

FILM STUDY GROUP
REPORT ON MICROFILM REEL NO. 36
Prepared by
SHELL DEVELOPMENT COMPANY

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Report on Roll 36 (formerly 4B) of
U.S. Technical Oil Mission Microfilm

This roll reproduces technical documents taken from the Ruhrchemie A.G., Sterkrade-Holten, Germany. This company was a leader in the field of Fischer-Tropsch synthesis, and the film contains considerable material concerning this important synthesis. The documents are mostly letters, short progress reports, and patent applications. Items that may be of interest are:

Miscellaneous information on Fischer-Tropsch process, including plant design, operations, and research at medium pressures and with recycling of various fractions.

Research on iron catalysts for Fischer-Tropsch.

Various novel catalysts for Fischer-Tropsch.

Conversion of hydrogen sulfide in gas to sulfur and sulfuric acid.

"Oxo" process patent applications.

Synthesis of lubricating oils from Fischer-Tropsch products.

Many patent applications on Fischer-Tropsch and other subjects.

Synthesis of wax.

All the material is covered by the following abstracts. These are identified only by item numbers, since there are no page numbers on the film. No translations or detailed abstracts have been made. Value ratings have not been assigned.

Abstracts

Roll 36 (Original Identification Roll 4B)
Target 30/5,01, Ruhrochemie A.G., Sterkrade-Holten.
Bag No. 3452 (cont.)

Item 34	<u>Synthesis plant for Spain:</u> Yield estimate, product distribution and cost analysis.	Holten, April 15, 1942	11 pg.
Item 35	<u>Methane for synthesis gas:</u> Yield estimate and cost analysis (partly illegible).	Holten, March 29, 1943	4 pg.
Item 36	<u>Yield calculation technique:</u>	Holten, September 15, 1941	9 pg.
Item 37	<u>Synthesis plant for Pechiney:</u> Discussion of catalyst to be used, cost analysis, and yields.	Holten, Jan. and Aug., 1943	19 pg.

- Item 38 Cost calculation for the production of a phosphoric acid polymerization catalyst. Holten, November 10, 1942 3 pg.
- Item 39 Project for using CO from electric steel furnaces for synthesis plant in Italy; cost estimate, etc. Holten, December 16, 1941 11 pg.
- ~~Item 40 Finnish synthesis plant project. Comparison of the Lurgi and Ruhrchemie proposals. Holten, December 18, 1941 16 pg.~~
- Item 41 Fatty acid production. Cost and yield estimates for production by the oxidation of aldehydes from the "Oxo" process, and by paraffin oxidation. Holten, 1942-43 11 pg.
- Item 42 Development of a test for asphalt content of aged lube oil which correlates well with ring sticking experiments. April 30, 1942 12 pg.

Bag 3454

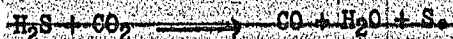
Target 30/5.01, Ruhrchemie A.G., Sterkrade-Holten.

- Item 1 Comparison of treating losses on refining gasoline with sulphuric acid and with clay. A literature survey. Holten 2 pg.
- Item 2 Mention of various processes used in connection with gasoline production and polymerization of olefins. Nothing novel. Holten, May 9, 1941 3 pg.
- Item 3 Vapor pressures of 10°C fractions of a synthesis gasoline. Holten 1 pg.
- Item 4 Some catalyst and reactor estimates for 100,000 tons/year synthesis plant. Holten, March 8, 1941 3 pg.
- Item 5 Data for converting primary synthesis products to lube oil and high octane gasoline. Holten, March 10, 1941 2 pg.
- Item 6 Various methods for carrying out the synthesis, outlined for the Mitsui Bussan. Holten, April 3, 1941 10 pg.
- Item 7 Conversion of cobalt low pressure reactors to iron catalyst at medium pressures. Holten, April 16, 1941 1 pg.
- Item 8 Motor vehicles with gas from wood and other solid fuels. Description of the fuels used, generator design, etc. Holten 15 pg.
- Item 9 Speech describing cobalt catalyst plant (no detail). Holten, June 6, 1941 3 pg.
- Item 10 Yield calculation method for synthesis plant. Holten, April 19, 1942 16 pg.

