

FILM STUDY GROUP

REPORT ON MICROFILM REEL NO. 34

Prepared by

THE ATLANTIC REFINING COMPANY

SCANNING OF REEL #34

(Orig. Ident. Reel 2B)

U. S. Government Technical Oil Mission

Bag 3440 - Target 30/5.01 - Ruhrchemie A.G. Sterkrade-Holten

SECTION 31. (Continued from Reel #33)

This material, as previously noted, appears to be original laboratory sheets showing tests on catalyst for synthesis of hydrocarbon. The information usually gives the composition of the catalyst, the conditions under which it was applied to the syntheses, and tabulated data showing products and yields. (280)

SECTION 32. ADDITIONS TO MISCELLANEOUS RUHRCHEMIE PATENTS

Item 1 - Feb. 8, 1940. (3)

Attention was called to the following:

(a) U.S. Patent 2019184. "On the other hand, it is in my opinion possible to confine the process to olefins or olefinic naphtha, whichever is available for the process."

(b) German Patent 475227 mentions the step-wise absorption in individual absorbers with decrease in temperature, whereby the naphtha can be separated into individual fractions.

(c) Raising the treating temperature. Calls attention to the fact that treating can be done at increasing temperatures with diminishing amount of polymer.

(d) Extraction of spent clay (U.S. Patent 2127654). Attention is called to the possible differences to the disclosure at hand.

All the above may be construed as comment upon the discussed patent disclosure which for the present we can only identify as R254.

Item 2 - Process for improving the octane properties of naphtha hydrocarbons (R452). (2)

Item 3 - Clay treating resin free naphtha (R458). Some doubt on the attainment of octane improvement claimed appeared warranted. (1) Clay treating of cracked naphtha. (R501) Enumerates conditions described by the invention and for cracking under intensive conditions. (1)

Cites objections to disclosure R513 which apparently is related to treating of paraffin, to disclosure R514 which appeared related to application of fatty acids and disclosure R515 which seemed to deal with the use of mixtures of free fatty acids for emulsifying wax. (7)

Further comment on disclosure R513 is found in notes of Jan. 22, 1941 and Sept. 8, 1941 and Dec. 2, 1941. This disclosure is now identified with R107858 IVd/12, entitled "Process for the production of high molecular weight fatty acids by oxidation of paraffin hydrocarbon." The claim is as follows:

Production of high molecular fatty acids characterized in that the so-obtained paraffin is treated at least four times consecutively, as in the familiar oxidation of montanwax with sulphuric acid bichromate solution and treating the resulting reaction mixture in the usual manner.

Disclosure 514 is outlined at considerable length in memorandum of Sept. 16, 1941. The patent claim itself is omitted. (4)

Disclosure 515 is commented upon in a note of March 15, 1941, in which one of the versions of the patent claim is as follows:

Process for the production of unctuous emulsions containing water, characterized in that one partly oxidizes solid paraffin derived from hydrogenation of carbon monoxide and in any case by addition of hard paraffin or fatty acids from carbon monoxide hydrogenation, emulsifies this with an alkali hydroxide or carbonate and water, which upon cooling produces a salve like emulsion. (3)

Process for the production of high molecular weight fatty acids from water gas paraffin. (R541) Comment under dates of Dec. 2, 1941 and Sept. 9, 1941. (2)

Disclosure R549 commented upon October 14, 1941 does not adequately reveal the invention. (1)

Improving the octane number of cracked gasoline (R455).

