

FILM STUDY GROUP

REPORT ON MICROFILM REEL NO. 40

Prepared by

THE ATLANTIC REFINING COMPANY

Mr. Newman

**SCANNING OF REEL #40
(Orig. Ident. Reel 8B)**

**U.S. Government Technical Oil Mission
Bag 3453 - Target 30/5.01 - Ruhrchemie A.G. Sterkrade-Holten**

SECTION 8. TRUE VOLUME OF PRESSURE VESSELS

Memo. Apr. 25, 1938 presents data to show that the true volume of pressure vessels may be calculated from the observed volume of gas released from a vessel which has been pressured to a definite degree. (4)

SECTION 9. POLYMERIZATION OF PENTENES AND HEXENES

Memo. Mar. 25, 1937 appears to have had its origin in the question as to whether catalytic polymerization of pentenes and hexenes in admixture with other olefins was covered by patents and is patentable. The writer cites literature and patents to show that this subject has been known, and adds his opinion there remain opportunities for patenting specific applications and variations of the process. (7)

**SECTION 10. DECLINE IN OCTANE NUMBER OF KOGASIN I BY
PEROXIDE FORMATION IN STORAGE; EFFECT OF INHIBITORS**

This appears to be a condensation of a report from the Kaiser Wilhelm Institute for Fuel Research, probably in 1938. Kogasin I is very susceptible to peroxide formation in storage, with attendant lowering of the octane number. The addition of 0.0015% naphthol, hydroquinone or pyrogallol imparts stability for at least a year. The addition of wood tar distillate in amount of 0.025% gave stability for 3 months. The prompt addition of fuel alcohol to the material being placed in storage lessens the danger of peroxide formation, but alcohol alone will not give stability for more than 1/2 year. Patents are cited on the use of inhibitors in motor fuel. (8)

**SECTION 11. CATALYTIC POLYMERIZATION OF UNSATURATED
HYDROCARBONS (27)**

Report Mar. 29, 1939 deals with polymerisation using solid phosphoric acid catalyst. Three principal studies were made:

- (a) Polymerisation of light naphtha.
- (b) Polymerisation of light liquid hydrocarbons (C₃-C₆).
- (c) Combination of charge stocks as in (a)(b) with and without the addition of ethylene.

The catalyst was of the Ipatieff type with the following composition:

60	grams	magnesium	chloride
50	"	"	oxide
100	"	kieselguhr	
50	"	starch	
50	"	activated clay	
600	"	phosphoric acid	(82%)

In making motor fuel with an end point not exceeding 200°C., it is hardly necessary to encourage polymerization beyond the formation of dimers. A relationship between extent of polymerization and quality of polymer was derived. The factor K is equal to the amount boiling above 200° divided by the quantity boiling above 70°. In other words, a low K value indicates an effective polymerization which produced much material in the gasoline boiling range and only a small amount heavier than motor fuel.

Polymerisation of Light Naphtha

A naphtha with initial point 25°, end point of 76° and an olefin content of 8.4% was subjected to polymerization at pressures between 1 and 10 atmospheres, temperature of 150 - 250° and with a threefold range of thru-put. It was shown that an increase in temperature or pressure or a decrease in thru-put velocity increased the polymerization. Tables I and II illustrate the effect of operating pressure.

Table I

Light Gasoline, E. P. 80°
Polymerized at 200°; throughput rate 250 cc/hr.

<u>Pressure</u> (atmospheres)	<u>Polymer</u> (%) (over 200°)		<u>K</u> value
1	7	-	.14
2	14	1.5	.11
4	17	2	.12
10	31	8	.25

Table II

Light Fraction (20 - 70°)
which had been subjected to polymerization at 5 atmospheres and 200°, throughput rate 400 cc/hr. gave a K value .20.
It is now subjected to polymerization at 200° and throughput rate 250 cc/hr.

<u>Pressure</u> (atmospheres)	<u>Polymer</u> (%) (over 200°)		<u>K</u> value
4	22	3	.14
10	42	6	.14
20	44	4.5	.10
50	48	4	.08
100	41	2.5	.06

The great advantage of elevated pressure is the ability to process more material per unit of time.

Cold pretreatment of the charge stock with Tonsil did not effect removal of gum and resin-forming substances. Two-stage polymerization was believed advantageous only when thruput rates above 2,000 cc per hour were used; below this charge rate simple processing was best.

At the very high thruput rates and mild polymerisation, more material boiling above 200° was formed than when polymerization was conducted at normal rates and the degree of polymerization was higher.

Polymerisation of Light Liquid Hydrocarbon

The charge stock consisted of 60% C₃H₆-C₄H₈ and 4.5% C₂H₄. In the first series, constant conditions of 200° and 100 atmospheres were employed. It was found that the conversion of C₃H₆ and C₄H₈ varied inversely with thruput rate; the polymerization of C₂H₄ was irregular. A second series at 10 atmospheres pressure showed even greater effect of thruput on degree of polymerization. Raising the pressure at lower thruput rates increases the conversion. The octane number of all the polymer gasolines made from light hydrocarbon charge was 96 - 98 (research method).