- Item 11 Iron Catalyst production and regeneration cost including chemicals and equipment required. Holten, 1941-42 16 pg.
- Item 12 Experiments with liquid phase synthesis (continuation of item 5, Bag 3452, reel 35). Recirculating a liquid diesel oil fraction over the catalyst. It appears that methane formation may be kept down to 2% of converted CO when 77% of the CO is converted. Holten, March 12, 1941 10 pg.
- Item 13 Catalyst start-up with oil spraying. It was felt that by spraying the catalyst with oil during the start-up higher molecular weight fatty acids would be washed off thus preventing the formation of cobalt soaps and thus the loss of catalyst. The experiments did not yield conclusive results. Holten, February 23, 1940 3 pg.
- Item 14 Comparison of gas conversion with synthesis gas and water gas over cobalt and iron catalyst. Holten, February 29, 1940 3 pg.
Performance of an "Eirichkorn" mixed catalyst consisting of 28.6% Co, 1.4% ThO₂, 2% MgO, 54.6% Kieselguhr. The gas production was very high which was attributed to the poor quality of the Kieselguhr. Holten, March 22, 1939 2 pg.
Comparison of cobalt-thorium and cobalt mixed catalyst. No essential difference. Holten, April 12, 1939 2 pg.
Test run for the production of highly olefinic gasoline by recycle operation at medium pressure. Temperatures had to be higher because of the lower CO + H₂ concentration. The olefin content of the gasoline ranged from 58-70%. November 5, 1940 2 pg.
- Item 15 Research Progress report, includes short notes on iron catalyst tests, recycle experiments, reactor start-ups, techniques, etc. Holten, March-July, 1940 7 pg.
- Item 16 Tests with the Krupp large tube reactor. It appeared to be no improvement over existing reactors. Holten, March 11, 1940 6 pg.
- Item 17 Test with various iron catalysts. The best appeared to be a precipitated catalyst containing 100 parts Fe, 10 parts Ca, 5 parts Cu, 100 parts Kieselguhr, precipitated with KOH. Operation was at 20 atm, and 240°C with gas circulation (2.7:1), 9% CH₄ was formed and 50% wax. The fraction up to 200°C contained 70% olefins but the Research octane number was only 47.5. The octane number of the 200-300°C fraction was 72 (65.5% olefins). Holten, September-November, 1940 8 pg.
Summary of experimental results with thorium and similar catalysts. Holten, June 29, 1939 4 pg.

Items

18 and 19 Recovery of Sulfur and Sulfuric acid from H₂S. Detailed description of a plant design for handling 3000 m³/h of gas containing 36% H₂S (the rest is CO₂ and water). The incoming gases are preheated in an exchanger with ceramic tubes to over 900°C and part of the gases react primarily according to the reaction:



Preheated air is added to complete the sulfur oxidation, raising the gas temperature to nearly 1300°C. The reacted gases exchange heat with the incoming stream, are further cooled in a steam generator, and then in an air cooler, heat exchanger and final cooler (steam generator at 2-4 atm. pressure) where the sulfur is condensed. Liquid sulfur is removed from the bottom as well as from the subsequent cyclone separator. The tail gases are re-heated in the exchanger mentioned above and are then taken to the contact sulfuric acid plant. The following compositions and estimates are based on experiments:

Quantity m ³ /h	Charge	Tail Gas	Air
	1000	1600	700
H ₂ S	33%v	4%v	
SO ₂	--	1.5%v	
CO ₂	64%v	38%v	
H ₂ O	3%v	18%v	
N ₂	--	35%v	
CO, H ₂ , CH ₄ , CS ₂ , COS, etc.		3.5%v	
S		28 g./m ³	

Sulfur balance

Liquid sulfur

67% of charged sulfur

96-98% H₂SO₄

31% of charged sulfur

Loss

2% of charged sulfur

Several flowsheets and reactor design drawings are included.

Holtan, July 29, 1944

29 pg.

Item 20 Patent applications: (primarily texts for applications outside Germany). Aromatization and dehydrogenation catalyst based on chromic oxide on alumina where the aluminum hydroxide is precipitated rapidly with acids from alkali aluminate solution and then quickly freed of all but a predetermined alkali content by washing. A starch-like product is obtained upon calcining under set conditions which is plasticized with chromic nitrate of fixed water and acid content with addition of certain alkalis, formed, slowly preheated and then calcined. Considerable detail is given in the application. Holten, August 20, 1943 7 pg.

Aromatization and dehydrogenation catalyst containing about 20% chromic oxide on alumina where cracking and carbon deposition are reduced by the addition of 2-7 gram atoms of alkali or alkali earth per 100 g. moles of chromic oxide plus aluminum oxide. In an example about 50% aromatics were obtained from a heptane-heptene mixture with 2.5%w cracked gas and 2.3% carbon on the catalyst. Holten, September 8, 1944 4 pg.

Methanization of CO in technical gases. This is an omnibus application which contains, among the 17 claims, the following: treatment with nickel containing catalyst at 170-190°C; magnesium activators; catalyst carriers such as Kieselguhr; removal of corrosive impurities by nickel containing catalysts at temperatures below 200°C; removal of organic sulfur, after H₂S removal, at 400-450°C over copper catalysts which is followed by treatment with luxmasse type catalyst (iron oxide + sodium carbonate). Holten, September 9, 1943 16 pg.

Steam cracking of Fischer-Tropsch gas oil where C₄ to C₆ hydrocarbons, preferably of a straight chain olefinic character, are added together with steam. Catalysts are regular cracking catalysts such as aluminum hydrate. Products are polymerized to high octane gasoline.

Holten, September 24, 1943 5 pg.

Determination of cycle time for fixed bed catalytic cracking so that equilibrium is established between the heat required for cracking and the heat released in carbon burning.

Holten, September 24, 1943 6 pg.

Oxidation of wax in the presence of sulfuric acid or nitrosyl sulfuric acid and nitrogen oxides (NO₂). The latter may be recycled and reoxidized. Inorganic or organic peroxides may also be added.

Holten, August 23, 1943 8 pg.

Catalytic cracking, dehydrogenation or aromatization where air preheated to the reaction temperature is passed through the catalyst after the carbon is burned off. Holten, September 2, 1943 6 pg.

Improvement of the aging characteristics of synthetic lube oils from the polymerization of olefins over aluminum chloride, by treating such oils at 170°C for some time with small quantities of aluminum chloride and elementary sulfur and then treating at the same temperature with clay or zinc oxide and/or magnesium oxide, subsequent heating to 260°C and then vacuum distillation.

