

**FILM STUDY GROUP**  
**REPORT ON MICROFILM REEL NO. 38**  
**THE ATLANTIC REFINING COMPANY**

SCANNING OF REEL #33  
(Orig. Ident. Reel 1B)

U. S. Government Technical Oil Mission  
Bag 3440 - Target 30/5.01 - Ruhrchemie A.G. - Sterkrade-Halton

SECTION 1. REPORTS ON TESTS OF LUBRICATING OILS

Note: The frames on this reel are not numbered and it will be necessary to refer to subject matter wholly by section location. However, an insertion showing the approximate number of frames involved has been made after each item. The first section consists of title items 101 - 147 with a German index. (2) The items appear in reverse order on the reel. The reviewer has arbitrarily scanned and commented upon those items which appear to be pertinent, and has omitted or commented very briefly on items of apparently a routine inspection nature.

Item 147: Low Temperature Starting of Auto Engine (3)

Starting tests on a Daimler-Benz engine led to the conclusion that modification of the fuel injection system was possible to give satisfactory performance.

Item 146: Testing of Aviation Oil Sample K-2015 (2)

The sample was comparable to Rotring in ring sticking and piston wear, and it appeared equally good for low temperature service. The product was believed satisfactory as aviation oil.

Item 145: Foaming in Lubricants (4)

Incomplete studies were made comparing the tendency of several lubes to foam, and parallel measurements were made on the persistency of the foam. The investigation was conducted with several types of equipment to afford intimate contact of air and oil. As would be expected, temperature was an important factor in the creation of foam and persistency in the oil.

Item 144: Test of Aviation Lube Oil S81060 for Cylinder Corrosion (1)

Item 143: Rotating Test with Rumanian Oil (6)

Comparison of the test oil with standard lubricants was made, wherein the number of revolutions per minute is plotted against temperature at intervals in the range  $-5^{\circ}$  to  $-30^{\circ}\text{C}$ .

Item 142: Pumpability of Recoil Oil (2)

The oil was believed satisfactory at temperatures as low as  $-40^{\circ}$ .

Item 142: Description and Operating Instructions for a Certain Boiler Construction (6)

Relates to German Patent 735795 and apparently describes work to substantiate patent claims.

Item 141: Pumpability of Lubricant at Low Temperatures (11)

Oils were tested to temperatures as low as  $-52^{\circ}\text{C}$ .

Item 140: Knock Test Measurements of Synthetic Gasoline Depending on the Ignition Conditions (9)

The text, like several that have been reviewed, mentions diagrams not included in this portion of the reel. It is inferred that the investigation should be continued, taking into account mixing temperature, pre-heat temperature and fuel-air mixture composition.

Item 139: Test of Motor Oil 3993 for Cylinder Corrosion (1)

The sample apparently fell within the accepted limits of several commonly used lubricants.

Item 138: Investigation of Ester Oil E-1 (4)

Esters made or found in the fatty acid and alcohol portions of the diesel oil fraction showed a very flat viscosity-temperature relationship, and their use in admixture with normal lubricants to depress the viscosity pole height appeared interesting.

Item 136: Investigation of 3 Winter Oils from IGs-Ne46, 48 and 49 (5)

Samples showed unduly high wear in use. The oils were compared to Rotring for several properties.

Item 135: Investigation of a Normal Army Winter Oil (Nerag N<sub>2</sub>) (4)

The military winter oil, Nerag N<sub>2</sub>, shows on the whole satisfactory properties. It is better than the research oil sample N<sub>1</sub>.

Item 134: Investigation of Motor Oil (Nerag N<sub>1</sub>) (6)

This oil showed by its low viscosity a high oil consumption. The conclusion is that it is less desirable than Rotring, but still usable. Instability and sludging were somewhat higher; tendency towards ring sticking corresponded somewhat to Rotring. The danger of cylinder corrosion is greater than with the usual military oils.

Item 133: Investigation of Motor Oil 3698 (4)

This oil was of possible military use, but consumption was twice as high as for Rotring and the tendency toward ring sticking somewhat greater.

Item 132: Aviation Oil E1951/2 from Inhibited RGH Bright Stock and Keranol (4)

The sample was considered suitable for aviation oil. Tendency to decompose is noticeably less than with the earlier sample 1951 made from non-inhibited bright stock.

Item 131: Influence of Oppanol Additives (6)

The additives were tried in an ROH and a military oil with particular reference to piston corrosion.

Item 130: The Effect of Oppanol Additive on the Behavior of Motor Oil (8)

Cold starting, oil consumption, deterioration, piston wear and ring-sticking were measured and commented upon.

Item 129: Aviation Oil 1979 from Main Laboratory (2)

The mode of manufacture of this oil is not stated; the examination led to the conclusion that it was satisfactory as aviation lubricant.

Item 128: Aviation Oil 3344 from Plant Production (3)

The sample did not have desired properties.

Item 127: Lubricating Properties of Thinned Motor Oils (Winter Oils) (10)

Item 126: Influence of Viscosity on Oil Consumption (10)

Oil consumption increases in general with lower viscosity and apparently with increasing volatility (at the same viscosity). The result with Oppanol additives was not wholly as expected. The experimental work was not conclusive in establishing relation of viscosity to differences of oil consumption.

Item 125A: Testing of Motor Oil 3370 (5)

The sample was considered as good in lubricating properties as usual military oil but was not better than pure synthetic oils made by ROH. Tendency toward instability and ring-sticking appeared to be unduly high. Oil consumption was not extraordinarily high. It was concluded that the sample 3370 was of doubtful utility.

Item 125: Examination of Sample 3370 (No.96-IG ester oil) (7)

Conclusions as for preceding item (Item 125A).

Item 124: Aviation Oil Mix K1951 from ROH Bright Stock and a Lower Viscosity Component from Nexag (5)

The above sample, with reference to stability, was better than Rotring oak oil and poorer than synthetic RCH aviation oil SS2007. The nature of the Nerag additive is not disclosed.

