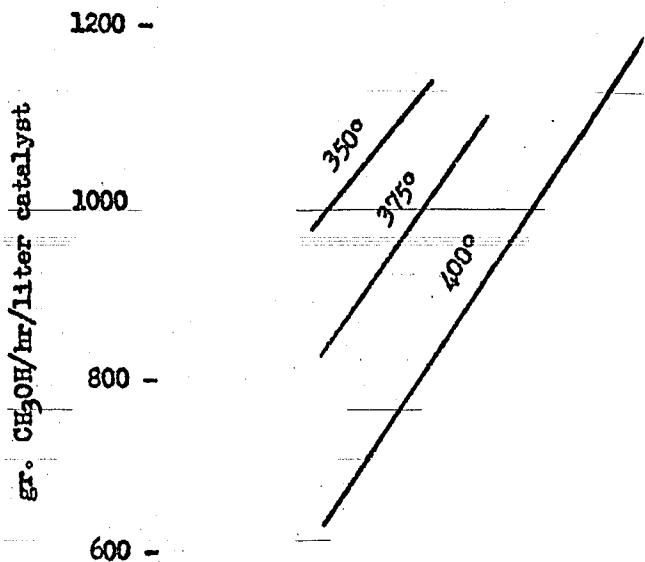
Conditions for ethyl alcohol addition were approximately the same, except the addition rate was about 50 cc/hr.



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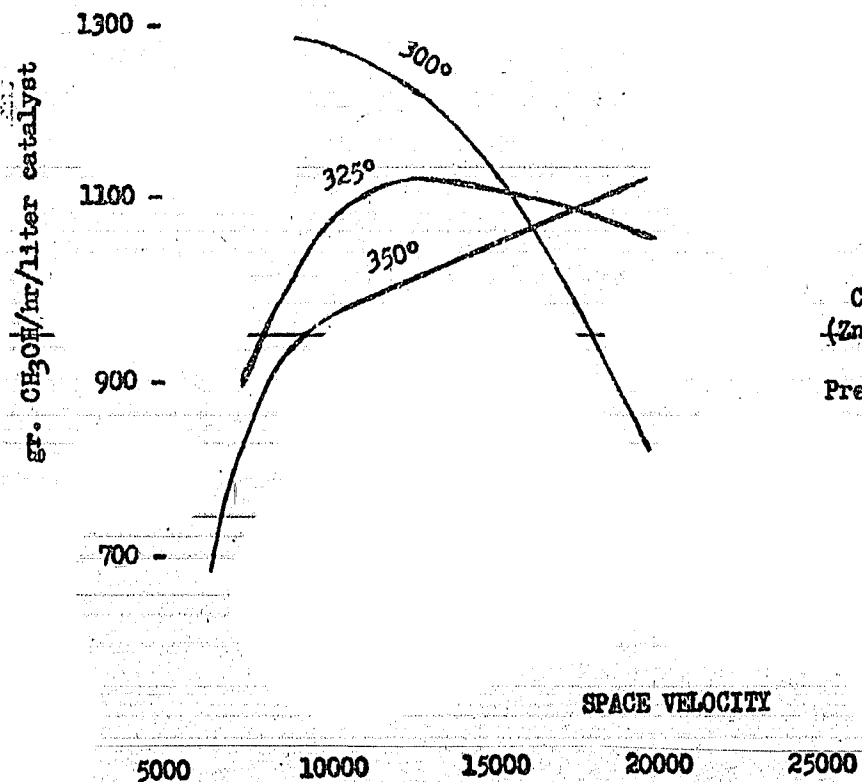
REEL #55

Sec. 5, Part 4



REEL #55

Sec. 5, Part 2



Cat. K15
(Zn-Cu-Cr)

Press. 250 atm.

SECTION 5. EXPERIMENTS WITH METHANOL SYNTHESIS

Part 1. Experiments with binary Zn-Cr catalyst. Report 2286, July 9, 1941, frame 427. The isotherms of space, time and yield for several binary Zn-Cr catalysts were established for 250 atmospheres. The composition of the raw methanol was studied. Several catalysts designated as U₁ and U₂ and Stal are adequately described.

Part 2. Zn-Cu-Cr catalyst. Report 2287, July 15, 1941, frame 456. This material describes experiments and data obtained for isotherms of space, time and yield in methanol synthesis. The catalyst derived from zinc oxalate and copper chromate was precipitated by ammonia. The composition is approximately 14% CrO₃, 70% ZnO and 14% CuO.

Part 4. Methanol synthesis with Zn-Mn-Cr catalyst. Report 2292, July 22, 1941, frame 463. This catalyst was very active and gave good yield of higher alcohol. The catalyst was made from zinc acetate, chromium oxide and manganese nitrate, dissolved, precipitated with ammonia, filtered, washed and dried as pellets. The approximate composition is as follows:

61% ZnO
22% MnO
16% CrO₃

The yields of isobutyl alcohol were considered remarkable. Other experiments, using a catalyst employing alkali in place of ammonia as the precipitant, were to be carried out.

SECTION 6. SEMI-ANNUAL REPORT FOR LAST HALF 1943 ON MEDIUM PRESSURE METHANOL SYNTHESIS

Frame 467, dated Jan. 15, 1944. At pressures of 30-50 atmospheres, methyl formate was synthesized from reaction mixtures ranging from that of normal water gas (ratio of CO:H₂ equals 1:1) down to ratio 1:4. Exploratory work was done on the production of methyl formamide and dimethyl formamide, particularly the latter, as starting material in the preparation of acetylene. Dimethyl formamide was prepared by reacting dimethyl amine and methyl formate. The reaction was said to be quantitative and readily carried out.

SECTION 7. SEMI-ANNUAL REPORT FIRST HALF 1943 ON MEDIUM PRESSURE METHANOL SYNTHESIS

Frame 470, dated June 21, 1943. Semi-works experiments were performed in continuous single-step production of methyl formate and in the two-stage hydrogenation of methyl formate. The preparation of this methyl formate appears to have been as follows: Methanol and CO in the presence of about 2% dissolved sodium are passed downward through a packed column at a temperature of about 82-88°. The effluent is cooled, unreacted CO is recycled and the methyl formate distilled from the liquid product. The two-stage hydrogenation

of methyl formate was done in the presence of an extruded copper chromate catalyst at 30 atmospheres, space velocity about 20 mols/liter catalyst/hr., and temperatures 160 to 185°. The yields of methanol were encouraging.