Holten, August 26, 1943 3 pg.

Isomerization of Fischer-Tropsch gasoline. Treatment with clay containing boron phosphate as activator, or the use of boron phosphate in the synthesis catalyst, yields gasolines of considerably improved octane number when the fraction is highly olefinic.

Holten, August 19, 1940 3 pg.

Reduction of aromatization and dehydrogenation catalyst by the use practically oxygen free H₂ which contains only the amount of water necessary for saturation at 0°C. Higher activity and lower carbon deposition are said to result.

Holten, September 17, 1943 5 pg.

Preparation of sulfuric acid esters of high molecular weight hydrocarbons where the acid (90%+) is mixed with unreacted wax from previous esterification and cooled to -20°C (no solidification). In this way the esterifications can take place slowly and evenly. The emulsion is separated into two layers with alcohol or water and the lower layer is extracted with chlorinated hydrocarbons such as chloroform which dissolve the esters preferentially. Other methods of separation are also claimed.

Holten, September 7, 1942 12 pg.

Preparation of oxygenated products by Fischer-Tropsch at about 300 atmospheres, below 305°C, and over catalysts suspended in saturated hydrocarbons consisting of metals, oxides or carbides of the 8th group and possibly activated by oxides of elements of the second and seventh group.

Holten, January 29, 1940 2 pg.

Item 21 I.G. "Oxo" patent applications

Reactivation of catalyst by passing CO, an organic solvent, and an organic acid to form soluble salts under pressure and increased temperature through the catalyst bed.

Ludwigshafen, October 3, 1942 5 pg.

Preparation of aldehydes and ketones by treating olefins with CO and H₂ at increased temperature and pressure in the presence of catalysts which contain metals of the 8th group, particularly cobalt.

Ludwigshafen, October 24, 1941 6 pg.

"Oxo" process catalysts consisting of organic compounds of the catalytic metal which are soluble in organic solvents.

Ludwigshafen, March 3, 1942 6 pg.

Preparation of alcohol sulfonates by hydrogenation and subsequent sulfonation of products from the "Oxo" reaction.

Ludwigshafen, September 20, 1940 7 pg.

"Oxo" process where the liquid or liquefied charge is passed continuously concurrent or countercurrent to the CO + H₂ gas and the entering charge is not mixed with the product leaving the reactor.

Ludwigshafen, August 8, 1942 7 pg.

"Oxo" reaction with sulfur containing charges where sulfur insensitive catalyst is used in the hydrogenation step.

Ludwigshafen, August 10, 1942 4 pg.

Recovery of cobalt carbonyl from reacted gases by scrubbing with a solvent, possibly the olefinic charge.

Ludwigshafen, August 10, 1942 7 pg.

"Oxo" reaction with sulfur containing charges where the organic sulfur is first removed and the hydrogenation carried out over catalysts containing metals of the eighth group.

Ludwigshafen, August 14, 1942 5 pg.

Hydrogenation of "Oxo" products where the hydrogen is circulated and its CO content maintained below 0.1%. This may be achieved by methanization of any CO formed.

Ludwigshafen, August 27, 1942 8 pg.

"Oxo" catalyst containing some cobalt and large quantities of easily reducible non-carbonyl forming metal oxides.

Ludwigshafen, November 23, 1940 8 pg.

Hydrogenation of "Oxo" products where the charge is introduced into the reacting liquid at a point where gas does not yet begin to separate.

Ludwigshafen, December 10, 1942 4 pg.

Suppression of Carbonyl formation in the "Oxo" reaction primarily by reducing the contact time.

Ludwigshafen, December 11, 1942 4 pg.

Use of a pipe coil for carrying out the reactions through which the catalyst and reactants are passed concurrently.

Ludwigshafen, January 23, 1943 5 pg.

Preparation of highly isomerized "Oxo" products by pretreating the olefins with CO and cobalt carbonyl, cobalt, or other cobalt compounds at about 100°C.

Ludwigshafen, February 2, 1943 7 pg.

- Purification of "Oxo" products by treating with H₂ under pressure over packing or high surface solids. Dissolved cobalt is removed in this manner. Ludwigshafen, March 10, 1942 3 pg.
- "Oxo" process in the presence of water which is at least partially liquid, Ludwigshafen, April 2, 1942 7 pg.
- Use of iron, cobalt and nickel oxides for the "Oxo" synthesis. The examples mention cobalt plus molybdic oxide, and a mixture of barium, chrome, copper and cobalt oxides. Ludwigshafen, April 9, 1942 5 pg.
- Purification of "Oxo" products. Practically identical with the application of March 10, 1942 listed above. Ludwigshafen, June 18, 1942 6 pg.
- "Oxo" process where the gases are free of CO₂. Ludwigshafen, January 10, 1941 12 pg.
- "Oxo" process starting at low temperature and using the heat of reaction to complete it at higher temperatures. Ludwigshafen, August 29, 1942 7 pg.
- Preparation of definite aldehydes by the use of olefins where one of the carbon atoms adjacent to the double bond contained no hydrogen and the other carbon one hydrogen. CO and H₂ addition then only takes place in one way. Ludwigshafen, September 17, 1942 4 pg.
- "Oxo" process using Fischer-Tropsch synthesis products and using hydrogenation conditions suitable for the conversion of esters to alcohols. Ludwigshafen, August 18, 1942 3 pg.
- Item 22 Patent. Lubricant for drawing wire which is prepared by evaporating spent caustic from scrubbing Fischer-Tropsch products. The residue is dried quickly at higher temperatures, powdered, and then put into a usable form. DRP 744022, Goldschmidt, A.G. Published, November 11, 1943 2 pg.
- Item 23 Patent Application: Nitration of toluene in the presence of SiO₂, Corundum, or other nitric acid resistant catalyst, between 150 and 200°C. 50% HNO₃ is apparently satisfactory. Holten, September 29, 1944 3 pg.
- Item 24 Patent: Method for determining the quality of lubricating oil. Accelerated aging test using metal oxide catalyst. DRP 493724, Siemens Schuckert, February 27, 1930 2 pg.
- Item 25 Patent Application: Preparation of cracking and dehydrogenation catalyst by treating silicates (aluminum or magnesium) at temperatures above 1000°C and then using as a carrier. Such catalysts are said to suppress gas formation and yield highly olefinic products. Holten, September 20, 1944 4 pg.