Polymerization of Light Gasoline & Light Liquid Hydrocarbon without addition of C₂H₄

A 1:1 mixture of light naphtha and light liquid hydrocarbon was subjected to polymerization in a bomb. C₃H₆ and C₄H₈ in the light gaseous charge was 43%. They polymerized in the mixture as though they were alone. No appreciable change in the 200° point was effected by the use of this mixture; for example, with severe polymerisation (92% conversion olefins) the volume was 86%, while at milder polymerisation (23% conversion of olefins) the percent boiling at 200° was 93%.

with addition of C₂H₄

A mixture containing 42% C₃H₆-C₄H₈ and 22% C₂H₄ was used. Polymerization of C₃-C₄ olefins occurred in the usual manner; the conversion of C₂H₄ was appreciably less, although increasing as the C₃ polymerization increases. At a point where about 90% of the C₃-C₄ was polymerized, about 18% of the C₂H₄ was reacted.

Investigation of the Phosphoric Acid Catalyst

The hydration temperature was found to be important and an optimum 250° was discovered. A test at 310° gave rapidly decreasing activity. Preliminary experiments were made in maintaining catalyst activity by introducing moisture during the run. The UOP polymerisation process was of continuing interest.

Polymerization of Light Hydrocarbon with increasing Thruput

Memo. June 12, 1939. A C₃-C₄ mixture was charged to an experimental unit, and it was found that by employing narrow reaction tubes it was possible to put through five times the volume prescribed by UOP without incurring conversions below 90%. The temperature prescribed by UOP was 190 - 205°; by increasing this temperature to 240 - 250° a ten-fold overall polymerization was accomplished with conversion not less than 80 - 85%. The strongly exothermic reaction did not cause any overheating in the reaction chamber, the heat being distributed throughout the tube by the high velocity of the material being processed. (6)

Reviewer's note: This work on polymerisation presents almost nothing new to American Technology. The employment of polymerisation for manufacture of aviation fuel blending components is not discussed and all the octane numbers reported are believed to have been made upon unhydrogenated material.

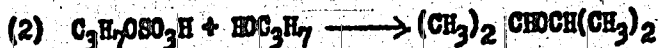
SECTION 12. PREPARATION OF ISOBUTANE

Memo. Feb. 13, 1939. The text (2) describes the laboratory preparation of isobutane by treating trimethyl carbinol with hydrochloric acid to form isobutyl chloride. This latter was then decomposed to form isobutane.

SECTION 13. PREPARATION OF ALCOHOL FROM C₃-C₄ HYDROCARBON AND THE PREPARATION OF ISOPROPYL ETHER FROM ISOPROPYL ALCOHOL

Memo. Jan. 16, 1938. It was possible to convert 65-70% of olefins into alcohol, and the writer believed that in continuous large scale equipment 75 - 80% alcohol yield was possible. About 14% is converted to naphtha or higher polymer; the remainder of the olefin passes through unchanged. The process depends upon the absorption of the olefin in concentrated sulphuric acid and subsequent decomposition of this addition product. It is not believed to have novel features over practice used in this country.

The production of di-isopropyl ether depended upon the reaction:



The optimum conditions for ether production were described as:

H₂SO₄ concentration, 70 - 80%; temperature below 69°; as large a proportion of isopropyl alcohol as can be secured (this increases the yield of ether); agitation of the materials undergoing reaction; the addition of 0.5-1% P₂O₅ to the sulphuric acid suppresses polymerisation completely. (33)

SECTION 14. UOP INHIBITORS FOR POLYMER GASOLINES

Memo. June 13, 1939. The UOP inhibitors Nos. 1 and 4 added in small amounts to polymer gasolines imparted stability without appreciable effect upon the octane number. (2)

SECTION 15. FURTHER WORK ON THE PRODUCTION OF ALCOHOL FROM C₃-C₄ HYDROCARBONS

An undated memo. (38) probably covering work in summer of 1938. Continuous countercurrent absorption was explored, using several means for dispersing the hydrocarbon into acid, such as the injection of hydrocarbon as a fog or as small bubbles. Apparently the contact time was too short because of the agglomeration of the hydrocarbon, and this type of absorption was abandoned in favor of batchwise treating in which dispersion of the acid and hydrocarbon phases depends upon stirrers. Using temperature about 30°, residence time about 1 hour, 75% H₂SO₄ and an acid-hydrocarbon proportion of 1:1, the one-stage absorption of olefins was about 75 - 80%; two-stage processing gave about 95% absorption. The polymer gasoline production from charge stock in which the C₃H₆ - C₄H₈ proportions were 1:2 was about 23% even when dilute acid and short absorption time was employed. It was concluded that the necessary reaction time is dependent upon the intensity of stirring, temperature, concentration of olefins and sulphuric acid. The regenerated acid was a somewhat better absorption medium than fresh acid. A type of contactor apparently equivalent to a turbomixer gave results parallel to those above.

Decomposition of the Acid-hydrocarbon Complex

The breaking down of the acid-hydrocarbon reaction product was studied both in batch and continuous units. A considerable amount of poly gasoline, presumably highly branched, could be hydrogenated to an octane number of about 96.

Perhaps the most enlightening part of this memorandum is the specifications written for a plant to treat 14 tons/day of hydrocarbon, having an olefin content of 44%. It may be presumed that this specification embodied Ruhrechemie's opinion as to suitable operating conditions.

Absorption Unit

Pressure, 15 - 20 atmospheres; operating temperature, 40 - 50°; batch processing 2 hours on stream; 75% sulphuric acid.