SECTION 8. MEDIUM PRESSURE METHANOL SYNTHESIS MONTHLY REPORT
NOV. 1942

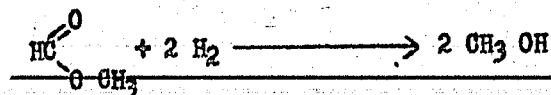
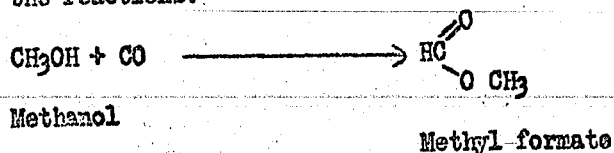
Frame 474, Dec. 15, 1942. Two hydrogenation experiments to produce methyl alcohol from methyl formate by a two-step process were reported. Other work was done on medium pressure one-stage methanol synthesis directly from CO and H₂. The detail in these summaries is usually inadequate.

SECTION 9. DRAWING OF REACTION TUBE FOR HYDROGENATION OF
METHYL FORMATE TO METHYL ALCOHOL

This assembly shows the tube and auxiliary fixtures such as valving, gauges, thermocouple wells, etc. No materials of construction are mentioned, and only the larger overall dimensions are given.

SECTION 10. OPERATING DESCRIPTION OF METHANOL PLANT AT WOLFGANG

Frame 477, Oct. 20, 1943. This plant employed the two-step process at 30 atmospheres wherein CO and methanol are reacted in the presence of sodium methylate to form methyl formate. The methyl formate is catalytically hydrogenated to methanol in the second step. In this and preceding reports on the same subject the reviewer does not understand the motive for this seeming contrary series of reactions, but surmises that methanol was a transitory component in the reactions:



The text refers to a flow diagram in which the several parts are numbered, but the diagram itself is missing. The text is more explicit than any of the preceding reports.

SECTION 11. CONTINUOUS PRODUCTION OF METHYL FORMATE

Frame 480, Aug. 11, 1943. This section consisting of a single frame is obviously incomplete. It is probable that the process resembles in all essentials the method described in the preceding report (frame 477).

SECTION 12. FLOW SHEET OF GLYCERINE PLANT - 50 TONS PER MONTH

Frames 481-483 show very generalized process flow in which the equipment items are numbered. There is no text at this point, and the diagrams themselves are inadequate.

SECTION 13. FLOW SHEET FOR PRODUCTION OF METHYL FORMATE FROM CO AND METHANOL

Frame 484. Schematic flow diagram showing valving and instrument location. The diagrams are of little value by themselves.

SECTION 14. FLOW SHEET FOR PRODUCTION OF METHYL FORMATE FROM CO AND METHANOL

Frame 485 appears to be a variation of the preceding process flow and the same comment applies to this diagram as given in frame 484.

SECTION 15. OPERATING DESCRIPTION FOR PLANT PRODUCING 28 TONS METHYL FORMATE PER MONTH FROM METHANOL

Frame 486, June 8, 1943. Incomplete value, because of the absence of a process flow diagram mentioned in the text.

SECTION 16. METHYL FORMATE-SYNTHESIS FROM WOOD-DISTILLATION GAS

Frame 488, Jan. 27, 1944. This report is more concerned with calculation of the economics of using wood-distillation gas containing about 33% CO and about 56% CO₂. The CO₂ may be removed by water washing under pressure whereby the CO content is increased to about 80%. The technical description of the process for making methyl formate is unimportant.

SECTION 17. PLANT FOR PRODUCTION OF 25 TONS PER MONTH METHYL GLYCERINE FROM CROTONALDEHYDE

Frame 493, Mar. 27, 1942. This report contains tables listing the individual pieces of equipment, identifying them by number, presumably referring these numbers to a drawing not shown. The size, material of construction, and commercial fabricator or location in a present plant is given.

SECTION 18. HYDROGEN PRODUCTION FOR PLANT MAKING ALLYL
ALCOHOL BY HYDROGENATION OF ACROLEIN

Frame 501, Feb. 3, 1941. By the catalytic reaction of steam and hydrocarbon and attendant removal of CO₂, there is obtainable a product gas containing about 0.5-1.0% CH₄, and a CO content of about 1-1/4% down to about 0.2%, depending on whether the conversion is made in one or two steps. If the process demands H₂ containing less than 0.2% CO, the catalytic purification of the gas using Ni is possible, reducing the CO content to the lowest possible value. The same Ni catalyst can be employed for this purpose as is used for the pressure hydrogenation step. In order to answer the question whether the conversion should be done in one or two steps, calculations were set up for coke oven gas and normal city gas.

The gas made in two-stage conversion and CO₂ washing is essentially sulfur free. The gas made from the large plant contained 1-2 mg. S/cu. meter after a caustic wash for removal of the residual CO₂.

Cracking is accomplished in a gas heated tube made from NCT3 steel or similar material at 900-1000°. The catalyst consists of clay or Mg and activated Ni on highly porous Sillimanite obtained from Koppers at Dusseldorf-Herdt. The Ni and Al, or Mg are introduced as nitrates and decomposed by heating in an air stream.

The conversion is done in one-step at atmospheric pressure. For two-stage processing with intermediate CO₂ washing, pressure conversion is preferred. In large plants a space velocity of 1500-2000 is permissible. The catalyst is not adequately described. A flow diagram showing principal equipment is included. Cost calculations were presented which show a probable figure of 22 pfg. per cubic meter H₂ of 99.9% purity. It is obvious that the principal title of this report should be Hydrogen Production: Method and Cost.