- Item 26 Patent Application: Preparation of mono- and di-nitro naphthene derivatives by treating the corresponding hydrocarbons with 50-70% nitric acid possibly with the use of catalysts such as iron nitrate.
Holten, September 29, 1944 2 pg.
- Item 27 Patent Application: Preparation of highly olefinic products by Fischer-Tropsch by the addition of 0.5-1.5 g./m³ of synthesis gas of carboxylic acids such as formic and acetic acid.
Holten, December 2, 1944 3 pg.
- Item 28 Standard-Kuhlmann process for lube oil synthesis; Gas oil and wax are chlorinated to 25-30% chlorine. The condensation of the chlorinated products takes place in the presence of aluminum powder, a little aluminum chloride, some dichloroethane, and benzene in three stages, with the temperature gradually increasing from 70-130°C. The dichloroethane serves as solvent and the benzene is to prevent pitch formation. The lube oil yield is 80-85% of the hydrocarbon charge. The viscosity is 12°E at 50°C and the best possible V.I. is 98.
Holten, April 6, 1943 2 pg.
- Item 29 Discussion of toluene distillation plant.
Holten, June 18, 1943 2 pg.
- Item 30 Lube oil synthesis from Fischer-Tropsch products. It appeared that better and more oil could be made from products synthesized over iron catalyst than over cobalt. It is possible to obtain 63% C₅-280° product in the synthesis of which 55% can be recovered as lube oil with 12% gasoline, 30% diesel oil, and 3% loss (including contact oil). Rough cost analysis is included.
Holten, August 15, 1941 6 pg.
- Item 31 C₄, C₅, and C₄ - C₅ polymer for aviation fuel. Polymerization was carried out at 60 atm. and 110-140°C, apparently over phosphoric acid catalyst. Unleaded octane numbers are somewhat above 90.
Holten, June 15, 1942 6 pg.
- Item 32 Short note on lube oil pilot plant.
Holten, January 12, 1942 1 pg.
- Item 33 Lube oil synthesis from Fischer-Tropsch products. (Miscellaneous notes.)
Lube oils from gasoline obtained by the recycle process.
Holten, December 3, 1941 11 pg.
Lube oils from gasoline obtained by the recycle process.
Holten, August 13, 1941 18 pg.
Lube oils from gasoline obtained by the recycle process, comparison of products obtained over iron and cobalt catalyst.
Holten, June 19, 1941 8 pg.

- Cylinder oil production from 200°C+ Fischer-Tropsch products.
Holten, May 20, 1941 1 pg.
- Lube oils from gasoline obtained by the recycle process.
Holten, May 6, 1941 4 pg.
- Lube oils from gasoline obtained by the recycle process.
Holten, March 10, 1941 11 pg.
- Lube oils from gasoline obtained by the recycle process.
Holten, January 22, 1941 2 pg.
- Item 34: Specifications and motor tests of lubricating oils (minutes on reports in Item 1, Roll 33).
- Delivery of lube oil to the Army. October 7, 1942 3 pg.
- Production of winter oils using synthetic lube.
April 9, 1942 2 pg.
- Aging of lube oil with special emphasis on effects in aero engines.
May 22, 1942 3 pg.
- Aero lube plant; atmospheric pressure distillation.
May 4, 1942 4 pg.
- Discussion of plant design for aero lube oil by the chlorination process. This report contains a few details including a very rough pencil flowsheet.
May 5, 1942 5 pg.
- Tests for gear oils. February 9, 1942 4 pg.
- Discussion of the Indiana test as a measure of aging properties.
November 19, 1941 2 pg.
- Discussion of the Indiana test as a measure of aging properties.
October 3, 1941 6 pg.
- Production of aero brightstock instead of normal aero-motor oil.
June 29, 1943 3 pg.
- Analyses of distillate oils.
Holten, January 20, 1941 1 pg.
- Preparation of synthetic cylinder oils; In contrast to motor oils these higher viscosity oils are prepared by:
1. lower polymerization temperature
 2. higher AlCl₃ concentration (2 instead of 1.2%)
 3. and longer polymerization (15-20 instead of 12 hours),
- Holten, January 13, 1941 3 pg.

Item 35 Synthetic lube oil (miscellaneous items)

Tests with an inhibited lube oil.