Ester Decomposition

Continuous operation about 16 hours daily in which the charge is 1250 kg ester per hour and 1875 kg H₂SO₄. The product is 350 kg pure alcohol/hr. (recovered here as aqueous solution) and 2500 kg 25 - 30% H₂SO₄. The decom-

position is accomplished with countercurrent exposure to direct steam for a period of about one hour. The mixture of hydrocarbon effluent and polymer naphtha is neutralized by exposure to solid caustic and is then distilled in conventional equipment.

Memo. June 2, 1939 on conference with Rheinpreussen on alcohol synthesis. Alcohols had been proposed as components of fuel, but objection had been raised because of low heat value, possible corrosive combustion products and an undesirable increase in vapor pressure imparted by the alcohols. This increase in vapor pressure in the case of methyl and ethyl alcohols was shown to exceed calculated values. However, in the instance of propyl and butyl alcohols, the change in vapor pressure by addition of amount of alcohol up to 15% is negligible. The Army's interest in alcohol as fuel is sustained. (2)

SECTION 16. CALCULATION OF WALL THICKNESS OF OVENS

This undated and unidentified item deals with the measurement of flowing gases and liquids in pipes. The title should read "fluid flow measurements with an orifice." (10)

SECTION 17. THE USE OF ACTIVATED CARBON FOR RECOVERY OF NAPHTHA AND LIGHT HYDROCARBON FROM RESIDUAL GAS

Memo. June 28, 1938. Operating cost for recovery with activated carbon at 7 atmospheres is only half as great as at normal pressure, and because of the high recovery showed to advantage when compared to the absorption oil process.

The carbon was identified as Supersobon FS. The amounts of naphtha and light hydrocarbon (C_3-C_4) in the charge gas were 250 - 400 and 150 - 350 gr per cu. meter, respectively. (2.5 - 4.0 and 1.5 - 4.0 G.P.M.) Total recovery of naphtha is wholly attained by the activated carbon, and 90% of the C_3-C_4 hydrocarbon will be recovered. Steam required for reactivating the carbon is 2 kilos per kilo recovered hydrocarbon; water requirements at 20° are 30 liters per kilo recovered product; carbon is used equivalent to 1 kilo for each 1.5 kilos product recovered.

Reviewer's note: This appeared to be a careful consideration of the application of activated carbon to recovery of hydrocarbons from gas. (7 frames)

SECTION 18. DRAWINGS AND TABLES (SERIAL #DVA) MEDIUM PRESSURE REPORT

Reviewer's note: It is presumed that the initials DVA stand for Pressure Research Division. There is no text in this section to permit absolute tie-up of these tables, graphs and drawings. Items appear in the following order:

Graph referring to ovens #4 and #5, in which CH_4 production, CO decomposition and contraction are plotted against time on stream.

Graph for oven #5, showing the same function.

Flow diagram showing valving and piping connections for activated carbon absorption plant - Drawing ZM103/52 dated Mar. 22, 1938.

Graph dated June 16, 1938 referring to oven #5 and showing contraction and temperature profile as a function of time on stream.

Item 551 - June 27, 1938 - table of data showing yields and inspections for synthetic products made at 7 atmospheres; the catalyst has been used for 5 months.

Sketch Aug. 1, 1938 showing insertion of sheet metal filler to lessen the free space in oven #2.

Sketch Aug. 17, 1938 apparently shows the form and chemical composition of catalyst charged to a number of ovens.

Graph #425, Dec. 3, 1937 temperature-pressure relationships for saturated steam.

Tabulated data on oven #1 for period Apr. 14 - May 19, 1938.

Graph showing contraction and temperature profile for ovens #1 and #7 plotted against duration of test in the period Apr. 9 - Apr. 12, 1938.

Graph showing contraction and temperature profile for oven #3 plotted against duration of test in the period Jan. 21 - 25, 1938.

Page of tabulated data, Aug. 29, 1938 resistance of different unreduced catalyst with respect to pressure (?).

Graph Sept. 1, 1938 showing a plot of volume of Diesel oil flowing through catalyst as a function of time.

Graph showing pressure drop of unspecified material through catalyst.

Sketch #11, Sept. 12, 1938 giving data for oven 132 and showing pressure drop relationship.

Sketch #12, Sept. 19, 1938 pressure drop measurement in oven #8.

Sketch #13, additional data on oven #8.

Graph undated, relating to oven 134 and showing plot of charge rate, temperature and contraction as a function of time in service.

Sketch #14 relating to Run #3 of the Research Laboratory and Runs #132 and #134 of Ruhrbensine in 1938. The graph shows throughput rate, contraction and vapor pressure as a function of time on stream.

Sketch #15 showing pressure drop measurements for ovens #8 and 132.

Sketch #16, Oct. 19, 1938 operating data. oven #5, second filling.

Sketch #17 continuation of data on oven #5, second filling.

Sketch #18 tabulated data of oven #1, third filling.

Sketch #22, Nov. 2, 1938 boiling point curves of normal paraffin and pressure paraffins.

Two unidentified pages giving properties of pressure paraffin.

Sketch #28, Nov. 11, 1938 boiling point curves on total product, ovens #8 and 131.

Sketch #42, Jan. 17, 1939, data on oven #4 which apparently is continued on item #43.

Sketch #51, Mar. 15, 1939 comparison of normal pressure and medium pressure synthesis (RB) using cobalt-thorium-magnesium catalysts.

