SUMMARIES

Microfilm 2

U. S. Government Technical Oil Mission

SUMMARIES OF MICROFILM 2

I. Summary on Isopropyl Ether

The I. G. file on this subject shows that engine tests convinced the German Air Ministry of the superiority of isopropyl ether over the iso-octane alkylate with respect to the supercharged operation. Previous objections to the water-sensitivity, lower calorific value and peroxide formation of the ether were dropped.

In 1943, the I. G, prepared a project to build an isopropyl ether plant at Heydebreck for the production of 63,000 t/yr. of isopropyl ether and 16,500 t/yr. of allyl chloride from 70,000 t/yr. of propane. This amount of a allyl chloride would be converted into 13,000-14,000 t/yr. of glycerine. Ultimate coal consumption: 80,000 t/yr. for gasification and 75,000 t/yr. for power. It was expected that the output of this plant would double the production of special aviation fuels in Germany.

The isopropyl ether was expected to have a boiling range of 65°-75°C. and an ON of 98.

The cost of the plant was estimated at 35 million RM ($9 million), amount of steel required 28,000 tons. The end of construction was planned by January 1, 1946 and full production by July, 1946.

Method of manufacture: chlorination of propane into 75% C_3H_7Cl (mono-) and 25% $C_3H_6Cl_2$ (dichloro-product). Isopropylene and allyl chloride, respectively, are produced by catalytic dehydrohalogenation. Isopropylene is converted into di-isopropyl ether by the H_2SO_4 method. The steps of converting allyl chloride into glycerine are not mentioned. By-product HCl is reoxidized into Cl using 70% $FeCl_3$-30% KCl catalyst.

Although correspondence indicates the inclusion of the project in the construction program of 1944, further outcome is unknown.

Introduction

In accordance with arrangement made by Dr. J. B. Rather, a review was made of reel #2 referred to in Mr. Albert Miller's circular letter of August 9, 1945 and of August 24, 1945 to Mr. P. V. Keyser, Jr. This is a set of microphotographs of about 1000 sheets of miscellaneous files taken in the office of I. G. at Ludwigshafen - Oppau. These files are mostly fragmentary correspondence, letters, telegrams, technical notes dated from 1935 to first half of 1944 and referring to current matters on allocations, construction plans, operational details, test data, etc. There is little correspondence for the second half of 1944, and none for 1945. The major subjects covered are as follows:

I. Isopropyl ether from propane

II. Alcohol synthesis from CO/H_2 gas

III. Iso-octane (Tanol, E.T. 100) from isobutyl alcohol

IV. Fisher-Tropsch gasoline process

V. Oppanol (polyisobutylene) from isobutyl alcohol

VI. Tonalon (basic Al chloride) from waste $AlCl_3$ solutions

VII. Crude oil refining at Lutzkendorf

VIII. Miscellaneous

Type of Information

The tremendous volume of microphotographs taken in a great hurry covers almost exclusively isolated items fully understandable to those who are in every day contact with the respective operations, but not to outsiders. There are no complete reports in reel No. 2 describing entire processes or new developments in a manner useful to a technical man who is not familiar with the local conditions.

Many terms are coded (catalysts, equipment, operations, uses); the fundamental operations are assumed to be known to the corresponding parties; the files are unilateral in that they contain replies to missing inquiries; statistical data refer to isolated periods, but do not give sufficient material for reconstructing a picture of the size of production through the war; many

subjects are reported in the state of tests the outcome of which is not reflected in the file.

Condition of the Reel

The individual sheets are not identified by order numbers or otherwise, and are not in a chronological sequence which makes the work of interpreting 1000 frames an extremely difficult task. Furthermore, all photographs were taken from carbon copies, sometimes typed on both sides of the copy sheet. As a result, over one third of the film is hardly legible and worthless. Mr. A. Miller's remark to the effect that direct work on the microfilm is impossible and that enlarged photostats are necessary, is confirmed by our experience. We have picked out 350 more promising frames according to their contents and condition, but even from this amount of photostats made by a professional firm for us, about 25% were still illegible.

