FILM STUDY GROUP

SUBJECT INDEX AND REPORT

T.O.M. REEL NO. 119

Prepared by

STANDARD OIL DEVELOPMENT COMPANY

STANDARD OIL DEVELOPMENT COMPANY

ABSTRACT AND INDEX OF TECHNICAL OIL MISSION MICROFILM

REEL NO. 119

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b) Manufacture of lube oils and resins from olefines	LU III 4(8)	Foot 23, Frame 8 to " 24 " 12

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Item LU III-2(2)

April, 1944 report on the synthesis of isoprene by the condensation of isobutylene with formaldehyde and on the polymerization of the isoprene in naphtha solution. 2% sulfuric acid may be used as the catalyst in the synthesis. The yield of the 4,4 dimethyl 1,3 dioxane is 90%. The dioxane is converted to the isoprene by treatment with phosphoric acid. 78% yield of isoprene based on the isobutylene is claimed. In addition to the preparation of isoprene there is also information on the preparation of dimethyl butadiene from trimethyl ethylene. Two dioxanes result -- 4,4,5 trimethyl, 1,3 dioxane and 5,5,6--1,3 dioxane. The latter can be converted to pinacolin by treatment with strong aqueous HCl. This pinacolin may be used as a blending agent in fuels since it has an octane number of about 114 or can be hydrogenated to tetramethylethane which has an octane number of about 93.

In connection with the isoprene, there is some data on the chlorination of the isoprene at -10°C. to give a granular product which is readily filterable and soluble in lacquer solvents. The authors also state that the polymerized isoprene after vulcanization is a good rubber formulating preparation.

Item LU III-3, Foot 11, Frame 9 to Foot 13, Frame 1

1939 report on plant for producing 15 kg. a day of lubricating oil from ethylene at Oppau. Although this report is of an early date, it gives information on equipment sizes, and flowsheets of the plant layouts with details of equipment used.

Item LU III-4 (1), Foot 13, Frames 3-4

1942 memorandum on the scrubbing of ethylene from coke oven gas with benzene at a temperature of 20°C. and a pressure of 20 atms.

Item LU III-4 (3), Foot 14, Frames 5-6-8-9-10

1944 report (Part 2) on isomerization of normal butane with aluminum chloride and aluminum chloride containing catalyst. This report presents the following conclusions:

1. Gamma alumina impregnated with aluminum chloride contains part of the aluminum chlorides in an inactive state which can be changed over to the active form by addition of HCl.

Item LU III-4 (3) (Cont'd)

2. A complex of aluminum chloride and polymerized olefins also was investigated.

3. A new carrier suitable for alumina chloride consists of bleaching earth bonded with 1% Al_2O_3.

This report stresses the need for complete removal of olefins from the butane feed for satisfactory catalyst life.

Item LU III-4 (5), Foot 20, Frame 6 to Foot 21, Frame 2

1943 laboratory data on the reaction of isobutyron with methyl magnesium chloride. (Grignard reaction) to make a carbonyl which can be dehydrated and then hydrogenated to 2,3,4 trimethyl pentane.

Item LU III-4 (8), Foot 23, Frame 8 to Foot 24, Frame 12

1943 report summarizing Oppau hydrocarbon research in the years 1939-1943. This report includes description of work in the following subjects:

1. Thermal and catalytic cracking.

2 and 3. Separation of olefins by extraction with copper-ethanolamine solution.

4. Selective hydrogenation of acetylene to ethylene.

5 and 6. Gas desulfurizing (especially COS removal).

7. Manufacture of naphthas from gaseous hydrocarbons by thermal or catalytic polymerization, by condensation and by alkylation.

8. Manufacture of hydrocarbons (lube oils, resins, etc.) from olefins.

9. Butadiene production.

A brief summary of the status of each of these subjects is included. This report includes a list of publications and patent applications made during this period.

Frames 7-8 give a list of the patent applications that have been filed in connection with this work.

LU III-4 (9), Foot 24, Frames 7-11

Developments in construction of apparatus for ammonia, iso-octane and methanol synthesis in Oppau in 1943. Equipment drawings are given in this report showing the old and the new types of equipment.

Item LU III-4 (10), Foot 26, Frame 1 to foot 29, Frame 6

1943 lecture by Pier on tungsten sulfide catalyst for vapor phase hydrogenation of middle oils obtained from sump-phase catalytic treatment of coal.

Item LU III-4 (11), Foot 30, Frame 8 to Foot 33, Frame 13

1944 report on hydrogenation of low temperature pitch from coal using either sump-phase operation with an iron catalyst on "grude" (coke from coal) or a solid pilled catalyst consisting of molybdenum sulfide. The pitch is preferably mixed with middle oil in the ratio of 60-40. By this process, high octane number gasoline, middle oil, and phenolic inhibitors are produced. In the case of the solid catalyst operation, it is necessary to de-ash the pitch with sulfur prior to catalytic treatment. It is stated that the liquid phase treatment with the solid catalyst gives double the yield obtained in the sump-phase operation and the catalyst life is good. The report includes numerous data and curves obtained in this operation.

On foot 30, frames 2-6, there is a letter which discusses this report and which also includes comparative data at Welheim and Ludwigshafen on the two processes for handling bitumen.

Item LU III-4 (12), Foot 34, Frame 1 to Foot 36, Frame 9

A report by Pier on the production of gasoline by hydrogenation. This appears to be a lecture by Pier in this field covering hydrogenation of natural oils and oils obtained from coal using sump-phase and solid catalyst in the liquid phase.