#52 - data on oven #2, 4th and 5th filling continued on #53.

Undated pressure differential measurements.

#56, Aug. 16, 1939 pressure temperature relationships of saturated steam.

#57, Schematic layout of activated carbon plants #5, 6, 7 and 8.

#58, Aug. 31, 1939, data on oven #4, fourth filling continued on item #59.

#60, operating data on ovens #1 and 8. This sheet is dated Sept. 4, 1939 and is continued on #61.

#62, Jan. 3, 1940, oven #10, first filling; graphs showing reaction data as a function of time on stream.

#64, Feb. 21, 1940, additional data on oven #10.

#65, Feb. 29, 1940, comparison of decomposition of synthesis gas and water gas by cobalt and iron catalysts at 7 atmospheres pressure.

#66, Mar. 1, 1940, oven #4, fourth filling; yield of liquid products as a function of CO decomposition.

#68, Mar. 22, 1940, oven #10. Graphs showing contraction, decomposition and liquefaction constants as a function of time on stream.

#69, Apr. 14, 1940, ideal CO₂ formation depending upon H₂:CO proportions in naphtha synthesis. This applies to #70 also.

#71, June 24, 1940. Graphs showing contraction and temperature as a function of time on stream.

#72 also relates to this type of data obtained from oven #10.

#73, Aug. 4, 1940, data obtained on ovens #3, 4, 10 and 12, showing CO liquefaction constant as a function of heat transfer surface in medium pressure synthesis.

#84, principal physical constants for hydrocarbons. Gives boiling point, density and molecular weight for hydrocarbons in the range CH₄ to C₁₉H₄₀.

Unnumbered page Mar. 24, 1941 showing calculated analyses and reaction constants in the production of city gas with iron catalysts.

SECTION 19. LUBE OIL PRODUCTION FROM C₃-C₄ HYDROCARBONS (GASOL)

One page memorandum Apr. 7, 1944 summarizes work on the following experiments: "2026, 2164, 2905, and 3385". Lube oils with viscosity pole height from 2.4 up to 2.9 were made.

SECTION 20. GRAPHS COMPARING PROPERTIES OF CRACKED NAPHTHA AND COBALT RECIRCULATION NAPHTHA

These graphs were unnumbered and undated, but apparently refer to oven #10, tenth filling. (2)

SECTION 21. DISTILLATION CURVES FOR IRON CATALYST NAPHTHA BEFORE AND AFTER PURIFICATION

Unnumbered graph sheets Aug. 16, 1940 probably referring to tests 2968. The treatment was with BaHSO₃ and sodium in unspecified amounts. (1 frame)

SECTION 22. OCTANE NUMBER OF MIXTURES OF POLYMER NAPHTHA AND RESIDUAL NAPHTHA FROM LUBE OIL SYNTHESIS

Memo. Dec. 27, 1940 - no significance. (1)

SECTION 23. LUBE OILS FROM MEDIUM PRESSURE PRODUCTS

A series of about ten reports. The first dated June 4, 1942 is entitled "Purification of Primary Naphtha from Alcoholic Residues by Passing the Vapor over Alumina". The writer has submitted this memorandum (3) in reply to a report on this subject June 1, 1942. It is accompanied by free hand sketches of equipment layout and outline of the operation as follows:

The catalyst is aluminum hydroxide held at a temperature between 240 and 320°. After heat exchange with incoming charge, the product is passed through a water separator with a residence time of about 2 hours. It is stated that the catalyst could be kept in service 10 - 15 days without regeneration. When the catalyst has about 5 - 6% carbon deposited on it, regeneration with air is specified. The writer cautions that large amounts of recycle inert gas should be employed to avoid overheating.

Production of Oil from the Primary Product of Naphtha Pressure-Synthesis

6th Progress Report - June 1, 1942

For a period of a year, research has been concerned with the separation of the alcoholic portions of recycle naphthas made with cobalt catalysts. The means employed for dehydration over aluminum hydroxide, temperatures of 230° increasing to 300° in a period of 8 - 12 hours appeared favorable. The catalyst surface is gradually carbonized, necessitating high temperatures which favor isomerization. The yield of naphtha was said to be 2140 l/kg alumina. The OH number should be less than 1 to give desirable oil synthesis. Aftertreatment to neutralise the naphtha is not necessary but is recommended because it increases the life of the catalyst. Detailed directions are given for preparation of the alumina catalyst. (18)

5th Progress Report - July 15, 1941

This memo. (17) reviews work with iron catalysts in the production of primary naphtha, dealing particularly with data from oven #11, 7th filling.

A characteristic of these naphthas was the high OH number (50 - 57) which yielded 63% normal oil with a pole height of 1.65. Material low in olefin which had been distilled over PCL₅ or sodium and completely freed of alcoholic components made an oil of pole height 1.6 with a yield of 54% from charge naphtha with boiling range 70 - 180°.

Investigations were made of charge naphtha for new research. It was shown that large amounts of concentrated phosphoric acid affords a treated naphtha suitable for the oil synthesis.

Activated alumina at 250 - 300° was found to be effective in removing the alcoholic portion from the charge stock for oil synthesis. This treatment substantially reduces the OH number. The treatment of the naphtha vapor with concentrated phosphoric acid at 170° also reaches the same objective, whereby cobalt catalyst naphtha with low OH numbers is obtained. Of special interest, particularly for iron catalyst naphtha, is the purification effected by concentrated phosphoric acid at 20 - 50° upon the fluid hydrocarbon mixture. There is an appreciable lessening of corrosion. Other means of purification were CaCl_2 , magnesium activated with AlCl_3 , and activated clays, which were less effective.