Identification of Items in Reel #2

The microfilm has no markings on the reel frames or on the 17 page index of subjects. In order to facilitate cross references, we have assigned order numbers from 1 to 279 as follows:

Page of Index	Item Nos.	Page of Index	Item Nos.
1	1 to 19	10	147 to 163
2	20 to 35	11	164 to 179
3	36 to 52	12	180 to 195
4	53 to 67	13	196 to 210
5	68 to 81	14	211 to 226
6	82 to 97	15	227 to 247
7	98 to 114	16	248 to 255
8	115 to 129	17	256 to 279
9	130 to 146		

Units such as tons, cubic meters, liters, etc., have been used without conversion to American units. They are sufficiently well known and their conversion is not always possible without the knowledge of auxiliary factors (e.g. density in the

conversion of tons to bbls.); only cost data have been expressed in U. S. $ assuming a Reichsmark equal to $.25.

Summaries of the major topics and brief abstracts of selected items are attached.

It is possible that we have overlooked and misinterpreted some points because of the fragmentary nature of the file material and our lack of familiarity with the coal conversion and other processes. Those specializing on Fischer-Tropsch and allied operations may wish to study the data further using our review as a supplement to the index of reel #2.

As far as the oil refining is concerned, the material includes data only on one small refinery as Lutzkendorf. This plant uses modern methods of distillation, propane dewaxing and phenol refining, which are common practice in this country.

In a letter of September 29, 1942 the I. G. advised the German Air Ministry that 15 tons of isopropyl ether, old American stock available at Polmin Wks., Galicia, could be utilized as follows:

(1) Aviation fuel 86 ON
85% motor gasoline 60-63 ON
50% @ 100°C., EP 150°C.
15% isopropyl ether
.85 cc. TEL (= 3.2 cc/gal.)

(2) Aviation fuel 96 ON
50-60% motor gasoline 60-63 ON
40-50% isopropyl ether
.85 cc. TEL (= 3.2 cc/gal.)

Reel 2, Section 10

II. & III. Summary on Isobutyl Alcohol and Iso-octane from CO/H_2 Gas

The production of isobutyl oil (mixture of various alcohols) and its utilization in the manufacture of iso-octane is discussed in correspondence between I. G. Farbenindustrie plants at Leuna, Oppau, Waldenburg, and Heydebreck in the years 1935-1938 and 1942-1944. The process discussed involves the reaction of CO and H_2 over a catalyst at elevated pressures. The manufacturing cost estimates of isobutyl alcohol and of iso-octane in units of the order of 4,000 tons iso-octane per year capacity show a wide discrepancy. A representative range for isobutyl alcohol seems to be 4.5-5.5¢ per pound. A corresponding price range for iso-octane appears to be 10-12¢ per pound.

The correspondence was investigated for clues as to special catalysts and reactions developed by the Germans in these years. It is possible that certain new and interesting engineering or production data were overlooked due to the fragmentary

character of the material and also to our lack of experience in this specialized field. However, very little concerning catalysts and reaction temperatures was found, and little of outstandingly new engineering principle was detected as far as we could judge.

The general process was as follows:

Charge Gases

Coke-oven or water gas is desulfurized over "Lauta" fillings to 2-3 mgs. per cubic meter.

Hydrocarbons such as methane are removed by a combustion method (treatment with O_2 over a catalyst) which lowers the methane content from 25% to 0.25%. This process for converting methane to CO and H_2 is described briefly in letters dated January 16, 1942 and December 8, 1942.

Ammonia, if present in the charge gases can be removed under 20 atm. pressure over moist silica gel.

The CO_2 content of the gas is also reduced at this point.

The synthetic gas thus purified together with enough H_2 to make the volume ratio of H_2 to CO equal to 2.3 (approx.) is compressed to 300-325 atm. and passed over a catalyst. Off gases rich in methane and a crude mixture of water and alcohols called isobutyl oil result. A decrease in the reaction pressure from 310 to 240 atm. was found to result in a 50% decrease in isobutyl oil production.