Item 123: Dilution of Motor Oil for Winter Use  
Influence on Piston Corrosion (2)

If one takes an otherwise unsuitable military motor oil and reduces the viscosity to a suitable point for starting at  $-40^{\circ}$  by the addition of normal gasoline or diesel oil, the piston lubrication will be decidedly poorer and in practice too great dilution must be counted upon. If the diluting substance has corrosive properties found in spindle oil, this will probably exceed allowable corrosion. The properties of the original oil must be such that upon dilution by diesel type oils the piston corrosion is not exceeded. The addition of low boiling materials is almost without effect, as these, at the elevated temperature at which corrosion takes effect, have been eliminated from the oil itself.

Item 122: Behavior of Several Commercial Aviation and Truck  
Motor Oils with Reference to Piston Corrosion (5)

Interesting comparison appears in the oils ASL, ASM and ASS whose press values are plainly associated with viscosity. In the remaining oils there was no correlation with viscosity.

Item 121: Development of a Method for Testing Motor Oils  
with Respect to Ring-Sticking and Stability (10)

The attempt to devise shorter test procedures for ring-sticking, sludging, oil consumption, etc., was not wholly successful. Five military motor oils showed values which lay close to those for aviation oil Rotring D.

Item 120: Thinning of Motor Oils for Winter Service (9)

There is a correlation between the boiling point of the diluting material and the interval before the material is evaporated from the oil. It depends upon such factors as outside temperature and service itself. Further research work is necessary. The effect of dilution on oil consumption cannot be derived from work up to the present.

Item 119: Oil Testing in NSU Engine (10)

In summary it may be said that engine sludging depends as much on the change and wearing out of the whole by other influences as upon the quality of the lube oil, but from the described experiments is discovered certain differences between the individual oils.

Item 118: The Immitability of RCH-Cetane (6)

An RCH fuel had a cetane number of 105 when tested in the IG test diesel engine. The RCH research laboratory said that a very pure normal cetane could be made by the Oxo synthesis.

Item 117: Testing of Four Motor Oils for Piston Corrosion (3)

The four oils tested were unsatisfactory for two stroke double cylinder motors.

Item 116: Engine Testing of Synthetic Oils to Observe the Influence of Viscosity and Different Additives on Piston Corrosion (3)

Two distillate oils 1906A and 1907A, and three residuum oils: 1908A, 1909A and 1910A, were tested in a Triumph motor. For comparison, there were two other series of experiments on the same oils by the addition of (1) 0.2% tricresyl phosphate and (2) 0.1% phenthiasin.

Item 115: Development of a Process for Testing of Motor Oils with Respect to Piston Corrosion (11)

A Triumph two-stroke motor was used. The Ruhrbensin synthetic oil behaved better with reference to viscosity than hitherto tested mineral and fatty oils. No direct and general correlation of viscosity and testing for corrosion was found. Oils of similar origin could, however, be so correlated.

Item 114: Engine Testing of Aviation Oil K1929 (4)

This oil had properties somewhat similar to earlier synthetic oils and in general is unsuitable. It was compared to Rotring D and oil K188E.

Item 113: Comparative Supercharge Test in NSU Engine and in BMW 132 Test Engine (4)

The above engines were respectively located at Ruhrbensin and the IG laboratory, Oppau. Four fuels were used: VT702, ET100 (iso-octane), and two fuels designated as aromatic, high octane agents. The text refers to curves which are not shown.

Item 112: Testing of Several Oils for Military Use, Using the Triumph motor with Reference to Piston Corrosion (7)

The following oils were examined: IG-Oppau, Motanol, Neragol, Rhenania-Ossag, Discobil and were compared with Aero-Shell Light. When tested by the current methods for determining piston corrosion, large differences between the individual oils were evident. These corresponded fairly well to road test results. Admixtures of oils with synthetic components was reported. The effect of graphite addition could not be established.

Item 111: Engine Testing of Synthetic Aviation Oil K1880 (2)

With respect to ring-sticking, oil consumption and stability, this oil was better than Rotring D. Testing in aviation engines was approved.

Item 110: Result of an Engine Test of Lubricant with Respect to Engine Corrosion (5)

The time required and the amount of material for the test was said to be small. A Triumph air-cooled motor BD-250 was used. The description of the test conditions is in greater detail than usual for this group of reports.

Item 109: Engine Testing of Synthetic Aviation Oil K1860 (Japanol) (2)

With respect to ring-sticking and oil consumption, this oil was particularly good. In stability, it resembled Rotring D. This oil was said to resemble K1880 in both properties. Actually this sample 1860 is a mixture of two other oils, namely K1858 and 1859.

Item 108: Engine Testing of Ruhrchemie Synthetic Aviation Lubricants (10)

The two oils in question are respectively SS2005 and SS2006.

Item 107: Engine Testing of Synthetic Aviation Oils with Low Pole Height in NSU Engine (6)

- 1769 - HL synthesis, aluminum chloride treated, undecolorized.
- 1773 - " " " " " " decolorized (SS2005).
- 1774 - " " " " " " " , with 0.1% phenthiasin (SS2006).
- 1814 - Aluminum chloride treated, finished in service.
- 1815 - Same as 1814 but twice treated with aluminum chloride.
- 1847 - HL synthesis, phanthiasin added before the synthesis, no aluminum chloride treatment.

Item 106 - Engine Testing of Aviation Oils in NSU Aviation Oil Test Motor (4)

The following oils were compared: Rotring D, Greenring, 1650, 1711, 2893, 1709, 1722, 1710, 2913, 1647.

Item 105: Development of an Engine Test Method for Aviation Motor Lubricant in NSU 501. OSL Engine (4)

The test was possible with two liters of lubricant and gave good reproducibility of results.

Item 104: Experiment with Fuels of Different Densities (5)

Engine tests on fuels ranging in specific gravity from 0.682 up to 0.882 were made, and the conclusion reached that the effectiveness of a fuel depends upon engine and carburetor design, and on engine service.

Item 103: Comparison of SS Fuel with Other Diesel Oils with Reference to Nozzle Coking (3)

Item 102: Supercharging in NSU-501-OSL motor. (Not on reel).

Item 101: An Apparatus for Measuring Bubble Formation in Gasoline (4)

Investigation, while not fully satisfactory, drew attention to the importance of the performance of the distribution system, the construction and condition of the fuel pump, and the inter-relation of the chemical and physical characteristics of the naphtha with its distillation curve.