4th Progress Report - June 24, 1941

This report (20) covers investigations of recycle pressure-synthesis using cobalt catalysts where a primary naphtha which has been subjected to certain treatment is converted to desirable oil. This processing did not entail the difficulties encountered in iron catalyst naphtha. Treatment with phosphoric acid was promising.

Note by reviewer: Primary naphtha is that liquid by-product resulting from treatment of water gas or other CO:H_2 mixtures over cobalt or iron catalysts to produce hydrocarbon. A very considerable amount of alcohol results from side reactions. Polymerisation of the olefins in the primary naphtha to obtain lubricating oils was developed in Germany. The text is concerned with product from oven #10, 10th filling.

3rd Progress Report - Mar. 15, 1941 (15)

In evaluation of run on oven #10, 10th filling in the period Nov.-Dec. 1940, the recycle naphtha exhibited lessening of the olefin content compared to fresh charge and the obtainable yield of normal oil drops from a figure of 55 down to 35-40%. At the same time, the viscosity pole height of the oil deteriorated from 1.64 to about 1.85. While ZnCl_2 and activated aluminum were found not wholly effective for pretreatment of the naphtha, it was found that by passing the naphtha vapor at 160 - 200° through concentrated phosphoric acid or by passing it over clay at 380° would accomplish reasonable results. A test run was made to explore the yield and properties of an oil made by pre-treating naphtha with metallic sodium.

2nd Progress Report - Jan. 10, 1941

This report (15) covers work on the pretreatment of naphtha with concentrated phosphoric acid. The naphtha in liquid form was reacted with the phosphoric acid or was vaporized at 80 - 150 mm. Hg and passed through the acid. Current production of naphtha was treated with substances such as ZnCl_2 or activated aluminum, and it was established that the treatment must follow and not precede the synthesis. It further established that the OH, NV and VZ values must be low for favorable oil synthesis.

1st Progress Report - Nov. 26, 1940

The work in this section (11) is largely identified as oven #9, third filling, and oven #10, tenth filling. Pretreatment of the naphtha with NaHSO_3 plus sodium, activated aluminum or SiCl_4 gave an appreciable increase in oil yield with simultaneous formation of contact oil. ZnCl_2 PbI_2 and SnCl_4 were used for the hot treatment of naphtha. All these were successful to some degree in eliminating the alcoholic character of the synthesis product. Present experiments pointed to the use of silicagel and clay for treatment of the naphtha vapor. It was observed that passing the naphtha over silicagel while perhaps not raising the yield of oil, tended to improve the octane number of the naphtha because of isomerisation.

Initial Report Oct. 31, 1940 on Production of Oil from the Primary Product of Naphtha Pressure-Synthesis

This section (16) reviews and comments upon the following period: oven #10, 9th filling; oven #2, 8th filling; oven #11, 5th filling; oven #11, 7th filling; oven #10, 10th filling. Research showed that a pretreatment of the naphtha from pressure-synthesis before polymerisation to oil is definitely necessary. Agents such as NaHSO_3 , followed by sodium, SiCl_4 , HgCl_2 , and activated aluminum were explored.

SECTION 24. LUBE OIL FROM MEDIUM PRESSURE PRODUCTS. OTHER REPORTS INCLUDING NAPHTHA REFINING

Memo. Feb. 17, 1945. Refining of recycle naphtha before oil synthesis by means of cold ZnCl_2 solution. A fraction of recycle naphtha 60 - 200° produced by cobalt or iron catalyst was cold treated with ZnCl_2 solution containing HCL in a continuous five-step cascade type equipment concentrated in order to free the naphtha of alcoholic substances, thereby making the naphtha more suitable for oil synthesis. The yield of oil is further improved by neutralisation of the naphtha at 200°. The properties of the naphtha, ZnCl_2 and alcohol layers were determined. (12)

Memo. Nov. 1, 1944. Refining of recycle naphtha by passing the vapor over clay (alumina). Alumina of type I gives good results. The highest activity is obtained by calcining the alumina at not higher than 400°. Splitting out of alcohol is done at about 350°; polymerisation starts at about 360°. A space velocity of 1-1.5 is chosen if the OH number of the charge naphtha is about 45. Neutralisation of the naphtha afforded only minor advantages. The refining of recycle naphtha made by iron catalyst and having an OH number of 111 seems more difficult. (9)

Memo. Oct. 13, 1944. Influence of addition of phenthiazin on the yield and viscosity of normal oil when added before cold synthesis to refined recycle naphtha made with cobalt catalyst. Two cobalt recycle naphthas, one without neutralisation, the other after passage over soda lime were used in a series of experiments employing 3% AlCl_3 in the cold. In both instances, the addition

of phenthiazin slightly depresses the yield and viscosity of the N-oil. The experiment again showed how important it is to neutralize the naphtha by means of soda lime. (4)

Memo. Oct. 6, 1944. Oil synthesis after separation of the naphtha into narrow boiling fractions. The subtitle speaks of this memo. as Part 3 - Cobalt Recycle Naphtha and refers to two previous memoranda, the first dated May 11, 1941 - cracked naphtha from cold pressed oil; the second, dated Mar. 15, 1942 - cracked naphtha from diesel oils.