An example of the quantities used in this step is as follows:

To produce roughly 2.5 tons per hour of crude isobutyl oil, 15,000 m^3/hr. of purified CO and H_2 are passed through a catalytic reaction chamber, 0.8 m in diameter and 12.0 m in length.

Off Gases

The fixed gases generated in this process furnish heat for part of the subsequent distillations and are then utilized in one or more of the following ways:

a. Fuel for steam generation

b. Recycle stock after the high methane content has been converted to CO and H_2

c. Charge stock to methane conversion units for ammonia synthesis.

Isobutyl Oil

The product from the above reaction consists chiefly of a mixture of alcohols. It is fractionated in a series of nine continuous columns.

a. Stabilization

From 1.2-1.5% (by wt. chg.) of fixed gased and dimethyl ether is taken off in the overhead. Part of overhead passes to a side column from which a methanol cut rich in butane is taken. Some olefines are isolated.

b. Methanol Separation

Most of the 51-55% (by wt. chg.) of methanol is taken off in the overhead.

An intermediate cut is passed to an auxiliary column in which 0.4-0.5% (by wt. chg.) of di-isopropyl ketone is separated from methanol. The residue from this distillation is recycled with the raw oil.

The residue from the main methanol tower is allowed to settle into a water rich layer and a layer containing small amounts of water.

c. De-oiling Column

The layer containing most of the water is passed to column c. The residue from this column is water. The overhead

contains propanol, butanol, and water. It is recycled with the raw oil.

d. Water Removal

The low water content layer passes to column d. The overhead containing water, benzol and propanol is recycled. The intermediate fraction contains most of the propanol and isobutyl alcohol along with some higher alcohols.

The residue contains most of the higher alcohols, from 6.5 to 8.0% (by wt. chg.). It is passed to a sixth column from which a 110-200°C. cut is taken.

e. Propanol Separation

The intermediate cut from column d is here distilled. Most of the 1.5 - 1.8% (by wt. chg.) of propanol is taken off in the overhead.

f. Isobutyl Alcohol Separation

The residue from column e is here distilled.

Most of the 10-13% (by wt. chg.) of isobutyl alcohol is taken off in the overhead at 105-108°C. The residue containing some higher alcohols is recycled through column d.

Methanol

In the isobutyl oil process, methanol, although making up about 50% of the crude product, is considered in most of these letters as a side product. It is possible under certain undisclosed conditions to manufacture methanol in concentrations as high as 88% of the crude product. The relative costs of manufacturing methanol, isobutyl oil, and Fischer gasoline in plants of 150,000 tons per year capacity are given as $26/ton, $40/ton, and $49/ton, respectively. The relative capital outlays for the same are estimated at $10 million, $14 million, and $22 million, respectively.

Amyl and Higher Alcohols

In 1943 it was planned to separate by distillation

roughly 58,000 tons per year of amyl and higher alcohols into their component parts. These alcohols were then to be used for the production of ester oils for low temperature aero, axle, and motor oils syntheses.

Iso-octane (Tanol and E.T. 100)

The planned production of isobutyl alcohol by I.G. in 1944 in plants at Leuna, Oppau, and Heydebreck was to increase from 5,000 to 9,000 tons/month. Utilization of this isobutyl alcohol for the production of iso-octane was to increase from 3,000 to 7,000 tons/month in the same period. The rest was to be converted chiefly to Oppanol. However, by October, 1944 the production of isobutyl alcohol had fallen to about 1200 tons/month. At times, during 1944, one or more of these plants were out of operation entirely while the others were well below 50% planned capacity.

The production of iso-octane from isobutyl alcohol incurs a number of steps. These steps, rates of charge, capacity of reactors, and yields for a typical 4000 tons iso-octane per year plant are described as follows. The figures are on an hourly basis.

