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THE FISCHER-TROPSCH PLANT OF RUHRCHEMIE A.G. STERKRADE-HOLTEN

(l.c.)
Hall + Haensel

REC'D: FEB 14 1946
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COMBINED INTELLIGENCE OBJECTIVES
SUB-COMMITTEE

RESTRICTED

THE FISCHER-TROPSCH PLANT OF RUHRCHEMIE A.G.

STERKRADE-HOLTEN, RUHR.

Report Compiled and Edited by

Capt. C.C. Hall, British, Ministry of Fuel and Power
Dr. V. Haensel, U.S., Petroleum Administration for War

on behalf of

British Ministry of Fuel and Po
and
United States Technical Industrial Intelligence Committee

C.I.O.S. BLACK LIST ITEM
30/5.01
Fuels and Lubricants

5 July, 1945

COMBINED INTELLIGENCE OBJECTIVES SUB-COMMITTEE

G-2 Division, SHAEF (Rear) APO 413

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Personnel of Investigating Teams.

In the Ruhr, April 6 to 23, 1945.

Lt.Col. A. Parker, British, Ministry of Fuel and Power
Mr. E. Cotton, U.S., Petroleum Administration for War
Dr. V. Haensel .. ..
Dr. E.B. Peck, ...
Dr. A.R. Powell, ...
Col. J.A. Oriel, British, Ministry of Fuel and Power
Lt. Col. R.N. Quirk .. ..
Lt. Col. H. Hollings, ...
Capt. J.H.G. Plant, ...
Capt. C.C. Hall, ...

In Central Germany, April 25 to May 2, 1945.

Dr. W.C. Schroeder, U.S., Bureau of Mines, Dept. of the Interior.
Dr. A.R. Powell, U.S., Petroleum Administration for War.
Mr. E.L. Baldeschwieler, U.S., ...
Dr. G. von Elbe, U.S., Bureau of Mines, Dept. of the Interior
Major R. Newmann, British, Ministry of Fuel and Power
Capt. C.C. Hall, ...

At Nienburg, May 11 to 13, 1945.

Major D. Morten, British, Ministry of Fuel and Power

At Leuna, May 15, 1945.

Major D.A. Howes, British, Ministry of Fuel and Power
Mr. J.G. Allen, U.S., Petroleum Administration for War
Mr. H. Schindler, ...

In London, April 25 and May 1, 1945.

Mr. G.S. Bays, Jr., U.S., Petroleum Administration for War
Dr. W.A. Horne, ...
Mr. J.P. Jones, ...
Mr. B.L. MacKusick, ...
Col. J.A. Oriel, British, Ministry of Fuel and Power
Lt. Col. R.N. Quirk .. ..
Major A.J.V. Underwood.. .. ..
Mr. A.R.M. Murray, ...

General Introduction

Nature of the Target

The Ruhrchemie A.G. was formed by a group of Ruhr Companies, the principle shareholders being :-

Gelsenkirchener Bergwerke A.G.
Gutehoffnungshütte
Harpener Bergbau A.G.
Fried. Krupp A.G.
Mannesmann Röhren-Werke A.G.
Essener Steinkohlen Bergwerke A.G.
Rheinpreussen.

About 1935, following the acquisition by Ruhrchemie of exclusive rights to the Fischer-Tropsch process, the Company started the construction of a plant for the commercial operation of this process, and a subsiduary company known as Ruhrbenzin A.G. was formed to serve as the operations organisation for the project. It is believed that the desire to find outlets for the surplus coke produced in the Ruhr was one of the main reasons for the new venture.

Not only did this plant represent the initial large-scale operation of this process, but it also served as the research and development centre for the process and many modifications and ancilliary and related developments which followed later. The other eight Fischer-Tropsch plants which were subsequently erected in Germany were licensed by Ruhrchemie and were based on the Ruhrchemie model.

The catalyst factory at Sterkrade-Holten supplied all catalysts required for the operation of the six Fischer plants in the Ruhr area.