A cobalt recycle naphtha after refining with $ZnCl_2$ was divided by distillation into cuts: $C_6 - C_{14}$. Oils made from these were subjected to thorough analysis, and in the direction of C_{14} , showed a slight increase in Conradson, a strong increase in the gum content and a pronounced decrease in verdampfbarkheit (tendency to volatilize?). No simple relation was discovered between flow point and the boiling range of the naphtha. (5)

Memo. June 30, 1944. Influence of neutralization of the cobalt recycle naphtha refined with alumina upon oil synthesis. Naphtha was vaporized and contacted with soda lime at 200° . The respective oil yields on neutralized and unneutralized stock were 49.6% and 46.2%, while the viscosity at 50° was 9.1° and 7.8° Engler, respectively. (2)

Memo. Jan. 27, 1943. Relationship between olefin content and oil yield based on recycle naphtha test. If the recycle naphthas which are used in oil synthesis are arranged in groups according to their olefin content, the widely scattered values obtained as average figures for yield, viscosity at 50° , and pole height of oils made with cobalt type catalyst, show a tendency to increase with the amount of unsaturates in the naphtha. As the oven conditions during syntheses also influence the yield and quality of the oil, these average figures are only directional. As a convenient figure, it may be kept in mind that 100 parts olefin will yield 73% of N-oil from the olefinic cobalt recycle naphtha. (9)

Memo. Aug. 3, 1942. Is a pretreatment to neutralize the primary recycle naphtha necessary before oil synthesis? The data were analyzed and the following conclusions reached. Treating of iron catalyst recycle naphtha in the vapor phase with $ZnCl_2$ to free it of alcohol, results in lowering the NZ and VZ numbers when treated with soda lime. The neutralizing treatment favorably affected the oil yield and the contact oil. (4)

Memo. Aug. 2, 1941. Status of work on recycle naphtha. This report particularly covers work on oven #10, 10th filling in the period Sept. 1940 to Feb. 1941 and on oven #10, 11th filling in the period March to July, 1941. (7)

Memo. July 9, 1941. Cold extraction of iron-catalyst and cobalt recycle naphthas for improvement of oil synthesis. This is a generalised discussion (2) with no supporting data. Naphtha was treated at room temperature for one hour with 84% phosphoric acid. About 2.5 wight % alcohol was taken up by the phosphoric acid. No ester layer was formed. New continuous experiments were in progress. Extension of the research was undertaken using sulphuric and acetic

acid. Washing naphtha with an equal weight of 80% $ZnCl_2$ solution for 5 hours at 30 - 35° formed a good ester layer. Such treated oils were particularly useful in oil synthesis, and show very good contact-oil formation. The quality was also good. There was recovered about 53 - 60% oil whose viscosity at 50° is 15.0°E. and with a pole height of 1.63. About the same figures were obtained by cold treating oils with phosphoric and with sulphuric acids. The details on research are said to have been reported in monthly summary May, 1941.

SECTION 25. LUBE OILS FROM MEDIUM PRESSURE PRODUCT - PRODUCT ANALYSES AND POLYMERIZATION EXPERIMENT FOR OVEN CONTROL - IRON CATALYST

A note Sept. 30, 1944 transmits data (6) on oil synthesis derived from oven #11, 14th filling, using iron catalyst. (10)

Memo. July 15, 1943 from the pressure research laboratory. Analysis and polymerisation of samples oven #15, 6th filling, using iron catalyst. The fraction 60 - 200° has an increasing tendency to produce oil. The average value is 34%. Therefore, there is a considerable portion of low utility; the high boiling residue at 320° in the oven effluent diminishes from 47 to 21%.

Engler distillation of the fraction 60 - 200° was not rigidly correlated with the resulting pole height of the oil. The data shows the P_2O_5 - H_2SO_4 numbers, density, NZ, VZ and OH numbers of the fraction 60 - 200° as the run progressed. A set of data gives inspections and yields of synthetic oils made with treated and untreated distillates.

Note July 10, 1943 transmits data on fractionation of iron recycle naphtha. The memo. (4) is concerned with data derived from samples obtained on ovens #14A, 3rd filling, during the period April 15-22, 1942. The sample consisted of 18.5 weight % activated carbon naphtha and 81.5 weight % condensate oil.

Memo. Jan. 25, 1943. Inspection data (2) on product from oven #11, 12th filling, water gas recycle over iron catalyst. The test number is 3452 and covers the period Nov. 15-16, 1942.

Memo. Dec. 4, 1942. Inspection data relating to samples from run on oven #15, 3rd filling, using iron catalyst. (2)

Memo. Aug. 25, 1942, showing data (2) derived from oven #11, 11th filling. Water gas recycle on iron catalyst in the period July 29 - 30.