Description of Steps	Kg./hr.	Yield (% Theor.)
Chg. of Isobutyl Alcohol (Distilled)	701.6	
Isobutylene from Dehydration of Alcohol (5 atms.) (Chg. 936.7 liters/hr. over 703 liters catalyst)	510	96
Di-isobutylene from Polym. (after topping) (25 atms.) (Chg. 1390 liters/hr. over 150 liters catalyst)	419	
Di-isobutylene from Cracking of Tri-isobutylene - Formed in Polym. step (Chg. 214 liters/hr. over 400 liters catalyst)	39	
Total Di-isobutylene	458	90

Description of Steps	Kg./hr.	Yield (% Theor.)
Iso-octane from Hydrogenation of Di-isobutylene (200 atm.) (Chg. with H recycle of 6560 m^3/hr. over 950 liters catalyst)	458	98.5
% Theor. Yield of Iso-octane from Isobutyl Alcohol =		84.5
Iso-octane Yield (% by wt. alcohol chg.) =		65.3

Reel 2, Section 13

IV. Summary on Fischer-Tropsch Gasoline Process

According to the index, more material is devoted to this subject in Reel 1. Reel 2 deals to some extent with the Lutzkendorf F-T plant which operates in conjunction with a hydrogenation unit and a crude oil refining unit. A combination flow sheet (Item 254) presents this general layout, while the synthetic gas production from brown coal is shown in Item 268.

This synthetic gasoline plant grew rapidly between 1941 and 1943, from 6,226 tons/yr. to 42,000 tons/yr. total liquid production. A further increase to 75,000 t/yr. was planned for 1944 and each of the following two years, but available monthly records show a production on the same level in April and May 1944 as in the middle of 1943. In this connection, the production plan 1941-1946 (Item 252) is of interest.

Typical yield and properties of products may be illustrated by 1943 production figures as follows:

	Tons	Sp. Gr.	°C Boil. Range	Other Tests
Gasoline	22,720	.695	E.P. 168	O.N. 54
Diesel Fuel	8,600	.743	162/246	Flash 42° (closed)
Kogasin II	8,600	.767	235/312	
Paraffinic bottoms	3,010	.797	318/450	
Total Liquid Products	42,000			
Contact Paraffin Wax	860			M.P. 100°C.
Fuel Gas	2,960			

Reel 2, Section 10

V. Summary on Oppanol

Oppanol, the German counterpart of the American Vistanex, is polymerized isobutylene made from isobutyl alcohol. 100 parts of isobutyl alcohol produce 72 parts of isobutylene (by catalytic dehydration), which in turn, produce 60 parts of Oppanol (by catalytic polymerization with boron fluoride at -100°C.). Manufacturing details do not appear in the file. There are several grades of Oppanol, from 80,000 to 200,000 mol. wt., the latter being Oppanol B. In 1944, I.G. was producing 700 tons/mo. of Oppanol (450 at Oppau and 200-250 at Frose Wks.). This involved an allotment of 1200 t/mo. of isobutyl alcohol which was about 25% of the total isobutanol production and over 50% of isobutanol used for purposes other than the manufacture of iso-octane. Correspondence indicates arguments among the Air Ministry (RLM), Army Forces (OKW) and allocating agencies regarding the relative proportions of iso-octane and Oppanol to be produced from the available supplies of isobutanol in 1944. While some Oppanol was used as additive to lubricating oils and synthetic rubbers, almost one half went into plastics for the army, presumably as a protective coating of military fabrics. Mention is made of Oppanol B being applied in the form of 10% solutions in carbon tetrachloride and naphtha

in 1942. Then, 50% emulsions were developed to conserve solvents. I.G. operated a 200 t/mo emulsion plant at Oppau in 1943 and considered the erection of a second unit of 300 t/mo capacity at Heydebreck. Their method of production is not given, but a competitive process of the Biener Co. tested by I. G. with satisfactory results appears in Item 208. This method calls for swelling Oppanol B in naphtha, mixing with pigments, several kneadings and millings with emulsifiers, stabilizers and water. The product was evidently used for water proofing of military fabrics in winter campaigns. Oppanol B was also converted into sheets using silica gel as a filler. These sheets were to meet certain mechanical specifications such as minimum tensile strength and elongation, but the use is not mentioned.