Plants erected (or projected) in foreign countries (e.g. Japan) were licensed by Ruhrchemie and depended on them for the basic technical information necessary for the operation of the process.

It is therefore clear that the Sterkrade-Holten works constituted a target of major importance for C.I.O.S. Item 30, and required thorough investigation. Other Fischer-Tropsch plants in Germany would serve mainly to confirm and amplify information obtained from Ruhrchemie.

Object of the Investigation

1. To obtain technical details of the operation of the Sterkrade-Holten plant and of the research and development work of Ruhrchemie in the field of hydrocarbon-synthesis.

2. To obtain information regarding the location, capacity and nature of Fischer-Tropsch plants erected in Japan or in Japanese-occupied territories.

Summary and Conclusions.

General.

There had been no increase in the number or capacity of the Fischer-Tropsch plants in Germany during the War, and the total, average annual production of primary products from the nine plants amounted to rather less than 700,000 tonnes, i.e., only about half that estimated in the Item 30 briefing documents.

The processes used in these plants were substantially those known or believed to be in use before the War. The cobalt catalyst (Co:100, ThO_2:5, MgO:8, kieselguhr: ca.200) had remained unchanged in composition since 1938 and was the only one employed on the full scale for both normal and medium-pressure (9-11 atmos.) operation. The methods employed for catalyst preparation, reduction and regeneration were substantially those known before the War.

Some increase in yield and catalyst life had been achieved in the atmospheric-pressure process by more rigorous purification of the synthesis gas and by improved operation and control in the catalyst chamber house - in particular, the starting-up of fresh catalysts, the methods and time schedules used for regeneration 'in situ' and the schedule for switching catalyst chambers from one stage to another. The average yield claimed for both normal and medium-pressure operation was 150 gm. C_3 and higher hydrocarbons per Nm^3 ideal gas; the catalyst life was given as 5-6 months for normal pressure and 8-11 months for medium-pressure operation.

No new design of catalyst chamber had been introduced. The rectangular, multi-plate vessel was still standard for normal-pressure synthesis and a vertical, cylindrical, double-tube chamber was used for operation at 9-11 atmospheres.

The Fischer-Tropsch process was regarded by Ruhrchemie primarily as a means of producing chemical products and was not thought to have much future as a fuel-producing process in a free world economy.

Even during the war, only the spirit fraction (e.p. 160°C.) and the light diesel oil fraction (160-230°C.) were used as fuel. The heavy diesel oil was sent to

I.G. for conversion to Mersol detergents and the soft wax to Witten (Deutsche Fettsäure Werke) for conversion to soap and edible fat. There had been no reforming of the motor spirit fraction or cracking of the heavy fractions (except to make raw-material for the manufacture of lubricating oils) during the war, although partly completed large-scale plants for catalytic cracking, polymer petrol production and conversion of the heptane cut to toluene, existed.

The main trend of the Ruhrchemie war-time research work was in the direction of producing chemical and special products which were in short supply.

The Sterkrade-Holten Plant

Water gas was produced from coke in standard generators and purified from hydrogen sulphide and organic sulphur compounds by the normal processes. A portion of the water gas was converted to hydrogen by the usual shift catalyst and the product blended with unconverted water gas to give the required ratio of carbon monoxide to hydrogen.

The synthesis step was carried out in two independent sections :-

1. An atmospheric section comprising 52 catalyst chambers in two stages supplied with gas of H_2: CO = 2 : 1.
2. A medium-pressure section of 72 chambers arranged in three stages which received gas of H_2: CO ratios 1.4:1, 1.6:1 and 1.8:1 respectively.

Direct condensers were employed on the atmospheric-pressure stream, and indirect condensers on the medium-pressure stream. Active carbon was used in both cases for recovery of light spirit and 'gasol', and the products were refined in conventional stabilising and distillation equipment.

The annual output from the whole plant was approx. 70,000 tonnes of primary products.

Synthetic Lubricating Oil.