Comment is offered in the memorandum of Nov. 9, 1941. (1)

Disclosure R665 - purification of high molecular weight wax acid is discussed in a memorandum of Aug. 13, 1943. (1) The patent claim is as follows:

High molecular weight wax acids derived by oxidation of high melting paraffin with alkali bichromate sulphuric acid, and with nitrous gases in the presence of nitrosyl sulphuric acid; saponification of the oxidation product with lye, subsequent extraction with the product resulting from hydrogenation of carbon monoxide, acidifying, washing and drying of the extraction residue, thereby characterized in that one carries out the oxidation step at 100 to 125°. (10)

The material contained in Section 33 is not regarded by the reviewer as of great importance. It represents some of the correspondence between the patent staff and the laboratories, usually of a nature indicating an attempt to substantiate claims made in the original disclosure. It is likely that the files of Ruhrhesmie, particularly those which concern the patent group, will be more satisfactory.

SECTION 33. SPECIFICATIONS FOR FUELS (5)

Item 1 - Liquefied fuel gas (gasol).

Item 2 - Fuel gas (Arsyn specifications of Oct. 24, 1939 and Sept. 19, 1940).

SECTION 34. LOW TEMPERATURE DISTILLATION ANALYSES

A letter of Oct. 9, 1942 transmits tabulated data upon 10 analyses, each performed by RCH and by Rheinpreussen. (2)

SECTION 35. EFFECT OF SUPER HEATED STEAM ON ALKAZID SOLUTION

A memorandum of July 31, 1942 is given. (2) Following observation of corrosive conditions in the alkazid plant, experiments were performed in which saturated solution taken from service and having a specific gravity of 1.157 was heated in glass, iron and aluminum vessels.

Glass - The temperature was raised to 152° during evaporation, at which the liquor had a syrupy consistency and specific gravity of 1.338.

Iron - Very pronounced foaming took place at the beginning, and the heating had to be interrupted from time to time. After a while the evaporation was normal. In this manner the liquor was heated to 139°, and a viscous liquid was obtained with specific gravity 1.322.

Aluminum - Very pronounced foaming occurred so that the temperature at the end of the experiment was only 109°. Specific gravity of the liquor was 1.250.

In order to establish whether this heating had harmed the liquors an absorption control test was made. The absorption value of the solution was satisfactory. From corrosion tests of solution on iron and aluminum, it was concluded that the superheating was not objectionable.

SECTION 36. CATALYST COMPOSITION AND ACTIVITIES

This appears to be an original tabulation of about 80 tests enumerating the following properties: precipitation temperature, washing temperature, reduction conditions, reduction values, color of product and percent contraction after 50, 100 and 200 hours. (2) Catalyst composition, but not proportions, is given.

SECTION 37. DETERMINATION OF SULPHUR IN GASES BY DIFFERENT METHODS

A single set of analytical values on the determination of H₂S and organic sulphur. Although the procedures are in some instances named, they are not described. (1)

SECTION 38. COMPARISON OF SULFUR REMOVAL BY CATALYST, AND THE INFLUENCE OF POROSITY

An evaluation for removal of sulfur was made on catalyst produced by RCH, Erbag and Schwarzside. The significance of the porosity measurement is not stated; the memoranda has the appearance of being incomplete. (7)

SECTION 39. REMOVAL OF ORGANIC SULFUR IN COARSE (GROBKORNIGES) MASS (1)

A memorandum Sept. 17, 1943

Information from Krupp indicates that in the coarse purification, 50% of the organic sulfur is firmly retained by the catalyst. A series of experiments was performed at different temperatures with bog iron ore, Luxmasse and a mixture of the two in proportion 1:1 under conditions comparable to commercial use. Dry charge gas, free of H_2S , was used. At $10^{\circ}C$, there is no appreciable removal of organic sulfur. Even up to 40° , the bog iron ore removes little sulfur. The Luxmasse and the 1:1 mixture at 40° , which is also the normal working temperature, over a period of 20 days removed 90% of the organic sulfur. These results were reconciled with the plant performance which gave only 10% efficiency, by the following observations:

(a) The plant coarse purification unit at the beginning of the research period had already been in service about 2 months.

(b) The H_2S content of the charge water gas was about 6 to 7 grains per 100 cu. meters, and after leaving the purifier was in the order of 0.1 grains. After two months the exit gas contained 1.5 grains per 100 cu. meters.