**SECTION 2. KNOCK TESTING - SYNTHETIC GASOLINE - June 20, 1944 (8)**

This investigation arose from reported discrepancies in determining octane number of fuels in IG and CFR engines. The synthetic fuel, at definite temperature conditions, exhibits a relatively high octane value and at lower or higher conditions the knock values are less favorable. The following data tables are given:

No. 1 - Showing the octane values on an IG engine with four different cylinder heads and using a synthetic gasoline with an octane number of approximately 52 and a gasoline-benzol mix with octane number approximately 69.

No. 2 - The effect of compressions in the range 4.3 to 4.7.

No. 3 - Gave parallel tests on IG and CFR motors with spark advance 22 to 30°, coolant temperatures 150 to 170°, and mixture temperatures 120 to 150°.

No. 4 - Influence of coolant temperature on octane number.

No. 5 - Shows the data for mixture temperature from 100 to 153° employing coolant temperatures of 100° and spark advance 22 to 26°.

No. 6 - Also shows the effect of mixing temperature but employed a constant coolant temperature of 150°. The spark advance varied from 10 to 30°.

**SECTION 3. DEVELOPMENT OF CATALYST FOR FISCHER-TROPSCH SYNTHESIS (9)**

A report by Otto Roelen, Aug. 18, 1939.

This report is of an historical and summary nature, the former part of which may be summarized in the table below:

<u>Year</u>	<u>Favorable Working Temperature</u>	<u>Method of Catalyst Production</u>	<u>Course of Reaction</u>
1922/23	400 to 450°	Compacted iron on activated surfaces	Only methane
1925	300 to 380°	Mechanical mixtures of oxide	Primarily methane, only minor quantities of higher hydrocarbon
1926/29	200 to 300°	Sintering of nitrates	Gives good yield of liquid product but has short life
Since 1930	200° and lower	Precipitation of carbonate on Kieselguhr	High yield - longer life

Looking back on the work it will be evident that increasing subdivision of the metal and the lower temperatures employed made for improved yield and life. Liquefaction of carbon oxide is better at lower temperature, though the speed of reaction drops off rapidly with decreasing temperature. In 1934, catalysts were developed by Franz Fischer and coworkers, which seemed to have technical applications because of conditions and yields. The most favorable composition was 100 parts cobalt, 18 parts thorium oxide, 100 parts kieselguhr, with the addition of two parts copper. The carbonate was precipitated from solution of



nitrate upon Kieselguhr, then washed and dried. After crushing and screening the mass, it was reduced with hydrogen at 350° (in the case of copper-containing material without previous reduction) or was placed in service without prior reduction with carbon monoxide and hydrogen. The yield of products was about 100 grams per cubic meter charge gas, and the life in technical use was about four weeks. At this point the work was taken over by RÖH. New methods had to be developed in this transition from small quantities to commercial production of catalyst.

A semi-works investigation was begun, from which it was established that other materials than thorium and of equal activity could be made. Granular catalyst mass was developed to avoid loss as dust. New analytical procedures were developed and methods devised for testing the utility of the catalyst. A great number of catalysts were placed in continuous service to establish their practical life, and for this purpose a new laboratory synthesis oven was developed which could run for months and years at constant temperature.

The spent catalyst containing valuable amounts of cobalt, thorium, etc. called for means of regeneration of these elements by leaching with nitric acid or the like. The life of the catalyst which at the beginning was about four weeks, has now been raised to four or six months. The catalyst cost per unit of naphtha under these conditions was so small that further work was considered unnecessary. By regeneration to activity equal to that of the fresh catalyst, the useful life of catalyst is now extended to two years or more.

Progress has been made in increasing the amount of higher hydrocarbons, i.e. ethane to high melting point paraffin. In 1934 a cobalt-thorium catalyst at usual pressure and service yielded about 60% of liquid products as naphtha. When one conducts the synthesis at low temperature, and from time to time extracts the paraffin deposited on the catalyst mass, about 30 to 40% of the recovered liquid product is solid hydrocarbons. In continuous service it is found one can make as much solid paraffin at 5-20 atmospheres as Fischer and Pichler made in medium pressures. Much work has been done in developing the synthesis at medium pressure, whereby more than 70% of the higher hydrocarbons formed were recovered as solid paraffin boiling above 320°.

A catalyst was sought which in normal pressure synthesis would be least influenced by paraffin deposition. The cobalt thorium catalyst must be dewaxed from time to time. Such catalyst now gives service of five months.

Catalytic materials were chosen because of availability and low cost. It is upon the development of finely divided metals of the iron group that the field of hydrocarbon synthesis is founded.

(The above discussion is not supported by reference to RÖH data.)

#### SECTION 4. MEDIUM PRESSURE SYNTHESIS

This appeared to be a summary of a lecture given by Dr. Pichler under date of December 6, 1937. (7)

First pressure experiments were conducted with ruthenium catalyst in a vessel repeatedly pressured with water gas. Ruthenium was shown to be an exceptionally good catalyst for hydrogenation of carbon monoxide. A catalyst now in service for 8 weeks at constant temperature, gives unvarying contraction and constant yield of 150 to 160 grams (liquid product per cubic meter?). The reaction product consists predominantly of paraffin.

It was also shown that the catalysts which at normal pressure were good for naphtha production, were also the best catalysts at elevated pressure. Favorable cobalt-iodalguhr proportions were 1:1 up to 1:2. Thorium is not necessary where pressure is employed. The presence of alkali in catalyst does not increase the paraffin yield.

Skeleton (diatomaceous earth?) catalysts were used under pressure. They yield only oil and naphtha.

The space rate of one liter of gas/gram cobalt/hour is also right for the higher pressure. The speed of reaction is dependent upon the catalyst surface which does not change with pressure.

Paraffins with melting point of 132° can be recovered. For this purpose, the catalyst was extracted with benzol and again with boiling toluol or xylol. Data is illustrated by graphs.