Holten, September 27, 1941 1 pg.

Continuous lube oil synthesis. A cracked gasoline was used for the tests. Preliminary experiments were made to explore the effects of temperature, $AlCl_3$ concentration, and reaction time.

In the main experiment aluminum chloride (1.5% and 2%) and contact oil (50% and 40%) were added to the gasoline in a pre-condensation vessel (50°C). The main reaction took place in a horizontal tube equipped with a mixer with several propellers and metal discs which divided the tube into 5 chambers and which permitted the oil to pass through perforations. The products are separated and the contact oil recirculated. The chambers are individually heated for temperature control. The temperature varied from 70°C to a final 110 or 120°C. The reaction time was 10 hours in one, and 5 hours in the other experiment. The oil yield was about 60%. Holten, May 12, 1941 6 pg.

Japan oil production. Holten, May 6, 1941 1 pg.

High grade synthetic lube from "cold press oil". Holten, April 4, 1941 2 pg.

Item 36 Miscellaneous Ruhrchemie patent applications (From 571-670)

Fischer-Tropsch where immediately following the cut-off of synthesis gas, the catalyst is flushed with nitrogen.

R571, Holten, May 10, 1941 3 pg.

Production of fatty acids by the mild oxidation of products of the "Oxo" process. R572, Holten, May 21, 1941 3 pg.

Production of fatty acids by the mild oxidation of products of the "Oxo" process. Olefins from other sources are used in the "Oxo" process. R573, Holten, May 21, 1941 3 pg.

Fischer-Tropsch without intermediate CO_2 removal. R574, Holten, May 21, 1941 3 pg.

Aromatization of hydrocarbons where interfering oxygen compounds are first removed with alumina at 100-400°C. R578, Holten, June 10, 1941 4 pg.

Increasing capacity of Fischer-Tropsch plant by increasing throughput and using tail gases for domestic gas. R579, Holten, June 17, 1941 6 pg.

Fischer-Tropsch: Removal of heat of reaction by vaporizing a finely dispersed liquid. R581, Holten, July 5, 1941 9 pg.

Removal of alcohols from synthesis products with chlorides such as zinc and calcium chloride.

R582, Holten, July 28, 1941 7 pg.

Treatment of soap prepared from free fatty acids with acetone at a definite pH.

R583, Holten, July 30, 1941 5 pg.

Separation from hydrocarbon-containing reaction mixture of sodium soaps prepared by aldehyde oxidation.

R584, Holten, August 1, 1941 4 pg.

Use of peroxides for the oxidation of wax.

R587, Holten, September 5, 1941 5 pg.

Improved method of preparing wax-like high molecular esters from hydrocarbons by addition of nitrogen oxide, nitrosyl sulfuric acid, and finally alcohols which have been substituted by alkyl-, aryl-, chlorine-, sulfate-, phosphate-, or amino groups.

R593, Holten, September 20, 1941 5 pg.

Combination of Fischer-Tropsch and domestic gas production.

R594, Holten, September 23, 1941 6 pg.

Conversion of aldehydes to acids in the presence of hydrocarbons.

R596, Holten, October 6, 1941 7 pg.

Removal of organic sulfur from low boiling hydrocarbon with mixtures of 1-2 parts of soda with 2-3 parts of reactive oxides or hydroxides of iron at temperatures between 200 and 300°C.

R597, Holten, November 10, 1941 4 pg.

Preparation of "Oxo" compounds from olefins by treatment with H₂ and metal carbonyls.

R598, Holten, December 30, 1941 2 pg.

Preparation of Emulsifiers from wax oxidation products produced particularly by nitric oxide and nitrosyl sulfuric acid by reaction in the liquid state below 130° with non-aqueous alkali (carbonate, NH₃, organic amines such as triethanolamine) until 25-80% of the fatty acids are neutralized.

R599, Holten, January 12, 1942 4 pg.

Preparation of ethers for plasticizers and solvents from "Oxo" products.

R600, Holten, January 26, 1942 4 pg.

Recovery of alcohols from "Oxo" reaction by using narrow boiling range olefin fractions.

R601, Holten, January 27, 1942 2 pg.

Conversion of organic sulfur in technical gases into an easily absorbed form by heating to 400-450°C over a copper catalyst.

R602, Holten, February 4, 1942 4 pg.

Same as R602 where catalysts contain as binding additive a compound of Ca, Mg, or Al.

R603, Holten, February 2, 1942 3 pg.

Methanization of CO and H₂ over nickel catalyst which contains magnesium as activator.

R604, Holten, February 2, 1942 2 pg.

Preparation of emulsifier. Same as R599

R608, Holten, April 8, 1942 8 pg.

Separation of isomeric fatty acids by partial saponification where the branched acids remain unsaponified.

R609, Holten, May 1, 1942 5 pg.

Regulation of a temperature dependent on another temperature by using the differential pressure between two gas thermometers.

R610, Holten, May 6, 1942 5 pg.

Dehydrogenation of C₈ + hydrocarbons to form olefins over catalysts such as chromic oxide on alumina, where the cyclization activity is suppressed by the addition of small amounts of water.

R611, Holten, May 6, 1942 5 pg.

Separation of Fatty Acids by incomplete saponification.

R614, Holten, May 14, 1942 4 pg.

Reactor for Fischer-Tropsch.

R619, Holten, June 6, 1942 4 pg.