(c) The water gas, which in the laboratory experiment was especially dried, in plant practice contains moisture.

SECTION 40. OPERATING METHODS AT THE RHEINPREUSSEN WORKS (25)

This material is also on Section #16 of Reel #33.

SECTION 30. EXPERIMENTAL RESULTS OF METHYL ALCOHOL AND HYDROCARBON SYNTHESIS FROM WATER GAS OVER COPPER-MANGANESE-THORIUM CATALYST AT HIGH PRESSURE

Note: This section was referred to in Reel #33. It consists of laboratory data sheets giving chemical composition of the catalyst, temperature, pressure, thrupt, and duration of test; product yields and inspections. (22)

SECTION 41. GRAPHICAL RECORD OF PRODUCTION APRIL 1940 TO DECEMBER 1944

Shows percent contraction, thrupt rate, period of extracting or discharging catalyst. (10) The reviewer presumes the graphs referred to Fischer-Tropsch synthesis.

SECTION 42. CALCULATION OF YIELD (FROM SYNTHESIS)

Memoranda of May 16, 1940. (6)

SECTION 43. MISCELLANEOUS TOPICS: GAS RATE FOR MEDIUM PRESSURE OVENS, ETC. (4)

Memorandum of conference with Hoesch-Benzin dated Jan. 6, 1942.

SECTION 44. CONDITIONS DEC. 5, 1941 IN THE NORMAL PRESSURE AND MEDIUM PRESSURE PLANTS

This report made to Prof. Martin, presumably refers to the plants at Holton. It enumerates ovens in service for each step, the number being emptied, those out of service through damage, the number in reserve and those which are known to be defective. (2)

SECTION 45. CALCULATION OF MONTHLY YIELDS (5)

Memorandum of a conference Mar. 14, 1939, to which representatives of the licensee companies were in attendance, dated April 6, 1939.

SECTION 46. CALCULATION OF THEORETICAL YIELDS FROM GAS ANALYSES

An order of Oct. 16, 1941 and apparently reissued Aug. 15, 1944, giving instructions on calculation of yields. It was emphasized that carbon and hydrogen balances must leave no remainder. (7)

SECTION 47. SYNTHESIS CONFERENCE

Memoranda reporting upon conferences are given as follows:

Dec. 12, 1939	on conference	Nov. 23, 1939
Jan. 15, 1940	"	Jan. 5, 1940
Dec. 20, 1938	"	Dec. 15, 1938

These memoranda serve as a background to the continued research under the guidance of Prof. Martin. (19)

SECTION 48. "FEINREINIGUNG", PURIFICATION OF WATER GAS WITH MINETTE (5)

The term Minette is unfamiliar, but the reviewer believes that it was a porous or fibrous carrier used to support the active agents. Three types were used: a so-called oxygen Minette, one moistened with 12 weight % of soda, and "gegluhte" Minette which was heated for 2 hours at 300°C. The oxygen Minette proved to be the most effective of the devices.

SECTION 49. OXO SYNTHESIS - DEVELOPMENT & ANALYTICAL METHODS (20)

Memorandum of conference July 3, 1940, under date of July 19, 1940. Representatives of IG and RGH attending. (3)

Memorandum on aldehyde catalysis - July 20, 1940. (2)

Rapid determination of sulfur phosphoric acid solution - Nov. 25, 1940. (2)

Aldehyde production Nov. 14, 1940. (1)

Acetal formation - Nov. 21, 1940. Splitting off of water, Jan. 6, 1941 and Nov. 19, 1940.

Cracked oils - Dec. 23, 1940.

It will be seen from the above that this section is really a group of memoranda relating to diverse subjects.

SECTION 50. PATENT POSITION OF IRON SYNTHESIS (6)

A memorandum dated Jan. 8, 1941 apparently in reply to an inquiry from Prof. Martin, Jan. 4, 1941.