#### SECTION 5. METHODS OF WORKING UP PRIMARY PRODUCTS OF SYNTHESIS AND THEIR APPLICATION TO PETROLEUM PROCESSING

A report by Dr. H. Velde, Dec. 28, 1940. (24)

The synthetic crude may be said to consist of  $C_3-C_4$  hydrocarbons, gasoline, diesel oil and solid paraffins. The  $C_3-C_4$  hydrocarbons have an olefin content of 20 to 50%. The gasoline has an end point of 200° and consists of hydrocarbons in the range  $C_5-C_{11}$ ; the diesel oil fraction boils between 200 and 320° consists of  $C_{12}-C_{18}$ .

The primary product of synthesis is wholly aliphatic, exhibiting complete absence of asphalt and resin in the higher boiling fraction. Considerable olefin differentiates it from crude petroleum. All fractions are practically sulphur free.

The author shows that in customary thermal cracking the octane number of the distillate is of the order 57 to 62 motor method but, by the FGH processing, an octane improvement as high as 24 numbers was possible. This improvement was obtained by passing the cracked gasoline over a contact mass at temperatures below cracking conditions. The vapor emerging from the catalyst mass is cooled somewhat, and in a second step at this lower temperature is passed over a

similar contact medium. Finally, vapor is fractionally condensed and a small amount of polymer separates from the otherwise water white gasoline.

Aromatization was distinguished in that no increase in molecular weight or evolution of hydrogen was incurred. The principal effect must be the isomerization of straight chained aliphatics; fractionation showed, however, very small amounts of branched product, as the boiling range of individual hydrocarbon groups was only slightly changed.

Isomerization ordinarily means production of branched product from straight chain. In this instance, however, where there is no appreciable change in boiling point, there appears to be a shifting of double bond from the end of the molecule toward the center. As the molecular weight of the hydrocarbon increases, there is a lessening of the octane number. Nevertheless, the blending octane number of the olefins exceeds that of the normal paraffins and the tendency for octane number to increase with the double bond at the center of the molecule holds throughout.

By comparison of olefinic fractions and the corresponding hydrogenated material, it was established that some branching takes place and that the hydrogenated raffinate is better than the hydrogenated original product. The olefin content of the charge stock governs the octane number of the raffinate. It may be taken as a general rule that the higher the olefin content of naphtha, the higher will be the octane number, but there are certain exceptions. It was established that petroleum fractions were susceptible to octane improvement by this method in about the same degree.

While it is necessary to crack severely (thermally) it is now possible to arrive at higher yields with equally good product quality by the new naphtha processing.

Application of this new refining process to catalytic cracking was undertaken. The primary naphtha can be used directly as a component of finished gasoline. A further improvement in the octane number of the light naphtha is afforded by the isomerization process.

Aromatization of the heavy naphtha fraction has two possibilities; one can separate out individual fractions, for example toluene. The yield of aromatic naphtha is about 85%. Very pure hydrogen is evolved, which can be employed for hydrogenation.

In catalytic cracking, as for example the Houdry process with once through passage of charge stock, there is separated out excellent naphtha, while the residue can be charged to thermal cracking. Some experimentation was done on recycling of cracking stock. A large amount of  $C_2-C_4$  hydrocarbon which can be polymerized is produced along with the naphtha. Thermal cracking of heavy naphtha gives yields (including polymerization of  $C_2-C_4$ ) of 65 to 75%. Contrasted to this, the yield by aromatization with octane number equal to that of thermal cracking gives 85 to 90%, and by catalytic cracking 75 to 80%.

One advantage of the new processing is the ability to work toward valuable lubricants and oxidation products. While the process was developed for synthetic charge stock, there appears to be no reason why it cannot be applied to petroleum.

Reviewer's Note: The author has discussed broad generalities and does not reveal the essential condition of processing which he advocates.

## SECTION 6. HYDROCARBON SYNTHESIS BY MEANS OF IRON CATALYST (23)

Report by Otto Roelen, Sept. 13, 1940.

This is a general, historical summary of probable interest to those concerned with the immediate subject. It was shown that the catalyst itself is a most important factor in determining the composition of products. The synthesis from water gas at 20 atmospheres and 245° employing two different catalysts, showed a range of 21 to 59% naphtha, 13 to 24% of heavy oil (200 to 320°), 17 to 14% of soft paraffin (320 to 460°), and from 4 to 50% hard paraffin boiling above 450°. Density of metal was found to have a considerable effect upon yield and type of products. Variations in the manufacture of the catalyst of similar composition have appreciable effect upon distribution of the product components. Altogether the iron catalyst gave more favorable results than the cobalt mass.

## SECTION 7. BEHAVIOR OF IRON CATALYST. Dec. 7, 1939. (3)

An iron contact mass, made without addition of alkali hydroxide when tested with water gas at atmospheric pressure and 245° for a period of 726 hours, gave a maximum contraction of 17% and a maximum yield of 21 cc per cubic meter of water gas. At the conclusion of the test period, the contraction was 5%.

Contrasted to the above are results where an iron catalyst activated with CaO\* and/or manganese, under similar test conditions gave the following results:

1. 100 Fe, 10 Ca  
Max. Cont. 35%; 796 hrs.-31%; 1468 hrs.-26%. Oil yield 42 cc/m<sup>3</sup>.
2. 70 Fe, 30 Ca  
Max. Cont. 35%; 804 hrs.-20%. Oil yield 28 cc/m<sup>3</sup>.
3. 50 Fe, 50 Ca  
Max. Cont. 31%; 852 hrs.-21%. Oil yield 21 cc/m<sup>3</sup>.
4. 75 Fe, 25 Mn  
Max. Cont. 30%; 900 hrs.-23%. Oil yield 45 cc

Other tests showed:

5. 90 Fe, 10Ca 270°, 10 atm.  
Yield = 80-90 g/m<sup>3</sup>; (50% naphtha, 20% diesel oil, 30% paraffin)

\* Oxide computed as metals.