Memo. Aug. 14, 1942 relates to the same test. (2)

Memo. July 13, 1942 summarizes 18 samples from oven #14A, 3rd filling, using iron catalyst. The fraction 60 - 200° whose SP number increased from 60 to 65% in 140 days on stream, was given a treatment with ZnCl₂ and showed an average yield of 16.9%. The pole height was about 1.60 to 1.80. The purpose of the experiment was to show the effect of run prolongation with iron catalyst. (11)

Memo. Feb. 18, 1942. Data on oven #14A, 2nd filling, using iron catalyst. This data included examination of the oven product and inspection of the distillate fractions 60 - 200° used in the production of lube oil. (6)

Memo. Feb. 17, 1942. Data on test of oven #11, 10th filling, recycle naphtha over iron catalyst for the production of lubricating oils. There was a steady improvement of the oven product with continued use of the catalyst. (8)

Memo. Feb. 12, 1942. Data on oven #11, 9th filling, using recycle naphtha on iron catalyst. (6)

Memo. Feb. 4, 1941. Inspection of oil made over iron catalyst. (2)
This and the following memorandum of Jan. 28, 1941 referred to tests made for Aresso. (See Section 46 of Reel #39).

Memo. Dec. 4, 1940. Oven #11, 5th filling, water gas recycle over iron catalyst at 20 atmospheres. Inspection data relating to the activated carbon naphtha and condensate oil recovered. (2)

Memo. Nov. 25, 1940. Data relating to oven #11, 7th filling, water gas recycle at 20 atmospheres over iron catalyst in the period Sept. 11-19, 1940. (2)

SECTION 26. LUBRICATING OIL FROM MEDIUM PRESSURE PRODUCT - PRODUCT ANALYSES AND POLYMERIZATION EXPERIMENTS FOR OVEN CONTROL - COBALT CATALYST

Memo. Aug. 15, 1944 giving inspection data on oven #15, 6th filling, using iron catalyst and oven #10, 26th filling, using cobalt catalyst. (3)

Memo. June 19, 1944. Inspections and data relating to the use of three naphtha samples in oven #10, 24th and 25th fillings, using cobalt catalyst. (7)
Four pages of tabulated data which appear separated from any transmittal sheet. They relate to oven #16, 1st filling, using cobalt catalyst.

Memo. Aug. 24, 1943. Report (8) on inspection of product resulting from oven #10, 22nd filling, using cobalt catalyst. The naphtha used was the portion boiling between 60 - 200°.

Memo. Sept. 19, 1942. Analysis and inspection of 4 samples made with naphtha produced in the pressure research laboratories over cobalt mixed catalyst. The following runs are involved: oven #10, 17th and 18th fillings and oven #15, 1st and 2nd fillings. (5)

Memo. Aug. 26, 1942. Data (2) on products made in oven #15, 1st filling, water gas recycle over cobalt mixed catalyst in the period July 20-21, 1942.

Memo. Aug. 5, 1942. Inspection of two recycle naphthas made by Hoesch and the polymerization product of these naphthas. These two naphthas were made from water gas. In order to make an oil with pole height 1.8, the fraction boiling above 105° (37.6% of total naphtha) must be used. (8)

Memo. July 20, 1942. Inspections relating to oven #9, 4th filling, using cobalt catalyst and naphtha made at normal pressure. (5)

Memo. July 9, 1942 relating to oven #10, 13th filling - inspection of medium pressure synthesis in recycle operation with water gas and a cobalt catalyst. (2)

Memo. Feb. 25, 1942. Inspection of product made in oven #10, 12th filling. The fraction 60 - 200° gave, after purification, about 15% on the total oven product, increasing to about 20% yield on normal oil. The viscosity and pole height of these oils suffered somewhat as the run progressed. This experiment on the 12th filling was considered less favorable than for the 11th; both made with cobalt catalyst. (11)

Memo. Feb. 5, 1942. Inspections of product from oven #10, 11th filling, of product made from recycle naphtha. (12)

Memo. May 22, 1941. Three naphtha samples made at medium pressure by synthesis from water gas recycle over cobalt catalyst. These inspections referred to the product made in oven #11, 8th filling, presumably in the period Jan. 29-30, 1941. (7)

Memo. Apr. 29, 1941. Inspection of 3 naphtha samples from oven #10, 10th filling - medium pressure synthesis on recycle water gas. (6) See also memo. Apr. 22, 1941 for period Dec. 29-31, 1940 (2); Apr. 17, 1941 for period Dec. 16-17, 1940 (4); Feb. 22, 1941 for period Oct.-Dec., 1940 (5).

Memo. Dec. 20, 1940. These inspections refer to oven #2, 8th filling, operating at low pressure on recycle water gas in the period Aug. 25-26, 1940 and to the product of oven #9, 3rd filling, in the period Oct. 4-5, 1940. (3)

Memo. Dec. 5, 1940. Inspection of sample mixture from ovens #9 and 10. (1)

Memo. Dec. 1, 1940. Inspection of sample from oven #10, 9th filling, non-recycle operation at 7 atmospheres. The sample represents the period July 27-28, 1940. (4)

Memo. Nov. 29, 1940. Inspection of 3 naphtha samples taken from oven #10, 9th filling, non-recycle water gas operation at 7 atmospheres in the period Aug. 13-14, 1940; oven #10, 10th filling, medium pressure recycle water gas operation in the period Sept. 1-2, 1940. (4)

Memo. Nov. 28, 1940. Inspection data from oven #10, 10th filling, medium pressure recycle water gas operation in the period Oct. 2-3, 1940. (2)

SECTION 27. MANUSCRIPT INDEX (GERMAN) RELATING TO RECYCLE NAPHTHAS AND THEIR OILS, COVERING SECTIONS 22 TO 26 (4 frames)

Bag 2744 - Target 30/5.01 - Ruhrchemie A.G. Sterkrade-Holten

SECTION 1. DIAGRAM OF CATALYST TRANSPORT KUBEL (1)

This drawing bears the designation Ruhrchemie PF9, Mar. 15, 1936. It is not accompanied by text. It appears to be a container with principal closures top and bottom and provided with a screen and heating coil near the bottom.