SECTION 51. THE P- GAS PLANT

This section consists of a single frame, showing a flow diagram and bearing the imprint of Ruhrchemie with the date Aug. 13, 1942. There are no clues as to the charge stock nor the products.

SECTION 52. COMMERCIAL DIESEL OIL: ANALYSES (1)

The inspection of 3 diesel oils is given; one of the oils is from petroleum. The alcohol content of this fuel was 1%, as contrasted to about 10 and 13% for the other two synthetic fuels.

SECTION 53. RECOVERY OF OIL WITH HIGH OLEFIN CONTENT

Memorandum, Aug. 19, 1940, of a conference held two days previously. The memorandum (2) outlines the proposed operating conditions, with instructions to the laboratory staff for carrying out the experiment.

SECTION 54. THE USE OF LUXMASSE IN CATALYST PREPARATION

Memorandum of Jan. 11, 1941 gives unusually complete details (3) covering the following:

- Grinding of the luxmasse with alkali.
- Analyses of the luxmasse.
- Preparation of the catalyst mass.
- Precipitation of catalyst mixture and
- Examination of product.

This memorandum will be of interest to those concerned with the synthesis reaction developed by Ruhrchemie.

SECTION 55. DEHYDROGENATION

Memorandum (2) Jan. 6, 1941 addressed to Herr Hanisch discusses the following:

- (a) Proposal to effect dehydrogenation with elementary sulfur.
- (b) Proposes the use of finely divided metals which form sulphide, and which presumably may be readily reduced with attendant loss of hydrogen by the hydrocarbon.
- (c) Points out that while a portion of the sulfur reacts to form H_2S , some part of the sulfur may react to form alkyl sulphides, which are undesirable. In the event that these are formed, they should be conducted over *FRM* (Fein Reinigung Masse ?).
- (d) The writer proposes to react octane with sulfur, using reflux, and to perform the experiment both in the presence of above-mentioned catalyst, and again without them.

SECTION 56. PREPARATION OF REDUCED CATALYST

Memorandum of Oct. 25, 1940 refers to correspondence of Oct. 16, 1940 and states that certain materials have been subjected to the requested treatment. The catalyst and brief properties are enumerated. (1)

SECTION 57. OIL REQUIREMENTS FOR LIQUID SYNTHESIS

The memorandum (1) was addressed to Prof. Martin, dated Dec. 1, 1941.

The experiments are not yet completed to show relationship of catalyst and oil yield.

SECTION 58. LIGHT LIQUID HYDROCARBON SYNTHESIS

A memorandum (1) Nov. 21, 1941. By simultaneously raising temperature and thruput rate, and employing iron catalyst, a paraffin and highly olefinic material resulted. The writer wishes to establish whether raising temperature and thruput will influence the yield of gasol (light hydrocarbon) without excessive gas formation or effecting the catalyst life unduly.

Reviewer's Note: Many of the memoranda in this reel appeared to be notifications or orders to certain of the staff to carry out previously discussed experimental work.

SECTION 59. IRON CATALYST

Memorandum (2) of Dec. 6, 1941 referring to correspondence of Nov. 29, 1941. This item is probably supplementary to item #58, above.

SECTION 60. DIESEL FUELS WITH CETANE NUMBER 200 TO 300

There was renewed interest in diesel fuels of extremely high inflammability, and with cetane number of 200 to 300. It appeared possible that such fuel could be made by employing the nitric acid esters of synthetic alcohol. In the simplest case, the olefinic primary product could be converted to alcohol-containing products by means of oxo synthesis and these converted to esters. In place of nitric acid, halogen containing derivatives might be used. The memorandum requests determination of ignition properties on a pure ester, or better still the esterified mixture of raw alcohol in the range C10 - C20. As in previous memoranda, this is really a suggestion to carry out the work, and we have no clue as to the actual performance nor the analysis of the resulting data. (1)

(This ends scanning of reel #34)