6. Catalyst composed of 100 parts Fe and 33 Ca at 236° was used in treating water gas in a recycle process at 25 atmospheres. Contraction was 60 to 65% and the yield was 130 grams per cubic meter of charge gas. The recovered liquid product consisted of 60% naphtha, 20% diesel oil and 20% paraffin.
7. Catalyst containing 50% Fe and 50% Ca, when used at 10 atmospheres and 250° with water gas in a recycle process, yielded 120 grams per cubic meter. The liquid product was 70% naphtha, containing 70% olefin and having octane number of 69.
8. Catalyst with a composition of 100 parts Fe, 33 parts Ca and 5 parts of Cu was employed with water gas at 245° and 20 atmospheres without recycle. After short service the liquid product amounted to about 43%, consisted of paraffin boiling about 320°.
9. The lessening of catalyst life by the addition of a few percent of nickel, cobalt or copper was observed and the following evidence drawn:
  - (a) Catalyst composed of 100 Fe, 33 Ca gave 20% contraction in 112 hours of service.
  - (b) Catalyst with proportions of 100 Fe, 33 Ca, 5% Ni, gave 20% contraction at 68 hours service.
  - (c) Catalyst with proportions of 100 Fe, 33 Ca, 5 Cu, gave 20% contraction at 16 hours service.
10. By careful washing of the precipitated moist catalyst with alkali hydroxide, improved activity can be attained. Two catalysts - 100 Fe, 33% Ca - with and without an activating wash gave 22% contraction, but that which was washed gave service for 398 hours as contrasted to the one which was washed giving 206 hours of service.
11. A catalyst composed of 95 Fe, 5 Mn for 267 hours gave a maximum contraction of 38% and an oil yield of 53 cc per cubic meter of water gas. After 267 hours in service the contraction was still 33%.
12. The activity of catalyst activated with CaO or MnO on carriers, was determined as having a useful life of about 150 hours. A catalyst composed of 100 Fe, 10 Mn, 5 Cu, 100 K gave a maximum contraction of 32%, and a maximum yield of 31 cc oil per cubic meter. Catalyst composed of 100 Fe, 10 Mn, 5 Co, 100 K gave 26% contraction and a yield of 37 cc per cubic meter. Catalyst containing 100 Fe, 30 Ca, 2 Cu and 40 K gave 33% contraction and 37 cc oil per cubic meter.

**SECTION 8. SUMMARY OF PATENT CONDITIONS COVERING THE PRODUCTION OF IRON SINTERED OR FUSED CATALYSTS FOR CO HYDROGENATION - Aug. 23, 1940. (5)**

The summary lists the patents on this subject, describing the principal ingredients and their proportions, together with the processing in manufacture of the catalyst.

**SECTION 9. DANGER OF FIRE IN GATSCH STORAGE TANK (12)**

Correspondence chiefly in the period May-June, 1941 concerning fire in the Odertal plant.

**SECTION 10. IRON CARBONYL EXPLOSIONS IN CATALYST SERVICE (1)**

A letter October 20, 1943 cautions that catalyst cases held in reserve should be pressured with inert gas.

**SECTION 11. IMPORTANCE OF STEADY GAS INPUT (2)**

A letter, April 28, 1943, from RGH to Braunkohle-Benzin AG at Schwarzhelde.

**SECTION 12. OUTPUT OF VARIOUS LICENSEE FIRMS, 1938-1942 (2)**

The summary is considered of little value, except that it reveals the following licensee locations:

Essener Steinkohle,	Bergkamen
Hoeschbenzin,	Dortmund
Krupp,	Wanne-Eickel
Rheinpreussen,	Moers-Meerbeck
Schaffgotsch, Benzin	Odertal
Brabag,	Schwarzhelde
Ruhrbenzin,	
Viktor,	Castrop-Rauxel

**SECTION 13. DISCUSSION WITH LICENSEE FIRMS ON GENERAL SYNTHESIS TOPICS**

Note: There are 8 sections, 13 to 19 inclusive, the first of which (#13) deals with Essener Steinkohle (60). This material consists chiefly of correspondence and analyses with comment upon isolated operations. The most important item is probably a report on operation of the naphtha plant for November, 1940 and is dated Dec. 18, 1940. No diagram is given, but the detail is better than usual. The process is as follows:

The synthesis gas derived from water gas reaction is treated in the coarse

purification plant by processing with bog iron ore and lumasse in proportions of one to one. The fine purification reduces the sulphur content of 13 to 18 grams per 100 cubic meters down to about 0.5 - 0.8 grams. The nature of the purification is not stated directly but it may be inferred that it was lumasse. Failure to remove sulphur before the converters shortens the useful life of the catalyst and results in higher sulphur content of the liquid products. It is hinted that a purification plant using activated carbon as the agent or carrier, was planned to follow the present fine purification unit. The converter was a Bamag unit operating at atmospheric pressure and its capacity was said to be 7200-cubic-meters-per-hour with a CO content of 12% or 6000 cubic meters per hour with 4% CO. The hydrogen plant is also of Bamag make and operates at 8 atmospheres. CO<sub>2</sub> is washed from the gas with alkasid liquor, type N. The CO<sub>2</sub> is thereby reduced to about 2% and residual H<sub>2</sub>S is eliminated. The average service of an oven was 1600 hours. Regeneration of catalyst was done by extraction, and was followed by hydrogen treatment. The solvent was a heavy naphtha fraction (90° - 100°) and is sent to a distillation column for separation of the extracted paraffin. An activated charcoal column was used for recovery of light liquid hydrocarbons from the synthesis gas. The refining of the synthetic crude appears to be conventional.

Note: A report dated June 7, 1940 gives further detail on the condensing system and upon catalyst activity.

#### SECTION 14. HOESCHBENZIN (16)

Several items appear:

Letter Feb. 19, 1942 describes a method for computing gas balances in the synthetic process.

A letter of May 11, 1942 comments upon control analyses and process evaluation. Several similar letters comment upon the operation of individual units such as the activated carbon plant, Lurgi stabilisation plant, etc.

#### SECTION 15. KRUPP. WANNE-KICKEL (4)

This section contains two letters commenting upon operations in the period 1938-1943, but the isolated data does not appear significant.

#### SECTION-16. RHEINPREUSSEN (27)

The contents of this section consist of:

Letter of Mar. 20, 1944 (3) - discussion of generator cinder dressing plant (ash was apparently treated for recovery of unburned fuel).