SECTION 19. HYDROGENATION OF CROTONALDEHYDE TO BUTANOL

Frame 514 is a memorandum of conference Sept. 3, 1941 in Rodleben. This conference was held between representatives of Dehydag and Degussa. The principal data relating to the process were as follows:

- 1 - Charge stock: 95-96% crotonaldehyde
- 2 - Hydrogen pressure: 30 atmospheres
- 3 - Temperature: 180-185°
- 4 - Thruput rate: 1 kilogram crotonaldehyde per unit catalyst per hour
- 5 - Catalyst: copper chromite
- 6 - Yield of normal butanol: 91.5-94.5% theoretical
- 7 - Residue: 6-7% branched octyl alcohol and some water

The heat of reaction is 41.1 Kg.Cal./mol. Operation in the liquid phase was said to be detrimental to the catalyst. Other evidence was presented which failed to confirm this.

Reviewer's note: It is observed that two processes developed independently were available. The discussion given here is so generalized as to be of little practical value to other workers in this field.

SECTION 20. RESISTANCE OF DIFFERENT STEELS, COPPER AND ALUMINUM TO CROTONALDEHYDE CONTAINING CROTONIC ACID

Memo. Nov. 4, 1941, Frame 517. The test specimens were exposed to crotonaldehyde containing 4% crotonic acid for 1248 hours at 220-240°. The steels and Cu were completely resistant, and the Al was considered sufficiently resistant for practical use.

SECTION 21. COMPARISON OF DEGUSSA AND DEHYDAG PROCESSES FOR HYDROGENATION OF CROTONALDEHYDE TO BUTANOL

Memo. Sept. 10, 1941, Frame 520. This conference probably had its origin in the discussions mentioned in Section 19, above. The principal data compared are shown below:

	Cu-Cr	Ni-Cr
1 - Catalyst	30	200
2 - Pressure, atmosphere	100-185°	120°
3 - Temperature	1.0	0.2
4 - Thruput rate, kg. butanol/catalyst/hr.	0.15 m^3/Kg	50 m^3/Kg
5 - Proportions of H_2 :butanol in product mixture	0	50 m^3/Kg
6 - Hydrogen recycle	120	50
7 - Residence time, seconds	91-95%	99%
8 - Yield of theoretical	125 KWH	490 KWH
9 - Total energy requirements		

(Some doubt was cast on the Dehydag figures, since they had had no practical experience with their chrome nickel catalyst. The yield from process was almost quantitative so no subsequent distillation of the butanol product is necessary. The higher charge rate and lower pressure required for the Degussa method was considered to more than compensate for the longer residence time.)

Reviewer's note: The tone of this conference as expressed by the writer was to give weight of support to the Degussa process.

Acetic Acid Anhydride - This memorandum also discussed certain experiments which indicated that the yield of anhydride with respect to reacted aldehyde was increased as the aldehyde concentration is increased. The question was raised whether the previous unfavorable anhydride yield in continuous type equipment could be improved if the maximum possible aldehyde content was employed in the first step. It was estimated that the highest concentration possible in the first step was 30%.

SECTION 22. METHOD FOR MAINTAINING CONSTANT REACTION TEMPERATURE IN EXOTHERMIC CATALYTIC REACTION

Memo. Feb. 26, 1942, Frame 524 - The reaction tubes are water jacketed. The writer proposes to take a portion of the steam evolved and by means of a heat pump to inject this somewhat compressed steam through nozzles into the base of the water jacket. The effect will be to create vigorous circulation of the water upwards through the jacket. Recirculation of the water is possible by means of a balancing leg from the steam separating space.

SECTION 23. PREPARATION OF CATALYST FOR HYDROGENATION OF CROTONALDEHYDE TO BUTANOL

Memo. Sept. 3, 1943, Frame 531 - The directions appear straightforward and adequate to permit repetition by others.

SECTION 24. HYDROGENATION OF CROTONALDEHYDE TO BUTANOL; CONTINUOUS PRODUCTION OF ALDOL AND CROTONALDEHYDE; HYDROGENATION OF ALDEHYDE TO ETHANOL

Conference Mar. 20, 1942, Frame 528 - The memorandum does not seem to be important.

SECTION 25. HYDROGENATION PLANT DESIGNED FOR CROTYL ALCOHOL USED ALSO FOR PRODUCTION OF 200 TONS BUTANOL/MONTH

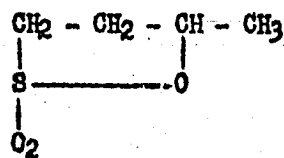
Memo. Feb. 25, 1943, Frame 532 - Compares the duty imposed upon the several parts of the equipment when alternatively making crotyl alcohol or the proposed 200 tons per month butyl alcohol.

SECTION 26. SEMI-ANNUAL REPORT JULY-DEC. 1941 - DR. BRENDLEIN'S ORGANIC LABORATORY

Report dated Jan. 13, 1942, Frame 540 - Crotyl alcohol. Certain precautions in preparation of the hydrogenation catalyst are discussed.

Methyl crotyl ether. According to a German patent, allyl ether may be used to prevent spoilage. By analogy it was thought that the ether of crotyl alcohol might have a similar effect, and the two isomers of crotyl chloride were reacted with sodium methylate by heating and reflux. While crotyl chloride II (boiling point 82-84°) is converted to methyl crotyl ether with a yield of about 80%, crotyl chloride I (boiling point 62-64°, which leaves the suspicion of a chloride of methyl vinyl carbinol) under the conditions employed reacted to a very small extent. The methyl crotyl ether was to be examined for insecticidal properties.

Sultone from methyl vinyl carbinol - Butane sultone (frame 541) was prepared with especial view to use as a detergent.



1,4-dichlorobutene from crotyl chloride - Experiments had so far not been successful. The reaction product contained small amounts of 1,2,3,4-tetrachlorobutane and larger amounts of 1,2,3-trichlorobutane. These experiments were being continued employing metal chlorides as catalyst.

Butanol for Fuerstenberg - Work was done on equipment for catalytic hydrogenation of crotonaldehyde.