Reactor for Fischer-Tropsch.

R620, Holten, June 6, 1942 5 pg.

Method of filling catalyst into Fischer-Tropsch reactor.

R621, Holten, June 8, 1942 7 pg.

Same as R621.

R622, Holten, June 24, 1942 3 pg.

Addition of carboxylic acids to lube oil where the acids are prepared (by "Oxo" process) from olefins in the lubricating oil range.

R625, Holten, August 4, 1942 3 pg.

Catalyst manufacture. Preparation of small pieces from strands by centrifuging against a solid wall.

R626, Holten, August 7, 1942 5 pg.

mono-olefins from paraffins by concurrent bromination and dehydrobromination at 300-500°C in a vacuum, where polymer formation is prevented by high space velocities.

R627, Holten, August 20, 1942 3 pg.

Oxygenated products by Fischer-Tropsch by addition of 5-7% acetylene or ethylene to the synthesis gas.

R629, Holten, August 25, 1942 2 pg.

Monocarboxylic acids from wax where the wax is dehydrogenated with chlorine or bromine at 250-300°C at low pressure with double bond shifting catalysts, such as activated clays or borates or phosphates which may be activated with metal compounds of the 3rd and 8th series.
 R630, Holten, August 28, 1942 5 pg.

Control of catalyst level in reactor.
 R632, Holten, August 31, 1942 4 pg.

Preparation of nitrated hydrocarbons from olefins and fuming nitric acid with reaction times of less than 5 minutes at 20-250°C.
 R634, Holten, September 18, 1942 6 pg.

Design of reactor for exothermic processes.
 R635, Holten, September 21, 1942 10 pg.

Olefins by Fischer-Tropsch by reducing the throughput (net) in a gas recycle process. R636, Holten, September 26, 1942 4 pg.

Preparation of nitrated hydrocarbons in the vapor phase over silica gel, clay, or other aluminum-magnesium silicates, calcined alumina, bauxite or other aluminum silicates.
 R637, Holten, October 3, 1942 5 pg.

Separation of sodium soaps from hydrocarbons.
 R640, Holten, November 4, 1942 4 pg.

Preparation of pure magnesia.
 R641, Holten, November 11, 1942 3 pg.

Preparation of water proof and water repellent fibers using fatty acids from paraffin oxidation.
 R647, Holten, December 14, 1942 5 pg.

Aromatization and dehydrogenation of hydrocarbons using catalysts which contain 1-3% manganese oxide.
 R643, Holten, November 17, 1942 2 pg.

Same as R643 where the catalyst contains 2-7 atoms sodium, potassium, or alkali earth per 100 molecules of the sum of chromic oxide and alumina.
 R642, Holten, November 14, 1942 4 pg.

Preparation of Nitro paraffins. Design of reactor.
 R644, Holten, November 28, 1942 3 pg.

Slide valve for catalyst storage vessels.
 R645, Holten, November 28, 1942 5 pg.

Preparation of acids from wax by treatment with chromic acid or nitric oxide in the presence of nitrosyl sulfuric acid, neutralization with concentrated KOH, extraction with heptane and treatment with a mineral acid.

R646, Holten, December 2, 1942 7 pg.

Separation of fatty acids from hydrocarbons.

~~R648, Holten, December 18, 1942 4 pg.~~

Same as R648.

R649, Holten, December 22, 1942 5 pg.

Use of pitch from residue of the wax oxidation.

R652, Holten, December 30, 1942 4 pg.

Preparations of liquid emulsions from pitch in the wax oxidation process.

R653, Holten, December 30, 1942 2 pg.

"Oxo" reaction below 200°C (135°C) in the presence of steam. The yield appears to increase.

R654, Holten, January 8, 1943 3 pg.

"Oxo" reaction where the catalyst is dissolved in water with possible addition of alkali such as soap,

R655, Holten, January 9, 1943 4 pg.

Dehydrogenation of cyclic hydrocarbons such as cyclohexane to cyclohexene over pumice, alumina, bauxite, clay, magnesium-aluminum silicate, etc., at temperatures above 500°C preferably in a vacuum by concurrent halogenation and dehydrohalogenation. Conversions of 20-30% are claimed with an ultimate yield of 95%.

R656, Holten, January 13, 1943 3 pg.

Increasing olefin concentration by fractionation.

R657, Holten, January 14, 1943 4 pg.

Concentration of soap-forming fatty acids.

R658, Holten, January 14, 1943 3 pg.

Design of shaken high pressure reactor.

R659, Holten, January 21, 1943 5 pg.

Removal of lime from magnesia.

R660, Holten, January 23, 1943 3 pg.

Purification of acids from wax.

R665, Holten, February 24, 1943 4 pg.

Iron catalyst for Fischer-Tropsch to produce olefins and oxygenated products preferentially. The additives used in connection with the usual Fe, Cu, Kieselguhr catalyst are V₂O₅, CeO₂ and MnO₂. Product contained about 60% olefin in the gasoline fraction besides about 20% oxygen compounds.

R667, Holten, March 17, 1943 4 pg.

Preparation of aluminum soaps from wax acids by heating the acid with $AlCl_3$ in an organic solvent such as heptane.

R668, Holten, April 1, 1942 4 pg.

Recovery of carboxylic acids from spent alkali obtained by scrubbing Fischer-Tropsch primary products.