SECTION 2. COMPAGNIE FRANCAISE DE RAFFINAGE PROJECT

Letter Aug. 2, 1941 addressed to Gutehoffnungslutte upon a project for naphtha synthesis involving Ruhrchemie Fischer-Tropsch process. Process conditions, charge stock requirements, and product are cited. There is no text to show whether this naphtha and lube oil plant was actually brought to construction. (9)

SECTION 3. ANIC (ITALY) PROJECT - DATA ON KOPPERS AND Lurgi GASIFICATION PROCESSES

Memo. Apr. 22, 1938 relating to a plant to make 100,000 tons/yr. finished naphtha from Baldarno lignite, containing 52.5% water. The material shows plant investment and operating costs based upon the alternative use of Koppers and Lurgi gas generators. (20)

SECTION 4. MISCELLANEOUS PAPERS CONCERNING LUBE OIL SYNTHESIS

Process for production of valuable lubricating oils. Material undated, refers to German patent 593455, class 230 group 1. Fractions derived from

mineral and tar oils are reacted in the presence of a condensing or polymerizing agent with the polymers, preferably the higher homologues of isobutylene. One of the examples cites 100 parts of a lube oil fraction with a VI of 55 was reacted with one part of isobutylene polymer made with boron fluorides at low temperature. The oil has a VI of 91. When this solution is reacted with two parts $AlCl_3$, undergoing stirring for two hours at 80° , there is recovered an oil with VI 99.3.

Memo. Jan. 27, 1940. Abstract of intermediate report #3. (Jan. 19, 1940) This memo. relates to utilization of a lubricating oil. Trial in 3 engines was reported. The experiment showed that utilization of oil in the engine depended upon numerous factors. The nature and source of the oil is not disclosed.

Memo. June 27, 1939. Aging of lube oils. Instructions for purchase and testing of lube oils - 1939.

Memo. Sept. 26, 1940. Experiment with recycle naphtha. Report of Aug. 29, 1940. Tabulated data relating to tests in oven #2 in the period August 1940 and an unspecified run September 1938.

Memo. Sept. 20, 1940. Production of lube oils with Index 120 from cracked products. (7) Cracked naphthas with an end point at least 280° are used in the production of lube oils with Index 120. If the total cracked naphtha is divided into two fractions, the higher boiling portion yields lube oils with the desired index; 50 - 60% of the total recovered lube oil made in this way will have the desired viscosity. The total amount of lube oil amounts to about 47%.

Memo. Dec. 16, 1940. Use of Ruhrbensin lube oils. This is a note from Prof. Martin to Dr. Hagemann, urging him to produce certain samples for trial. (1)

Memo. Oct. 19, 1940. Inspection data on two samples K-1773 #2922 and K-1814 #3001/6. These were aviation oils.

Undated abstract which seems to refer to Swiss (?) patent 112241 IVa/23c. The patent claim is as follows: Lubricating substances for combustion engines, consisting of white oils which are practically free of unsaturated hydrocarbons and with a viscosity of about 4 - 15° Engler at 50° .

Memo. Sept. 14, 1940. Production of lube oil for the main laboratory.

Memo. Nov. 29, 1940. Application of Ruhrbensin lube oils.

Report of Oct. 10, 1940. Cylinder and compressor oils were tried in service.

Memo. Nov. 13, 1940. Process for neutralisation of high boiling hydrocarbon oils treated with sulphuric acid. This appears to relate to patent application V.33405.IVa/23b dated Dec. 24, 1935. The patent claims that the

treatment for a long time at 300 - 350° results in decomposition or separation of objectionable organic acids. Distillation is with superheated steam.

Nov. 25, 1940. Process for polymerization of isobutylene. Application 61446 IVc/39b. The patent claims production of polymer by treating isobutylene with catalyst, preferably boron fluoride, for the Friedel-Crafts reaction, at temperatures below -10° and in the presence of small amounts of monovalent alcohol.

Production of High Octane Naphtha

Abstract of patent application J.51351 IVa/23b. Naphtha is extracted with acetonitrile or mixtures of acetonitrile with water formamide or glycol. The second claim operates as in claim 1 and states that one takes two high boiling naphtha fractions, of which the end point of the lightest and the initial point of the heavier are about 100 - 130°; extract these fractions and mix the extracts with each other or with other fuels, or with portions of the residue remaining after the extraction.

Memo. of conference Feb. 19, 1942, between Dr. Schaub and engineers of the Berlin Technical Hochschule regarding an oil testing machine.

Abstracts of letter Hagemann to Valde Oct. 5, 1942, giving examination and specifications for certain lubricating oils for winter use.

Production of High Molecular Weight Material

Patent Application J.58607 IVd/120. The halogen derivatives of hydrocarbons are decomposed by means of acid reactive inorganic halides made from such unsaturated hydrocarbons which contain an aromatic residue. The acid reagent or acid reactive inorganic halide, or extended surface polymerizes these to substances with molecular weight of at least 600. The text cites the use of chlorides of Al, Fe, Zn, Ti, B, etc.

(This ends scanning of Reel #40)