Letter of Oct. 21, 1943 (4) - description of synthesis operation. Additional material will be found in the letter of Feb. 12, 1943 (1).

Memorandum of Apr. 9, 1941 (3) - discussion upon CO balance.

A report of Jan. 16, 1941 which gives a rather complete description of the

plant, including gas cracking, purification, conversion, synthesis, process control, catalyst handling, etc. with numerous analyses to support the descriptions. There is no flow diagram but the material is better than usual. (10)

Letter of May 24, 1940 (2) supplementing memorandum of a conference May 20, 1940 between Rheinpreussen and Moers-Heerbeck and Ruhrbenzin.

Memorandum of Nov. 23, 1936 (2) commenting upon process conditions.

#### SECTION 17. SCHAFFGOTSCH-BENZIN

Material found in this section is as follows:

Memorandum May 20, 1940 - visit to this plant to examine water gas installation. (4)

Monthly summary Oct. 1942 showing analyses of fuel and gas streams together with data on liquid products, catalyst operation, chemical utilities, etc. for this plant. The data are unusually complete. (15)

Memorandum Dec. 29, 1942 relating to operations. (2)

Feb. 6, 1942 - referring to Ringrohröfen. (2)

Letter May 31, 1941 (3) - answering a number of questions such as "What is the CO<sub>2</sub> content of the washed oil?", "Give the analysis of the crude gas before and after washing", etc.

Memorandum Apr. 24, 1941 relating to gas generator operations. (1)

Memorandum Sept. 24, 1937 relating to the gas plant and accessory equipment. (2)

Memorandum of Sept. 21, 1937 (6) which gives fairly good description of individual operations such as catalyst unit, CO<sub>2</sub> washing, etc. However, the date (1937) makes it questionable whether the information was applicable to the operations which have yielded data discussed in the summary of Oct. 1942.

#### SECTION 18. BRABAG, SCHWARZHEIDE

Memorandum Mar. 23, 1944 contains an excellent description of conditions in this synthetic oil plant (11). It discusses catalyst quality with respect to its reduction values, size and shape, deposition on a carrier, and the cobalt content; synthesis with regard to proportions of CO and H<sub>2</sub>, age of oven in service, regeneration of catalyst, filling and emptying the catalyst cases, gas purification, activated carbon plant and general discussion on the operation. There is no flow diagram nor supporting tables of data, but this section should be of value when correlated with such information to obtain a clear understanding of the process.



Memorandum May 3, 1943 also is intimate discussion of process details for current operations. (7)

Memorandum Oct. 10, 1942 deals particularly with gas purification, intermediate regeneration of catalyst and a premium system involving costs and efficiency of operation. (7)

Dec. 29, 1941 - Memorandum relating to gas balances, general questions on synthesis, activated carbons, purification and general matters. (8)

Memorandum of Aug. 25, 1941. Relates to an electro-filter for gas streams, sulfur removal from synthesis gases, extraction of the catalyst mass, operation of the activated carbon plant, questions on corrosion, carbon balances, etc. (8)

Letter of June 13, 1940 transmits a summary of analytical data with reference to the period April, 1939 to April, 1940. (2)

The sum total of aforementioned memoranda are considered useful in that they throw light upon an operation viewed by an outsider who was alert to note details which to the local staffs might be regarded as routine or of little significance.

#### SECTION 19. VIKTOR, CASTOP-RAUXEL

This section contains items:

Memorandum Aug. 12, 1943 - Dust filtration difficulties in the primary naphtha recovery unit. (1)

Memorandum Oct. 23, 1941 - Comparison of product measurements by Ruhrbenzin and Rauxel. (6)

Memorandum May 21, 1940 - relating to calculation based on analyses. (1)  
The memorandum is incomplete.

#### SECTION 20. RUHRBENZIN REPORT ON VARIOUS PLANTS

A memorandum Jan. 5, 1939 entitled "#14, Report on visit to gasoline plant", gives detailed discussions on the use of catalyst in several plants, particularly upon their composition, sizing, form, extraction after use, regeneration and emptying from the catalyst case. (11)

Memorandum #13 dated Oct. 4, 1938 gives a report (16) upon visits to the gasoline plant of Rheinpreussen, Viktor and Erzbag. The nature of this memorandum is as for the previous memoranda #9, July 27, 1938 (8), #8, July 19, 1938 (6), #7, July 11, 1938 (4), #6, July 5, 1938 (6), #4, June 8, 1938 (7), #5, June 30, 1938 (5), #3, May 31, 1938 (8), #2, May 23, 1938 (8), and May 18, 1938 (15), which apparently are a continuous record of intimate discussions on the synthesis process. They should be valuable when studied with flow diagrams because of the wealth of discussion. In some instances there is tabulated data presumably representative of the operation in the period commented upon.

SECTION 21. VARIOUS RUNS WITH COBALT CATALYST  
AT MEDIUM PRESSURE

This section consists of about half a dozen memorandum in the period 1940-1941. Their dates and titles are given below:

- (a) Nov. 3, 1941 - Paraffin Production by Recycle Hydrogen Operation. (2)
- (b) June 21, 1940 - Report #7. Experiments on Different Catalyst Loading and Saturation. (6) It was shown that after 190 hours in service, the paraffin was white, whereby one of the conditions of the experiment was fulfilled. The experiment at one-quarter the normal rate was to check the oven for its heating capacity at normal load, so that overheating and attendant severe gasification would be avoided. The used catalyst showed no evidence of carbon deposition.
- (c) Memorandum July 29, 1940. (6) Naphtha having a boiling range of 40 to 145°, recovered from activated carbon, was injected into the system in the course of the synthesis experiment. Comparison of data before, during and after this naphtha addition, showed a decidedly adverse effect from which the catalyst never fully recovered.

Reviewer's note: This experiment may have had two objectives

- (1) To exert a possible continuous cleansing of the catalyst and
- (2) To determine the effect of hydrocarbon concentration on the course of the synthesis reaction.