R669, Holten, April 19, 1942 4 pg.

Preparation of low temperature iron catalysts for Fischer-Tropsch, by adding the bulk of the Kieselguhr after precipitation of the iron and in such quantities that the iron content is between 150 and 350 g./liter of catalyst. Alkali is added and the catalyst is reduced at temperatures below $300^\circ C$.

R670, Holten, May 20, 1943 4 pg.

Bag 3451

Target 30/5.01, Ruhrchemie A.G., Sterkrade-Holten.

Item 1 Synthesis with cobalt catalyst.

A 6 month life test of a cobalt mixed catalyst at 63% $CO + H_2$ conversion. 55.8%w of gasoline containing 60%v olefins was produced.

Holten, August 1943 15 pg.

Analysis of olefinic condensate for "Oxo" reaction.

Holten, February 2, 1943 1 pg.

Comparison of yields with different reactors.

Holten, September 5, 1941 4 pg.

Discussion between Krupp and Ruhrchemie concerning the medium pressure synthesis with recycle for high olefin production.

Holten, June 16, 1941 5 pg.

Effect of inerts in the synthesis gas. Conversion decreases at constant throughput and temperature. At constant temperature and inert content, the effect of throughput was also studied.

Holten, September 24, 1941 2 pg.

Fischer-Tropsch synthesis where the tail gas can be used for domestic and industrial gas.

Holten, June 12, 1941 4 pg.

Item 2 Synthesis with iron catalyst.

Short conference on iron catalyst for low temperature operation.

Holten, February 8, 1943 2 pg.

Experimental program with iron catalyst.

Holten, June 20, 1941 2 pg.

Wax production with gas recycle (short note).

Holten, November 3, 1941 2 pg.

- Tail gas composition for different synthesis gases.
Holten, November 6, 1941 1 pg.
- Estimate of commercial yield with iron catalyst: 147 g./m³ CO + H₂ including C₃ and C₄ at 90% conversion.
Holten, December 4, 1941 1 pg.
- Effect of catalyst age on wax yield (decreases with age),
Holten, January 19, 1942 1 pg.
- Note concerning method of determining guaranteed yield.
Holten, February 26, 1942 3 pg.
- Same as above. Holten, May 19, 1942 2 pg.
- Method of extracting and drying a wax forming catalyst.
Holten, December 22, 1942 2 pg.
- A 46 day test with an olefin and wax forming catalyst. Yields and boiling range are similar to those with former catalysts.
Holten, July, 1943 7 pg.
- Part of material covered in Item 1, Bag 3452, Roll 35
Holten, May 19, 1942 2 pg.
- Item 3 Increase of olefin concentration in Fischer-Tropsch products from 39 to 61% in the gasoline fraction by gas recycle.
Holten, July 1, 1941 3 pg.
- Item 4 Use of tail gas of Fischer-Tropsch for heating gas; examples for patent application. Holten, September 12, 1941 6 pg.
- Similar to above, November 17, 1941 2 pg.
- Similar to above, September 22, 1941 1 pg.
- Item 5 Yield comparison for preparing fatty acids from Fischer-Tropsch products by wax oxidation and by "Oxo" process.
Holten, Jan. 31, Feb. 1 and 2, 1943 6 pg.
- Item 6 Synthetic Wax
- Dewaxing experiments with a universal extraction experimental filter press. February 7, 1936 5 pg.
- Visit to the wax plant of the Rieback-Montan A.G. at Gerstewitz. May 18, 1937 3 pg.
- Wax vacuum distillation experiments. October 10, 1936 3 pg.
- High melting point wax. February 21, 1938 3 pg.

<u>Description of a wax crystallizer</u>	June 7, 1938	3 PG.
<u>High melting point wax, specifications, effect of benzene-alcohol extraction, uses, etc.</u>	Holten, September 23, 1938	3 PG.
<u>Deodorization of wax by treatment with steam.</u>	Holten, July 28, 1940	2 PG.
<u>Discussion of operation of wax plant.</u>	Holten, July 30, 1941	7 PG.
<u>Oxydation products in grease production.</u>	September 12, 1941	2 PG.
<u>Synthetic lube oil as plasticiser in the rubber industry.</u>	November 7, 1938	4 PG.
<u>Construction of high vacuum distillation plant.</u>	October 27, 1941	2 PG.
<u>Use of synthetic wax for candles.</u>	January 30, 1942	2 PG.
<u>Use for waxes.</u>	April 15, 1942	2 PG.
<u>Peroxide formation in waxes.</u>	May 6, 1942	3 PG.
<u>Wax production.</u>	December 18, 1941	3 PG.
<u>Wax yields.</u>	June 27, 1942	2 PG.
<u>Work-up of waxes.</u>	June 27, 1942	2 PG.
<u>Processing costs for the refining of crude hard wax.</u>	September 22, 1942	2 PG.
<u>Inspection of the Moesch vacuum distillation plant.</u>	December 22, 1942	2 PG.
<u>Inspection of the Schaffgotsch vacuum distillation plant.</u>	January 19, 1943	4 PG.
<u>Discussion of hard wax work-up with N.V. Was-Import-, Export-, Fabricatie. Rijswijk, bei den Haag.</u>	March 3, 1943	5 PG.
<u>Changes in the composition of hard wax.</u>	December 29, 1943	4 PG.

Item 7 Properties of the wax used in the fatty acid synthesis.
October 20, 1938 4 pg.