At Sterkrade-Holten, 1400 tonnes per month of high-grade synthetic lubricating oil was produced by aluminium chloride polymerisation of the olefines derived from soft cracking of the over 170°C. portion of the primary products. The oxidation stability of these oils had been markedly improved by the incorporation of phenathiazine or, more recently, elemental sulphur in the polymerisation process.

The oils were blended with petroleum oils and used in army vehicles.

Research and Development Work.

The OXO Process. The Sterkrade-Holten works included an almost completed plant for the production of 10,000 tonnes /annum of C_{12} - C_{18} alcohols by the reaction of water gas with C_{11} - C_{17} Fischer-Tropsch olefines, using a powdered cobalt catalyst in the liquid phase at 135°C. and 150 atmos. pressure to form the C_{12} - C_{18} aldehydes, which were then hydrogenated to the corresponding alcohols at 180°C. and 150 atmos. The process was to be operated by the OXO Gesellschaft (Ruhrchemie + I.G. + Henkel et Cie.) with the object of producing detergents from the alcohols. The OXO reaction appeared to be generally applicable to olefinic compounds.

The Cobalt - Water gas - Recycle Process. Arrangements were almost complete for the operation of the Sterkrade-Holten synthesis plant with all the 72 medium-pressure ovens in one stage at 11 atmos. using water gas as the feed material and recycling 3 parts residual gas to 1 part fresh gas. After adjusting the H_2: CO ratio to 2 : 1 the tail gas was passed through two atmospheric-pressure stages.

The products from the medium-pressure stage were said to have a high olefine content and would have provided suitable raw-material for the OXO process.

Iron Catalysts. Research work which had started before the War had resulted in the development of an iron catalyst of the general type:- Fe:100, Cu:2-5, CaO: 10, kieselguhr: 30-150, which gave good performance with water gas at 215°-230°C. and 20 atmos. pressure. The process was preferably operated in two stages with a 2:1 recycle-gas : fresh gas ratio in the first stage. The products were rich in olefines and contained a high proportion of hard wax; the yields and life of catalyst were said to be similar to those obtained with cobalt.

This process had only been operated on the pilot-plant scale ($100m^3$ gas /hr. = 1/10th. full scale).

Apart from the question of War-time availability of materials, there was no suggestion that this process was superior to that based on cobalt.

The iron catalyst was said to be more expensive to prepare, it required higher operating pressures, and tended to give products contaminated with oxygen-containing bodies. Its use was not essential for the production of olefine-rich products; these could equally well be obtained by the cobalt - water gas - recycle process. The production of hard wax was the only virtue specifically claimed for the iron catalyst.

Chemical Products. A considerable amount of research work had been carried out along the following lines :-

1. The extraction of the small amounts of alcohols and fatty acids present in the normal products and attempts to modify the process in such a way as to increase the proportion of these compounds.

2. The synthesis of n-primary alcohols at 200°C. and 200 atmos. pressure using cobalt and iron catalysts.

3. The oxidation of the hard wax with nitrosyl sulphuric acid to produce fatty acids of greater chain length and freedom from byproducts than are obtained by the Witten (aerial oxidation) process.

4. Chlorination and dechlorination of the waxes to produce olefines which yield special lubricants on polymerisation and detergents by sulphation.

5. The production of new products by the addition of acetylene to the synthesis gas.

Japanese Intelligence.

The Directors of Ruhrchemie appeared to have little knowledge of value concerning Japanese developments in the Fischer-Tropsch field during recent years. The exchange of information appears to have been 'one-way'.

Such information as was obtained has been passed to the appropriate authorities.

Report 1 **Inspection of the Plant**

Date of Inspection: April 6, 7 and 8, 1945

Personnel of Inspection Team:

Lt. Col. A. Parker (Leader), British, Ministry of Fuel and Power
Mr. E. Cotton, U.S., Petroleum Administration for War
Dr. V. Haensel, ...
Dr. E.B. Peck, ...
Dr. A.R. Powell, ...
Col. J.A, Oriel, British, Ministry of Fuel and Power
Lt. Col. R.N. Quirk, ...
Lt. Col. H. Hollings, ...
Capt. J.G. Plant, ...
Capt. C.C. Hall, ...