Hydrogenation product - 1-methylol tetrahydro pyran was made from 2-formyl-2,3-dihydro pyran, and 1,2,6-hexanetriol was made from oxyadipin aldehyde by catalytic hydrogenation. No details are given.

SECTION 27. MONTHLY REPORT OCT. 1942 FROM BRENDLEIN LABORATORY

Frame 544, Dec. 6, 1942 - Reactions with liquid ammonia. It was observed that halogen derivatives of crotyl and allyl alcohol are converted to amines by ammonia. The amines may be converted to corresponding nitrates or if possible to nitramines by nitric acid.

Methanol synthesis at medium pressure - Laboratory equipment was built for hydrogenation of formic acid esters, especially methyl formate.

SECTION 28. SEMI-ANNUAL REPORT JAN.-JUNE 1941-BRENDLEIN LABORATORY

Frame 547, July 1, 1941 - Crotyl alcohol and crotyl derivatives. Crotonaldehyde was hydrogenated to crotyl alcohol. By shaking crotyl alcohol with 5 to 6 times its volume of concentrated aqueous hydrochloric acid, there was attained a yield of 98% crotyl chloride as 2 isomers. The proportion of isomers I and II were respectively 34 and 66. Crotyl chloride II was readily saponified to the extent of 97% in about one hour by N/2 alcoholic potash, while the chloride I was saponified to the extent of 73% in 4 hours. Other derivatives were prepared. This report also touches upon the Fuerstenberg plant and the process for making allyl alcohol.

SECTION 29. CROTYL CHLORIDE FROM CROTYL ALCOHOL, AND ITS SAPONIFICATION

Report Sept. 19, 1943, Frame 551 - The production of crotyl chloride from crotyl alcohol was simple. Shaken with concentrated aqueous hydrochloric acid, crotyl alcohol gives about 95% yield of the isomers I and II in proportions 34:66. By heating, these isomers may be made to pass from one to the other, although the isomer II appears more stable. Saponification of the higher boiling isomer (I) is readily accomplished with alcoholic potash, the

reaction being 97% complete. The lower boiling isomer is not completely saponified even when heated for several hours. Both isomers are quantitatively saponified with aqueous sodium hydroxide only by prolonged heating at 130° under pressure. Saponification of the chloride yields methylvinyl carbinol as well as crotyl alcohol, and when crotyl chloride I is employed, the carbinol will be the major product. This report is better than average for detail.

SECTION 30. ETHYL ACETATE FROM ACETALDEHYDE
(This report is in four portions)

I. June 14, 1941, Frame 562 - Laboratory batch experiments.

Research on the production of ethyl acetate by condensation of acetaldehyde by means of aluminum butylate discontinued in 1931 was again taken up in order to obtain further fundamentals to assist in the planning of a proposed plant at Fuerstenberg. For complete reaction of the aldehyde charge, 7-8 hours reaction time is required. The amount of catalyst calculated on the aldehyde consumed was increased from the former figure of 3.5% up to 5.5%. The yield of acetate under these circumstances is about 88-90%, besides forming 4-7% of higher boiling by-products. Experiments to lessen butyl acetate formation which occurs with dilution of the catalyst were not successful. Dilution of butylate with anhydrous ethyl alcohol gave as good yield as with butanol. Addition of aluminum chloride to the butylate increased the aldehyde decomposition, increased the yield, and lessened the formation of side reaction products.

II. Aug. 23, 1941, Frame 577 - Batch operation experiments.

The experiments were performed in copper equipment having a stirring device. The acetate yield was 89-90% of the reacted aldehyde. The information obtained agreed with the laboratory experiment. The addition of $AlCl_3$ to the catalyst improved the yield. The catalyst is aluminum butylate although the preparation of the material is not described in detail.

III. Nov. 18, 1941, Frame 581 - Continuous laboratory experiments.

Catalyst and aldehyde were brought simultaneously and continuously into the reaction zone in the proper proportion; reaction product was continuously withdrawn. The properties of the aluminum butylate made necessary the batch production of the catalyst, and in lack of a suitable suspension medium, a portion of the product ester is used to dilute the butylate. The principal portion of the aldehyde and the diluted catalyst is introduced to the reaction vessel continuously. The yield of acetate was about 86% of the aldehyde reacted; side reaction products averaged about 8%. The addition of $AlCl_3$ to the catalyst in continuous experiments increased the yield of acetate.

IV. Dec. 6, 1941, Frame 589 - Continuous Operation experiment.

The research on continuous operation was conducted in steel equipment, and a schematic flow diagram of the equipment is shown in the text. The thru-

put rate was about 150-170 liters per day. These experiments covered periods of between 3 and 18 days; some difficulties were encountered by the separation of catalyst suspension, thereby causing blockage. Since iron is strongly attacked by acetaldehyde, and the latter on its part is thereby diminished in activity, copper is used throughout, except for the aldehyde tank which is aluminum. The attack of acetaldehyde on metal, especially at the start of the experiment, depresses the yield of acetate and correspondingly increases the yield of side reaction products. With non-ferrous equipment, an acetate yield of 82-83% of aldehyde was obtained with a corresponding formation of 8-12% of oily side reaction products.

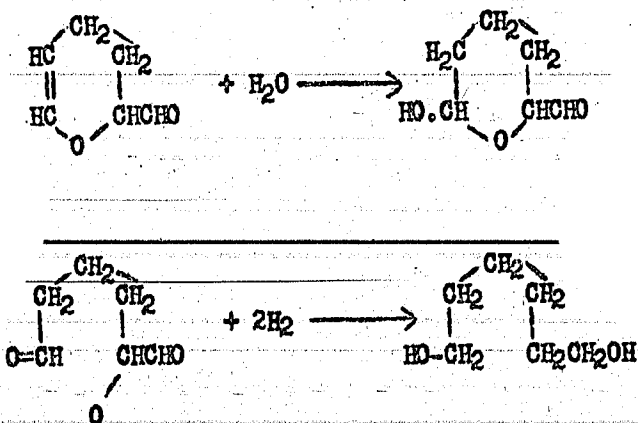
Reviewer's note: This series of four memoranda does not contain original data but it does appear to be an adequate description and summary of the experimental work.