Item 8 Abstracts of some issued patents on gasoline synthesis, lube oil and motor fuels. 6 pg.

They include:

Methods of carrying out the Fischer-Tropsch synthesis.

Fischer-Tropsch catalysts and equipment.

Lube oil synthesis and recovery of old lube oil.

Polymerization of low boiling olefins. DRP describes the use of aqueous aluminum fluoride (DRP 742052).

Item 9 Fischer-Tropsch synthesis with iron catalyst and gas recycle.

Tests with iron catalyst F. 1427.

Holten, October 7, 1941 2 pg.

Tests with iron catalyst precipitated with KOH (100 Fe, 10 Ca, 5 Cu, 100 Kieselguhr). This catalyst was far superior to a similar one precipitated with NaOH (25 g. more liquid product per m³. The gasoline fraction (38%) contained 75% olefins including oxygenated compounds.

Holten, November 29, 1940 8 pg.

Report on first six pressure pilot plant runs with different iron catalysts.

Holten, September 11, 1940 6 pg.

Report on performance of an iron catalyst precipitated with NaOH.

Holten, September 11, 1940 6 pg.

Report on water gas consumption of the catalyst reported on in the previous item.

Holten, June 26, 1940 14 pg.

Report on water gas consumption of the catalyst reported on in the previous item.

Holten, July 10, 1940 6 pg.

Report on performance of an unreduced Fe, Ca, Cu catalyst impregnated with NaOH.

Holten, February 21, 1940 6 pg.

Experiments with two iron catalysts.

Holten, January 27, 1940 2 pg.

Item 10 Fischer-Tropsch synthesis with cobalt catalyst at medium pressures.

Report on the effect of gas recycle on catalyst wax deposits. It was found that wax deposition was not reduced and that hydrogenation without prior extraction was not adequate to remove the deposits.

Holten, August 27, 1942 1 pg.

Carbon deposition in gas-recycle operation. Poor Kieselguhr was blamed for the deposition. Only high H₂CO ratios prevented deposition.
 Holten, April 17, 1942 2 pg.

Discussion of various methods of operation with gas recycle, purpose, and comparative calculations.
 Holten, December 23, 1940 15 pg.

Experiments with olefin s thesis with gas recycle over mixed catalyst. Reduction of throughput (net) increased the total yield. Gasoline yield decreased but olefin content increased in both gasoline and gas oil. The yield of hard wax increased. Increasing CO partial pressure has an effect similar to decreasing throughput. Increasing recycle ratios give better results. Increasing temperature has an unfavorable effect in every respect.
 Holten, March, 1942 9 pg.

Comparison of a regular tubular reactor and one with jacketed tubes.
 Holten, March 6, 1941 6 pg.

Experiments with gas recycle over a mixed cobalt catalyst (100 Co, 5 ThO₂, 8 MgO, 200 Kieselguhr). The run lasted 204 days with 1:3 fresh gas to recycle. It was found that it was important to remove the gasoline from the recycle gas in order to maintain catalyst activity and high olefin concentration in the gasoline fraction. On the other hand, gasoline recycle increased the gas oil yield by reducing the wax production. Increasing the CO concentration in the recycle by increasing the conversion (higher temperature) does not increase the olefin content appreciably, but causes higher gas formation and reduced wax production.

The effect of recycling gasoline with the recycle gas was to increase the C₃ yield considerably (more than double) at the expense of C₄, particularly the butylenes.
 Holten, November 1, 1941 26 pg.

Report on a test run with gas recycle containing data similar to that in the report abstracted above.
 Holten, April 29, 1941 18 pg.

Report on gas recycle experiments using a low cobalt concentration catalyst.
 Frankfurt, February 6, 1939 13 pg.

Report on gas recycle experiments.
 Holten, May 23, 1938 9 pg.

Item 11. Medium pressure synthesis with gas circulation.

Report on gas recycle without removal of water or oil.
 Holten, July 5, 1940 7 pg.

- Report on gas recycle without gasoline removal.
Holten, July 10, 1940 6 pg.
- Report on gas recycle at the Hoesch plant.
Holten, September 26, 1939 9 pg.
- Report on gas recycle operation by Lurgi.
Holten, January 23, 1939 12 pg.
- Comparison of straight through and gas recycle operation.
Holten, April 20, 1938 14 pg.
- Recycle experiments performed in cooperation with Lurgi.
Holten, September 26, 1939 3 pg.

Item 12 Medium pressure synthesis without recycle.

- Comparison of results with water gas and synthesis gas. It appears that water gas was considered more desirable.
July 4, 1940 2 pg.
- Results using water gas at 7 atm.
Holten, September 3, 1940 5 pg.
- Results using water gas at 7 atm.
Holten, March 15, 1940 6 pg.

Item 13 Medium pressure synthesis.

- Observations in medium pressure experiments.
Holten, September 7, 1939 5 pg.
- Effect of pressure on gasoline synthesis. One to seven atmospheres.
Holten, March 1, 1939 6 pg.
- Comparison of synthesis at 7 and 5 atmospheres.
Holten, December 20, 1938 5 pg.
- Summary of medium pressure experimental work up to April 1939.
Holten, June 29, 1939 7 pg.
- Effect of pressure on the synthesis. Five and ten atmospheres.
Holten, November 15, 1938 3 pg.