- (d) Memorandum #5, March 30, 1940. (5) Experiment at 178° with about 25% of normal thruput, and increasing the thruput to normal at 37 hours in service. At 25% thruput rating and 178°, the contraction was 61%, carbon monoxide decomposition was 99% and the liquefaction coefficient was 39. When the loading was increased to 100% (normal) at the same temperature, contraction was 56%, the CO decomposition 86% and the liquefaction coefficient 46. After 160 hours, these factors had changed to respectively 37, 47 and 83, and continued with no change up to approximately 260 hours. At this point the temperature was changed to 184°, resulting in slight increases in contraction and CO decomposition. A further increase in temperature again gave a slight increase in contraction, a rise to 63% in CO decomposition, and a pronounced drop in liquefaction coefficient.
- (e) Memorandum Apr. 23, 1940. Ideal Gas Composition in Naphtha Synthesis. Discussion and graphs. (3)
- (f) Report #4, Feb. 26, 1940. Experiments with Synthesis Gas in One Step at Low Thruput and Quick or Rapid Raising of the Temperature. (6) Comparison of results with thruput at 25% and at normal thruput rate, showed that by increasing the load to normal, contraction and CO decomposition was reduced, while the liquefaction coefficient remained about constant.
- (g) Report #1, Feb. 22, 1940. Experiments in Oven #10 of the Pressure Research Units. (6) Oven #10 had a thruput of 100 cubic meters gas per hour. The work reported showed a progressive rise in temperature from 167° to 184° over a period of 175 hours, during which time the contraction progressed from 25 to 61%. The data, while not complete, have in part been assembled in graphical form and show the general type of information sought by the organization. The catalyst was a cobalt mixture 2-3 mm. in size.

(h) Memorandum, Oct. 26, 1939 outlining a program in the pressure research plant. Oven #10 was to be filled with normal cobalt catalyst and used for the following:

- (a) Operating with synthesis gas according to the Ruhrbenzin Ofenhaut conditions, observing all the product characteristics and the cobalt deterioration, in accordance with the instructions and information already gathered by Dr Feist.
- (b) Repeating the above work without the use of the water circulating pump. Each experiment was to be carried out in 14 days.

(1) Memorandum of Oct. 18, 1939. Program for Pressure Research Plant. This memorandum enumerates the available ovens and broadly states their use. (5)

#### SECTION 22. THE EXAMINATION OF BLACK WAX. (5)

This work conducted by the ROR Laboratories had its inception in the recovery of paraffin apparently discolored by the inclusion of catalyst. An insoluble substance high in ash was found after extraction of the paraffin. This residue contained cobalt, thorium and magnesium. By means of suitable solvents, it was treated for examination of the organic portions.

#### SECTION 23. NORMAL PRESSURE SYNTHESIS CHARACTERISTIC DATA. (2)

A memorandum of July 14, 1938 transmits certain requested data. This is a single page of data, derived under the following conditions:

Temperature of 100 to 195°, space velocity, one cubic meter of synthesis gas per kilogram of cobalt per hour in the first step. The synthesis gas contained CO and hydrogen in the proportion 1:2. The information is not believed to be important.

#### SECTION 24. MEDIUM PRESSURE SYNTHESIS; EXAMINATION OF PRODUCTS

A memorandum (13) Sept. 19, 1939 reports upon paraffin and naphtha researches in the pressure laboratory. Extensive data was secured on three ovens, one containing cobalt mixed catalyst operating on gas with a CO hydrogen ratio of 1:1.91 - a second oven containing thorium catalyst on purified kieselguhr, operating on the same type of charge gas, and a third oven containing somewhat coarser thorium catalyst on purified kieselguhr but using as charge gas a water gas with the proportions of CO to hydrogen are 1:1.25. Pressure was approximately 7 atmospheres and the temperature approximately 190°. Several pages are devoted to the statement of product inspection data.

## Investigation of Primary Products of Pressure Synthesis in the Naphtha Boiling Range. (97)

A report December 7, 1938. This report includes 30 tables of data and about an equal number of pages of graphs, and apparently had as its main objectives, comparison of fuels made from treated and untreated naphtha.

Generally speaking, the naphthas were those portions of condensate which when fractionated in a good column the portion coming over up to 200° is mixed with raw activated carbon naphtha. In the first series, the vapor pressure was measured that the engine value might be computed to a common value. Later, such vapor pressures were adjusted to a common level by the addition of pure butane in the order of 2 to 5%. One oven was charged with synthesis gas in once thru processing and another was used in cycle operation with water gas or synthesis gas.

While it was possible to obtain a correlation of octane number with boiling point, it was not possible to find a correlation between exposure and CO decomposition. Correlation of mid-boiling point of the product and the octane number was found.

Extensive studies were made on the treated naphtha derived from the primary products discussed in the first part of this work. The untreated naphtha showed only a qualitative relationship between olefin content and octane number but, the chemically treated naphtha showed a direct relationship between octane number and olefin content, of which only the partly aromatised T.V.P. cracked naphtha afforded an exception. The nature of the treatment given the naphtha is not made clear.

Other data in this section is given for several experimental runs.

## SECTION 25. LUBE OIL PRODUCTION FROM RECYCLE PRODUCT

A memorandum Feb. 27, 1941 changing the quality of recycle product. (5)  
This work had shown that the quality of naphtha was readily correlative with other properties. Over an extensive period of time the fractions boiling up to 200° had olefin content ranging from 58 to 63%. The octane number, too, showed no decided change. Treatment of naphthas with activated clay, phosphoric acid, zinc chloride, activated alumina, etc., was employed. It was shown that the pole height of the oil became poorer and poorer, and at first it was assumed that the effect was associated with the pretreatment. A series of oils was made in which the oxygenated compounds were treated out with metallic sodium. This method resulted in practically no deterioration of the pole height. Another series of tests were given a pretreatment with large amounts of aluminum chloride. The results do not show great disagreement with other tests and it may be concluded that the observed degradation of the naphtha does not stem back to the pretreatment. Beside the olefins of whose characteristics very little is written, other properties were observed. In the diesel oil fraction, the pole height and yield remained practically constant with the olefin content. The discussion becomes of a speculative nature leading up to consideration of a large scale plant. Several pages of data relating to this subject are found in this section. (10)

## SECTION 26. IRON CATALYST SYNTHESIS: EXAMINATION OF PRODUCT (14)

Memorandum Nov. 9, 1942 - Summary of Products from Iron-Catalyst Oven. (4) Present information gathered over an operating period of three months shows that the liquid products, exclusive of light hydrocarbons, contains about 40% total paraffin of which about 50% is hard paraffin. After four months on stream, about 35% total paraffin can be counted upon with a hard paraffin content of 45%.