SECTION 31. RING CLEAVAGE OF FORMYLDIHYDROPYRAN TO MAKE
1,2,6-HEXANTRIOL AND ITS DERIVATIVES

Report July 3, 1943, Frame 603 - Opening of the ring of 2-formyl-2,3-dihydropyran to form 1,2,6-hexantriol was undertaken covering the following principal topics:

- (a) The use of freshly distilled pyran
- (b) Using aqueous solutions not higher in concentration than 40%
- (c) The use of toluol sulfo acid for the hydration, avoiding temperatures higher than 40°
- (d) Hydrogenation in aqueous solution

Ring cleavage of the esters of hydrogenated formyldihydropyran was attempted with acetic acid anhydride and acetylchloride. The yields were poor.



Experimental procedure and an interpretation of results appeared to have been carefully done.

SECTION 32. CORROSION TESTS: CROTYL ALCOHOL, CROTON-
ALDEHYDE, TRIOXYBUTANE

Memo. May 4, 1943, Frame 616 - The origin of this work was the desire to use the crotyl alcohol plant for production of trioxybutane.

SECTION 33. TRIOXYBUTANE PLANT IN RODLEBEN

Memo. 1207/0 Jan. 26, 1943, Frame 618 - Apparently relating to a conference between Degussa and Dehydag. The discussion centered around materials of construction, particularly their resistance to corrosion.

SECTION 34. DESIGN DATA FOR TRIOXYBUTANE PLANT

Memo. Jan. 9, 1943, Frame 620 - Includes sketch of unit and major dimensions. The text describes the duty and process conditions for the several pieces of equipment.

SECTION 35. CENTRIFUGE FOR TRIOXYBUTANE PLANT

Memo. Oct. 24, 1942, Frame 624 - Relates necessity for this type of equipment.

SECTION 36. TRIOXYBUTANE PLANT SILVER COOLER

Memo. Dec. 17, 1942, Frame 625 - The filter approached closely to VA in corrosion resisting properties, but was preferred because of somewhat greater ease in working. The proposed conditions anticipated that the mixture of butanol, crotonaldehyde and butyraldehyde would be refluxed, the vapor entering at 104° and the condensate leaving at 30°. Other materials of construction are commented upon.

SECTION 37. TRIOXYBUTANE. 2,000 TONS PER YEAR PLANT FOR
FUERSTENBERG. HIGH PRESSURE HYDROGENATION PLANT

Memo. 1221, Feb. 16, 1943, Frame 627 - Conference with Dehydag in Rodleben. This plant was assumed to charge crotonaldehyde and secondary butanol in proportion 368:552 to effect the following yields, all calculated as weight percent of crotyl alcohol or crotonaldehyde: trioxybutane from crotyl alcohol-74%; crotyl alcohol from crotonaldehyde-66%; butanol from crotonaldehyde-24%; oils from crotonaldehyde-10%. The equipment, its duties and operating conditions are described. A summary is given for materials of construction. There was no flow diagram, but the text is considered above average in lucidity.

SECTION 38. LABORATORY EXPLOSION IN CROTYL CHLORIDE PLANT

Memo. July 28, 1942, Frame 638 - Reports an explosion which took place in the laboratory where crotyl chloride was being reacted with sodium nitrite. The autoclave, fitted with a shaker, was designed for 300 atmospheres pressure and had a capacity of 1 liter. The contents were 180 grams crotylchloride, 150 grams sodium nitrite and 150 grams of water. In a period of 45 minutes the interior temperature rose to 103°. Shortly thereafter there was a violent explosion.

SECTION 39. HYDROGENATION OF ACROLEIN TO PROPIONALDEHYDE

Memo. Dec. 29, 1942, Frame 639 - The hydrogenation of crotonaldehyde to butyraldehyde and of acrolein to propionaldehyde is relatively easy. It was found that Raney catalyst at 20-30° or 100° for less active catalyst was sufficient to avoid undesirable resin formation in the latter reaction. Pressures as low as 5 atmospheres may be used. An example is given wherein a 43% methyl alcohol solution of acrolein is processed with about 4% of Raney nickel in a V2A shaking autoclave which is cooled with water to hold the reaction temperature between 20 and 25°. The initial H₂ pressure was 100 atmospheres; after 40 minutes the pressure had fallen to 20 atmospheres. No double bonds could be found in the reaction product. The yield was 95% theoretical, the remainder being propanol.

SECTION 40. HEKANDIOL

Letter Apr. 5, 1943, Frame 640, to Dr. Helberger (Text was concerned with manufacture of 1,3-trimethylene glycol; 1,5,6-hexantriol, and hydroacrylaldehyde from acrolein.) The text is not specific.

SECTION 41. LIST OF CATALYSTS GIVEN IN CORRESPONDENCE MAY 14, 1942 WITH AUER GESELLSCHAFT

Frame 642. This material cites catalysts 1Q through 14Q, B15 through B22, W23 through W27 and S28 through S33. This listing does not adequately describe the manufacture of the catalysts and can only be regarded as identifying their gross composition.

SECTION 42. EFFECTIVENESS OF CERTAIN INSECTICIDES

Material dated April 15 and May 15, 1940, Frames 644 and 645 - This is largely a tabulation of material without text to clarify it. This section of the reel appears to be a poor carbon copy and it is probable that a more detailed account will be found.

SECTION 43. INSECTICIDAL EFFICIENCY OF CHLORAMINES

Memo. Mar. 13, 1943, Frame 647 - Calls attention to two preparations:



Memo. Apr. 27, 1943, Frame 646 - Reports that the two preparations were ineffective as insecticides as breathing poisons against corn beetles.

SECTION 44. FURFURAL HYDROGENATION

Memo. June 20, 1939, Frame 648 - Relates that Dr. Brendloin has succeeded in hydrogenating furfural to tetrahydrofurfural alcohol, and obtained good yields of a clear liquid without objectionable odor. The alcohol and the acetate of this alcohol were to be examined as lacquer solvents. The operating conditions and the catalyst used in the hydrogenation step are not stated.