Reel 2, Section 11

VI. Summary on Tonalon

(Items 236, 237, 238, 239, 240, 241, 242, 243)

This subject appears to have been of interest to I.G. as an outlet for waste aluminum chloride.

Tonalon, a basic aluminum chloride, $Al(OH)_5Cl$, is available as a 37% aqueous solution, and in various solid forms for the dye and pharmaceutical trade; as a solid, Tonalon has an Al_2O_3 content of 46-48%. Its solutions have the same acidity as aluminum triformate and aluminum triacetate but have an advantage of a higher content of effective Al_2O_3.

Tonalon is produced simultaneously with ethylene-chlorohydrin when ethylene oxide in concentrated or diluted gas streams is passed into aqueous aluminum chloride solutions. Laboratory work was carried out in batch, semi- and continuous units on absorption of ethylene oxide. The ethylene chlorohydrin is removed under vacuum from the aqueous solution; the

Tonalon solution remains. The ethylene chlorohydrin production for 1942 was 247, 196 kg. Industrial production for Tonalon was 121, 542 kg. in 1939.

Tonalon is used for impregnation of cloth, in the dye industry and pharmaceutical trade.

Tonalon H, an intimate mixture of Tonalon (80%) with urea (20%), is used for the impregnation of cloth and related materials. It was introduced in August 1939. Tonalon H has a solubility in water as high as 400 grams per liter of water; a 37% solution by weight has a specific gravity of 1.18. An advertising circular is given on the use of Tonalon H for impregnation of cloth by various methods.

A related subject is the conversion of waste $AlCl_3$ into aluminum formate by double decomposition with sodium or calcium formate and crystallization. Item 243 describes laboratory work along these lines.

Reel 2, Section 13

VII. Summary on Crude Oil Refining

This topic is covered in Reel 2 only in connection with the Lutzendorf plant. A part of their operations is refining of 100,000 tons/yr. of crude oil. From the American point of view, this is a very small plant of 2000 bbl/day capacity, but the refining steps appear to be up-to-date as they include two stage atmospheric-vacuum distillation, propane deasphalting of residue, propane dewaxing, phenol solvent refining and clay contacting of lubricating oils. As distinguished from American practice, there is no production of heavy fuels from crude, all residues such as asphalts and phenol extracts being sent to the hydrogenation plant for conversion into hydro gasoline and Diesel fuels. The disposition of kerosene, gas oil and waxy by-products is not shown, but they are not cracked since the plant

has no cracking units. There is, however, a cracking installation in the Fischer-Tropsch plant at the same location to process heavier than gasoline cuts from synthetic oil. The crude oil refining at Lutzendorf is essentially centered on the production of motor, cylinder and aviation oils by conventional methods.

The tie-in with Fischer-Tropsch operations at Lutzendorf appears to be only in the blending of gasolines. The 50,000 ton/yr. hydrogenation plant at the same location picks up the heavy residues and low value by-product oils for conversion into gasoline and Diesel fuels. In addition, it also handles coal tar from outside sources.

Reel 2

VIII. Miscellaneous

Synthetic Rubber

Of the two items on this subject, an excerpt from some report on the Russian production of Buna N by the Lebedev process may be of some interest. Up to 1941, there were 5 Buna plants, 30,000 t/yr. each, in operation. Some operating details are given in Item 247.

Dimol

Brief notes and a flow sheet for the production of 3 tons/day of Dimol indicate that this material is a condensation product of 1.6 parts of vinyl acetylene with 1 part of acetone (in the presence of solid KOH). Dimol was to be co-polymerized with butadiene in the ratio of 2:7. Outcome of project not indicated.

Hydrogenation

A general layout for hydrogenation of heavy residues from oil refining and cracking of Fischer-Tropsch gas oil is given in connection with the Lutzkendorf plant of I.G. Hydro gasoline and Diesel fuel are produced in about equal amounts. The process and production figures are briefly outlined in sections on crude oil refining and Fischer-Tropsch operations at Lutzkendorf.