Item LU III-4 (13), Foot 36, Frame 10 to Foot 39, Frame 9

A lecture given in 1942 in Germany by K. Peters on the manufacture of synthetic fuels.

Item LU III-22, Foot 41, Frame 4 to Foot 42, Frame 11

1942 report on the dehydration of butylene glycol over a phosphate graphite catalyst in the presence of hydrogen. In the presence of 10 liters of hydrogen, per liter of contact, per 24 gms. of butylene glycol per hr., the yield of butadiene is

Item LU III-22 (Cont'd.)

greater by an average of 6% over the approximate 80% obtained without the use of hydrogen. In addition to butadiene, the by-products of this dehydration include: propylene, allyl carbonyl, butyroaldehyde, and high boiling oils. Other gases than hydrogen do not seem to have this promotional effect.

Item LU III-27, Foot 47, Frames 1-4

Emulsion copolymerization of acrylonitrile and methyl acrylic acid.

Foot 47, Frame 7

Emulsion copolymerization of styrene and methylacrylate and acrylic acid using Neopon N as the emulsifier.

Item LU III-27, Foot 48, Frame 5

Preparation of catalyst #4046.

Item LU III-27, Foot 53, Frame 1

Emulsion copolymerization of vinyl acetate with vinyl ethers to produce a material giving adherent films. The novelty lies in the use of emulsion copolymerization.

Item LU III-27, Foot 55, Frames 9-11

Copolymerization of isoprene with styrene. The importance of having pure isoprene for this purpose is emphasized.

Item LU III-27, Foot 57, Frames 10-14

Memoranda on polymers of esters of acrylic acid (made by reacting acrylic acid with aliphatic acids, glycols, naphthenic alcohols and aromatic alcohols).

Item LU III-27, Foot 58, Frames 3-6

Memorandum on polymers from a series of vinyl ethers with some information on the properties of the products.

Item LU III-27, Foot 58, Frames 9-10

Memorandum on the use of various polymers for water-proofing paper.

Item LU III-27, Foot 58, Frame 13 to Foot 59, Frame 2

Memorandum on the effect of aldehydes on isoprene polymerization in concentrations as low as 0.1%. The aldehydes have a slight promoting effect but in concentrations of 1/10 or higher, they have a pronounced effect on yield, particularly in the cases of propionaldehyde and crotonaldehyde. It is also stated that analytical tests carried out show the absence of aldehydes in commercial isoprene.

Item LU III-27, Foot 59, Frame 11

A memorandum which states that decalol-vinyl-ether and methyl-phenyl-carbonyl-vinyl ether can be polymerized at very low temperatures with boron fluoride to give solid polymers. Furthermore, mixed polymers can be obtained by the reaction of the above ethers with other vinyl ethers, e.g. vinyl isobutyl ether.

Item LU III-27, Foot 60, Frame 1

Polymers of cyclo octatetraene (made by polymerization of acetylene) by treatment with peroxides or with acid catalyst such as boron fluoride-dihydrate or with iodine. These polymers are stated to be unstable in the presence of light.

Item LU III-27, Foot 60, Frames 3-10

Memorandum on a calender having a tolerance of the foil thickness of about ±2 microns.

Item LU III-27, Foot 60, Frame 13-14 to Foot 61, Frames 2, 3, 4

Memorandum on the preparation and utilization of propionaldehyde. The propionaldehyde is made by oxidation of n-propyl alcohol with air over a silver catalyst with an 85% yield. The normal propyl alcohol is stated to be obtained along with ethyl alcohol from synthesis gas by the use of a five-component catalyst whose composition is not given. Among the uses for propionaldehyde discussed are:

1. Preparation of isoprene involving the condensation of propionaldehyde with acetaldehyde to produce methyl ~~aldol, and the hydrogenation of the latter to methyl~~ butylene glycol with the dehydration of the latter to isoprene. An overall yield of 80% is reported.

2. Preparation of amyl alcohol. This is accomplished by the steps involving condensation of the propionaldehyde ~~with acetaldehyde at elevated temperatures with the~~ loss of water to produce tiglic aldehyde (unsaturated C_5 aldehyde) and hydrogenation of the latter.

3. Preparation of trimethanol ethane which is used as a glycerin substitute.

Item LU III-27, Foot 63, Frames 7-11

Memorandum on the cost of the preparation of acrylic acid by the reaction of acetylene with alcohol, HCl, and nickel carbonyl. The basis for the cost calculations are given. This information may be of interest in arriving at a cost calculation in U.S. money.

Item LU III-27, Foot 65, Frame 13 to Foot 66, Frame 2

1940 memorandum on the comparative polymerization of butadiene and isoprene. This does not appear to contain much information but suggests some catalysts for polymerization that may be of interest.

Foot 75, Frames 2-3

1939 memorandum on the preparation of a continuous process for the preparation of succinic acid by the oxidation of tetrahydrofurane with nitric acid.

Foot 75, Frames 8-10

1939 memorandum on the conversion of adipic acid-dinitrile to hexamethylene-diamine, at 90-110°C. at 200 atms. pressure with a yield of 80-90%.

Foot 80, Frames 12-13 - Patent application No. I 69,678

Patent application on the use of residues from the dehydration of butylene glycol as insulation material.

Foot 84, Frames 1-13

A review of research work in 1940-1941 in the form of tables. This gives a rather complete list of all the projects worked on at that time under Dr. Reppe, and at Leuna.

Foot 85 - Frame 1

Table of technical products derivable from propargyl alcohol and butadiene.