SECTION 45. PROPERTIES OF DIMETHYL FORMAMIDE

Memo. Oct. 20, 1944, Frame 652 - Acetone and dimethyl formamide when tested at 15° and one atmosphere partial pressure, showed relative absorptions of acetylene as 23 and 46, equivalent to a maximum filling per liter of container space for these two materials as 0.222 and 0.295 Kg. acetylene. There is no mention that the dimethyl formamide has supplanted acetone as a carrier for acetylene.

SECTION 46. METHOD FOR PREPARATION OF HALOGEN- AND NITROGEN-CONTAINING COMPOUNDS

This record of invention Dec. 15, 1943, Frame 655 bears the number D89500 IVc/12, and covers paraffin or substituted paraffins, or their derivatives with at least 3 carbon atoms which contain 3 adjacent halogen atoms which react with ammonia in the presence of solvent materials. The example cites that 1,2,3-trichlorobutane is reacted with liquid ammonia for 3 hours at 100° in an iron shaking autoclave, and after discontinuing the heating is shaken for 16 hours longer. The unreacted ammonia is distilled off. The remaining reaction product is diluted with ether and filtered. Ammonium chloride remains on the filter. When the ether is distilled from the reaction product, two fractions were identified. (The reader's attention is called to material in frame 647)

SECTION 50. REACTION OF AMMONIA AND METHANOL

Memo. Sept. 28, 1944, relating to a conference pertaining to Fuerstenberg, Frame 678 - It does not reveal any process conditions except that the proposal is made to react methanol in place of ethanol with ammonia.

SECTION 51. QUARTERLY REPORT OCT.-DEC. 1940 FROM DR. BRENDLEIN'S ORGANIC LABORATORY - Frame 680

Note: The reviewer presumes that the material described in these reports is given in great detail in some final report and he has confined comments to a statement of subjects under investigation with a brief indication of the extent of the work.

Hydrogenation of Acrolein. In addition to allyl and propyl alcohol, other higher boiling liquid polymerization or condensation products are likely to be formed. A series of experiments in which hydrogenation was performed at normal pressure and a temperature of 275° was successful in that over a period of several hours no resin formation was observed.

Separation of saturated and unsaturated hydrocarbons by wash (azeotropic) distillation. Experiment with methanol as the wash material was not encouraging.

Naphtha fractionation. Experiments with a 60 plate column and a packed tower.

Hardening of fat with Raney nickel. These experiments had as their objective the development of a continuous process, and further sought reaction conditions as low as 100°.

Hydrogenation of cyanhydrins. The hydrogenation step could only be carried out in acid solution.

SECTION 52. QUARTERLY REPORT JULY-SEPT. 1940 - Frame 683

The following subjects were covered:

Hydrogenation of alpha-beta-unsaturated carbonyl compounds to the corresponding unsaturated alcohols. A principal objective was the production of allyl alcohol from acrolein.

Production of pure furfural by wash distillation. Twofold treatment increased the furfural concentration from 80 to 91%.

Separation of acetic acid-formic acid mixtures with toluol. It was shown that an original mixture having only 2.2% formic acid could be enriched to 62% when toluol is used as the azeotrope.

SECTION 53. QUARTERLY REPORT APR.-JUNE 1940 - Frame 685

Hydrogenation of alpha-beta-unsaturated carbonyl compounds to the corresponding unsaturated alcohol. Croton aldehyde was hydrogenated to crotyl alcohol and a lesser amount of butyl alcohol.

Wash distillation experiment. This subject relates to separation of complex mixtures by azeotropic distillation.

Fat hardening. Meat's-foot oil was to be hydrogenated for pharmaceutical purposes. Raney nickel deposited on a carrier was the catalyst. Temperatures of 150° or lower were sought to avoid loss of vitamins in the product.

SECTION 54. QUARTERLY REPORT JAN.-MAR. 1940 - Frame 687

Hydrogenation of alpha-beta-unsaturated carbonyl compounds to the corresponding unsaturated alcohol. The catalysts were a combination of cadmium and copper to convert acrolein to allyl alcohol and crotonaldehyde to crotyl alcohol.

Separation of crotyl-butyl alcohol mixtures by azeotropic distillation. Advantage was taken of the difference in solubility of water in these two chemicals; namely, 1.7% and 9%.

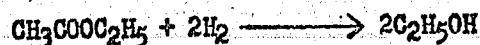
SECTION 55. QUARTERLY REPORT OCT.-DEC. 1939 - Frame 689

1,3-propendiol dialkylether. Attempts to convert acrolein to the ether in concentrations above 65% were not successful.

Hydrogenation of acrolein to allyl alcohol. The use of cadmium catalyst permitted yields of allyl alcohol up to 28% of theoretical, together with propyl alcohol and lesser quantities of other side reaction products.

SECTION 56. MONTHLY REPORT DEC. 1942 - Frame 691

A two-stage process was being developed for synthesis of ethyl alcohol from CO and H₂.

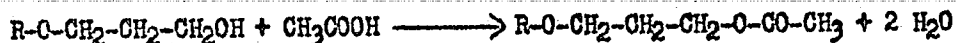


The first step was performed in continuous equipment which is silver-plated. The catalyst was tungstic acid with small amounts of the nitrates of bismuth, zinc and copper. Temperature inlet 320°, reactor outlet 360°, pressure 200 atmospheres. The charge is one mol methanol to two mols water. The methanol is 79.4% decomposed to yield 36% of theoretical.

The second step consists of hydrogenation of ethyl acetate to ethyl alcohol. A temperature of 245°, pressure of 30 atmospheres is employed in the hydrogenation step, using copper chromite catalyst. The thruput rate of ethyl acetate is 415 grams per liter catalyst per hour. About 63% is reacted to give a yield of 100% theoretical.