Memorandum Aug. 27, 1942 - Refining of Iron Paraffin. (2) Treating wholly refined iron paraffin with 50% sulphuric acid was regarded as very promising. It was proposed to explore this treating method further.

~~Reviewer's Note: These iron paraffins refer to waxes recovered in synthesis using iron catalyst.~~

Memorandum Nov. 21, 1940 - Product of No. 11 Oven and Experiment 336 & 339. (7) A determination of the amount of oxygenated product in naphtha and diesel oil was undertaken to show its relation to physical properties, particularly specific gravity and refraction. The amount in total naphtha was about 5 to 10% and in diesel oil a maximum amount of about 15%. Further experiments are still in progress to determine split-out water and the OH number, as the amount of oxygenated product seemed somewhat low.

## SECTION 27. OVEN #11, CHARGE #11 (4)

This section presents data on a series of experiments in which the charge was water gas to an iron catalyst in recycle operations. The data relates to the period July 1 and 2, 1942.

## SECTION 28. ANALYSES AND LUBE OIL RESULTS FOR COBALT CATALYST (8)

Memorandum Aug. 26, 1942 is a report of a test on oven 15 first filling, water gas recycle, with cobalt catalyst. The data includes atmospheric distillation of the synthetic crude, Engler distillation of the fraction boiling between 60 and 200°, physical data on the fraction from 60 to 200° and upon this fraction after treatment with 80% zinc chloride solution, supported by graphs showing continuous operation conditions and average data.

## SECTION 29. OFFICIAL TEST OF SIX IRON CATALYSTS

Report on official test with iron catalysts at medium pressure and straight service. Reference Braunkohle-Benzol A.G. Letter Aug. 21, 1944, Schwarzhede. (9) There is a comparison of results of synthesis using the iron catalyst of the following firms:

Ruhromann, Rheinpreussen  
Lurgi, I.G., KWI and Erabag

Conditions were specified as even temperature 225°, pressure 10 atmospheres, water gas containing 88% CO and H<sub>2</sub> in the proportions 1:1.25 to be tested for duration of three months. Tabulated results for the six catalysts is given for the following items:

C<sub>1</sub> - C<sub>2</sub>, C<sub>3</sub> - C<sub>4</sub>, Naphtha (C<sub>5</sub> to C<sub>10</sub>), Diesel Oil (C<sub>11</sub> to C<sub>18</sub>), Hard Paraffin above 250°, Lower Boiling Alcohol, Total Alcohol, Total Water, Total Olefin, Yield in grams per cubic meter of charge gas, Ratio of CO to H<sub>2</sub> reacted, and CO decomposition.

The report then proceeds with evaluation of the catalysts, rating them in groups as they apparently favor any of the above items.

Much of the significance of this test is lost because of the inadequate description of the catalysts other than identifying them by origin. The reviewers should be alert to discover from individual company correspondence identification, properties and mode of manufacture of the catalysts involved in this test.

A letter from the Kaiser Wilhelm Institute for Fuel Research dated Aug. 18, 1944 to Ruhrchemie transmits a report on the possibility of substituting iron catalyst for cobalt catalyst. A fairly good case is presented for the iron catalyst, but as in the preceding report there is no adequate description of the catalyst. (10)

More detailed tests originating with Rheinpreussen and for R.C.H. are given. (6)

A memorandum of R.C.H. Aug. 28, 1944 is entitled "Calculation of Yields According to Daily Condition in the Synthesis of Higher Hydrocarbon" shows methods of computation and application to the test data of the official runs. (10)

A supplement to the report on the official tests was made using iron catalyst and is dated June 5, 1944. (10) This description by Braunkohle-Bensin is carefully prepared and contains additional analytical data. Like the other reports it does not identify the catalyst. There is a considerable amount of data extending back to 1943 and gives a flow diagram of the synthesis test procedure. (10)

Under date of Sept. 22, 1943 Brabag submit their comment on the tests. (6)

A memorandum May 8, 1943 reports (10) the conference held in Berlin the preceding day in which representatives of the several companies interested in synthesis discussed the ground work for tests described in the preceding part of this section. This appears to be a verbatim reporting of the conference and inasmuch as high placed officials of the several organizations were there, it probably represents a good cross-section of German opinion.

A rating of the catalysts in order of effectiveness for a large number of functions was submitted by Lurgi and will be found attached to their letter July 19, 1944 addressed to Dr. Roelen of Ruhrchemie. (10)

Rheinpreussen under date of July 5, 1944 submit their discussion of the catalyst test. The film at this point is illegible in many places. (15)

The formalized test data sheets (110) worked up by Braunkohle-Bensin are displayed, but no cover letter for this report is found. The appearance denotes careful and systematic handling of the information. No analysis of results is shown.

From the Kaiser Wilhelm Institute dated June 1, 1944, discusses the occurrence of iso compounds in the distillate. (9)

Reviewer's Note: This entire section 31 will be seen to consist of test data accumulated by each of the participating organizations in the official comparison test. It is evident that the file is incomplete in respect to candid discussions within a single organization.

### SECTION 31. EXPERIMENTAL RESULTS FOR IRON CATALYST SYNTHESIS

Nos. 629-750 three parts. Part 1 (11) and Part 2 (60).

This material which occupies the entire section to the end of the reel is not identified by name, but presumably is data from Ruhrombe Laboratories. It is in the form of a laboratory note book sheet or page in the handwriting of the man who has done the experimental work. Basic data relating to the composition of the catalyst and its test in synthesis is given. The date of the experimental work is uncertain, although one of the pages bears the notation Feb. 12, 1944, Dr. Leucke (?). The value of this original data will be enhanced if other reels disclose the appraisal of results and decisions upon use of particular catalyst.

(This ends scanning of reel #33)