SECTION 57. PRODUCTION OF ETHER ESTERS (ACETATES) FROM MONOALKYL ETHERS OF THE 1,3-TRIMETHYLENE GLYCOLS

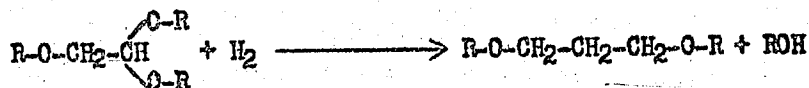
Report 1581 Jan. 12, 1939 - Frame 693. The monoalkyl ether of 1,3-trimethylene glycol made by hydrogenation of alkyl propionaldehyde was converted to ether ester by de-esterification of the free hydroxyl group. The reaction is shown:



The monomethyl, monoethyl and monobutyl ether esters of the glycol were made, and samples were sent to the lacquer laboratory for testing as solvents.

SECTION 58. HYDROGENATION OF METHOXY-PROPIONALDEHYDE-DIMETHYL-ACETAL AND ETHOXY-PROPIONALDEHYDE-DIETHYLACETAL

Report 1554 Oct. 14, 1938 - Frame 697. Hydrogenation of methoxy-propionaldehyde-dimethylacetal yields the dimethyl ether of 1,3-propylene glycol; the corresponding ethoxy-diethylacetal yields the diethyl ether of 1,3-propylene glycol. The reaction may be represented:



The experiments were performed in a shaking autoclave of V2A steel using Raney nickel catalyst described in report 1553. The pressure was 80-111 atmospheres, and the temperature rose to 179° over a period of 90 minutes.

SECTION 59. REPORT OF CONFERENCE (A) RECOVERY OF ACETYLENE FROM EFFLUENT GAS IN ACETYLENE KETONIZATION, (B) BUTANOL RESEARCH, (C) ACETIC ACID ANHYDRIDE, (D) ETHYL ACETATE

Memo. dated Dec. 3, 1941 - Frame 701. Recovery of acetylene from gases by washing with acetone. The dissolved gases when evolved from the solvent are about equal proportions of CO₂ and C₂H₂ which may be admixed with fresh C₂H₂ and charged to the ketonization step.

Butanol research was being delayed by difficulty in obtaining ammonium chromate used in the catalyst.

The summary speaks of work done upon solubility of catalyst in the reaction mixture, and also relates that certain metals are being tested for corrosion resistance against acetic acid anhydride.

The general discussion does not reveal the exact means of making ethylacetate, but it may be inferred that the process may have employed aluminum butylate in ethanol or butanol, or perhaps the reaction of alcohol upon acetaldehyde.

SECTION 60. HYDROGENATION OF FERULIC ACID AND AMMONIUM FERULATE

Report 1606, June 1, 1939 - Frame 706. Using Raney nickel at 100° and 100 atmospheres hydrogen pressure, ferulic acid may be hydrogenated to hydroferulic acid with a yield of 85%. Similarly ammonium ferulate gave good yields. For hydrogenation of the acid, the reactants were in the following proportions: Acid: methanol: Raney nickel, 97: 200: 10. For hydrogenation of the ammonium salt the proportions of salt, methanol and Raney nickel were 28: 250: 5.

SECTION 61. PREPARATION OF 1,3-PROPENEDIOL DIALKYLETHER FROM ALKOXY PROPIONALDEHYDE DIALKYLACETAL

Report 1651, Dec. 5, 1939 - Frame 711. The diethyl ether was made from the corresponding ethoxy diethylacetal and the methoxy dimethylacetal was used to make the dimethyl ether. The catalyst, reaction conditions, purification and identification of the product are described adequately.

SECTION 62. SEPARATION OF ALLYL ALCOHOL-PROPYL ALCOHOL MIXTURES BY AZEOTROPIC DISTILLATION

Report 2079, June 20, 1940 - Frame 719. In the selective catalytic hydrogenation of acrolein to make allyl alcohol, there is obtained a mixture of this alcohol with propyl alcohol whose separation by fractional distillation is difficult because of the closeness of the boiling points. A satisfactory separation was obtained when 300 grams of a mixture of alcohols (allyl: propyl equals 17:30) was distilled with 400 grams of water at 175 mm. mercury in a 60 plate height column.

SECTION 63. SEPARATION OF METHYL CYCLOPENTANONE AND FURFURAL BY AZEOTROPIC DISTILLATION

Report 2080, June 26, 1940 - Frame 722. Hydrogenation of furfural oil to tetrahydrofurfural alcohol yielded by-product methyl cyclopentanol which is separated away with great difficulty. The addition of water and subsequent distillation at 150 mm. Hg in a 60 plate column effected successful separation.

SECTION 64. SEPARATION OF CROTYL-BUTYL ALCOHOL MIXTURES BY AZEOTROPIC DISTILLATION

Report 2022, Apr. 8, 1940 - Frame 725. The catalytic hydrogenation of crotonaldehyde yields a mixture of crotyl- and butyl-alcohols which may be separated by the addition of water and distillation at 150 mm. Hg.

SECTION 65. HARDENING (HYDROGENATION) OF NEAT'S-FOOT OIL

Report 2031, Apr. 23, 1940 - Frame 733. Neat's-foot oil was hydrogenated to a solid fatty like product with Raney nickel at 140-150° and a hydrogen pressure of approximately 15 atmospheres. Products with solidification points as high as 55.5° were made. The fat was said to be used for pharmaceutical purposes

SECTION 66. SEPARATION OF ISOPROPYL ALCOHOL AND TERTIARY BUTYL ALCOHOL BY AZEOTROPIC DISTILLATION, USING WATER AND BENZOL AS AZEOTROPES

Report 2084, June 29, 1940 - Frame 740. This and the several other reports describing separation of close boiling components are described with sufficient detail to permit ready repetition and checking of such work.

SECTION 67. SEPARATION OF ACETIC ACID-FORMIC ACID MIXTURES WITH TOLUOL AS THE ADDITION AGENT

Report 2131, Sept. 14, 1940 - Frame 744. The equipment and processing is somewhat more complicated than in most of these azeotropic distillations, and the text is accompanied by a schematic flow diagram.

SECTION 68. EXPERIMENTS WITH ALKALIZED ZINC CHROMIUM CATALYST. EFFECT OF DIFFERENT ALKALI ADDITION IN BUTANOL SYNTHESIS

Report 2291, July 21, 1941 - Frame 752. The formation of higher alcohols by alkalized Zn-Cr catalyst has been established. Catalyst "ka1" gave high yield of isobutanol. Catalyst "Stal + RB" gave some normal propanol in addition to isobutanol. Catalyst "Stal + Kac" yielded products principally boiling above 110°. The description of the catalyst and the operating conditions is in more detail than usual.

(b) REACTIONS OF CO AND H₂ ON OLEFINS - OXO REACTION

The following group of reports showing the status of work for individual months in the period Feb. 1941 to Dec. 1943 is indexed as Sections 69 to 85 inclusive. The reviewer has examined the data in reverse order, namely, chronologically, beginning with section 85. Much of the text is illegible, being a very poor carbon copy. There is little numerical data given, and the reviewer has confined his remarks chiefly to an enumeration of the principal work reported.

SECTION 85. FEB. 1941 - FRAME 871

Intentional poisoning of the catalyst with H₂S or CS₂ was done to lessen the hydrogenation effect and increase the opportunity for alcohol formation. Catalyst reduction appears to be a continuing project.

SECTION 84. APR. 1941 - FRAME 868

Used catalyst was regenerated by leaching with light naphtha and methanol, followed by drying and reduction. The original activity was secured in this manner. The cycle was repeated three times.

SECTION 80. DEC. 1941 - FRAME 849

Contains a discussion on the constitution of the oxo alcohols.

SECTION 79. FEB. 1942 - FRAME 843

Mentions the reaction of C₂H₄ and water gas using nepasin as a fluidising agent, and the separation of CO away from H₂ recycle by methanization.

SECTION 77. JUNE 1942 - FRAME 830

Sulfonation and separation of neutral oils from alcohol-sulphate is reported. Throughout the summary there is extensive work reported on the examination of liquid products and identification of specific compounds.

SECTION 72. JUNE 1943 - FRAME 793

The aldol reaction attendant upon the oxo reaction is becoming more detailed. Throughout these reports there is evidence that close association with Ruhrchemie has been maintained.

SECTION 69. DEC. 1943 - FRAME 774

Oxidation of liquid hydrocarbon products obtained by low temperature carbonisation of steinkohl at Blechhammer was used as charge in the oxo process, as well as raw tar from the Leuna alkylation plant.

(c) SYNOL WORK

The subject matter reported in items 69-85 concerning the reaction of CO and H₂ with olefins in the oxo reaction was reported as project 813. The greater part of the present work reported upon Synol was performed as project 628 and 820.

The material in sections 86 and 87 (frame 875 to 896) covers semi-work experiments in alcohol synthesis, recycle operation, influence of drying temperature, the effect of carriers composed of iron or pulverized glass as the medium to support precipitated iron catalyst, heats of reaction and absorption, and the use of several types of clay as refining media.

(d) WORK ON OXO AND SYNOL ALCOHOLS

Sections 88 to 93 (frames 898 to 961) are bi-monthly reports for the annual period Feb. 1943 to Feb. 1944, conducted as problem 820. The principal topics discussed were:

Production of cleaning agents from carbonization naphthas, including the reaction of oxo alcohols with aromatic material such as benzol, toluol and naphthalene.

The sulfonation of oxo alcohol hydrocarbon mixtures with SO₃ dissolved in SO₂.

The alkylation of short chain oxo alcohol to long chain alcohol sulfate.

Studies on shifting of the double bond in branched olefins by means of cobalt carbonyl.

Studies upon the extraction of synol alcohol.

Hydrogenation of oxo and synol products.

Studies on the constitution and isolation of individual components.

Despite the fact that much of the material is illegible, these bi-monthly summaries appear to possess importance because of their serving as a background to the development of these important processes.

(e) HYDROCARBON SYNTHESIS FROM CO AND H₂

Progress reports, sections 94-104, covering the period Oct. 1940 to Dec. 1943 (frames 963 to 1079) seem to form a continuous story on project 628 with the exception of period Oct.-Nov. 1943. Note that items 86 and 87 above are on the same project as items 94-104. The summaries are given in reverse chronological order. The summary of Oct. 1940 states the purpose of the project is the recovery of hydrocarbon oils of paraffinic and olefinic nature as charge material for synthetics and cleaning agents. It is said that the work has been in progress for several years and a comprehensive report was written by Wenzel Nov. 18, 1940.

The following phases of investigation were reported:

(a) Influence of reduction time on the synthesis with fused iron catalyst.

(b) The effect of geometry of the catalyst case.

(c) Analysis and refining of the synthesis product.

(d) Improvement to the catalyst itself.

(e) Synol synthesis, that is, material of an alcoholic nature (in the summary for April 1942, section 101, it was established that in the synol process the alcohols were practically unbranched and that the OH group is at the end of the molecule).

The principal investigators associated with this work were Breywisch, Geiseler, Reisinger, Wintser, Pobloth and Wenzel. The value of these summaries may lie in the detailed discussion of research which proved to be unimportant, impracticable or susceptible to development and improvement in subsequent work. The reviewer believes that to persons interested in the general subject of hydrocarbon synthesis, and particularly in the field of synol, review of this subject matter will yield valuable impressions and suggestions to short-circuit much experimental effort.

(This ends scanning of Reel #55)

PATENT DISCLOSURES REEL #55

<u>In order of appearance</u>		<u>In numerical order</u>	
<u>No.</u>	<u>Frame</u>	<u>No.</u>	<u>Frame</u>
1279	2	1245	38
1280	7	1246	41
1281	9	1259	44
1282	11	1260	46
1272	14	1261	48
1276	18	1262	50
1277	20	1263	54
1275	24	1264	56
1271	27	1265	60
1268	30	1266	63
1269	33	1267	66
1270	35	1268	30
1245	38	1269	33
1246	41	1270	35
1259	44	1271	27
1260	46	1272	14
1261	48	1275	24
1262	50	1276	18
1263	54	1277	20
1264	56	1279	2
1265	60	1280	7
1266	63	1281	9
1267	66	1282	11