Reported by : Dr. A.R. Powell, U.S., Petroleum Administration for War

General.

The information gained from the mere visual inspection of the plant at Sterkrade-Holten was very slight and in part was rather confusing. This was true to a greater extent than any other target visited and was due to three reasons :

1. Key personnel familiar with the plant was not present, nor could they be readily located at the time. The few employees there at the time of the visit of the investigating team had only a hazy knowledge of plant operations as a whole, although each one had some knowledge of a specific operation or research project.

2. Pertinent documents, including process flow diagrams and research reports had been evacuated before the arrival of the team.

3. The bomb damage at the Sterkrade plant of Ruhrchemie was very severe, so that it was impossible to prepare any kind of flow diagram based on undamaged pipe lines and equipment. On the other hand, bombs had blown open some of the equipment so that some knowledge of internal construction could be obtained that would have been impossible otherwise.

The Ruhrchemie works on the northeast side of the main road passing through the plant comprised a synthetic ammonia plant, a nitric acid plant, research and development laboratories, and a plant for the preparation, regeneration, and reduction of Fischer-Tropsch cobalt catalyst.

The Ruhrbenzin works on the other side of the main road contains the Fischer-Tropsch synthesis plant with its various ancillary units, T.V.P. and Dubbs cracking units, a partly constructed catalytic cracking plant, clay treating unit, a polymer gasoline plant, synthetic lubricating oil plant and the OXO process plant. At the extreme south end is a large unfinished plant for production of toluene from heptane.

Apparatus in the development laboratory could not be definitely identified, but information obtained indicated that work on iron synthesis-catalysts up to semi-technical scale and also work on oxidation of wax had been carried out.

The Preparation and Purification of Synthesis Gas.

The first stage in the process was the production of blue water gas from coke. The battery of generators appeared to be of the standard Humphreys and Glasgow type and were not therefore investigated in detail.

Following the water-gas generator building was the gas holder and the necessary blowers to carry the gas through the purification system. Removal of hydrogen sulphide or "Grobreinigung" was carried out in the usual vertical cylindrical towers containing layers of iron oxide. These were standard design and no detailed examination was made. Following this was the "Feinreinigung" or removal of organic sulphur from the gas. This unit consisted of gas preheaters for heating the water gas to approximately 200°C. before entering the catalytic purification chambers. The chambers were vertical cylindrical towers with the catalyst held in heavy screen baskets in such a way that the catalyst layer was in the form of an annulus in the chamber, with empty gas space between the annular layer and the chamber walls (which were thermally insulated) and also empty gas space in the core of the annular catalyst layer. Later a drawing of this chamber was obtained and will be included in the final report. The preheated gas entered the center gas space and left the chamber through the inner empty core. Two of these chambers operated in series with a temperature control between the two chambers so that the temperature in each could be regulated independently. Examination of the catalyst showed it to be hard particles about ¼ to ½ inch in diameter and of a typical ferric oxide color, and it was expected that later information would show it to be the usual 70% iron oxide-20% sodium carbonate composition.

Following the gas purification units were the towers containing the usual shift catalyst for conversion of the carbon monoxide in the water gas into hydrogen so that the desired ratio of hydrogen to carbon monoxide could be attained for the synthesis gas. Since only a portion of the water gas passes through this conversion plant, by-pass lines were provided so that unconverted water gas could be mixed with converted gas in any proportion to give a desired hydrogen:carbon monoxide ratio. Since synthesis gas was delivered to both the normal pressure and the medium pressure catalyst chamber systems, and since each system might require different ratios, the mixing system was arranged to give independently made mixtures to each.

Normal-Pressure Catalyst Chamber System: (See Fig. 1)

This consisted of 52 catalyst chambers (exact count was difficult because of extensive bomb damage). The general design of these normal or low pressure chambers was fairly well known and furthermore complete drawings of their construction were later obtained from Gutehoffnungshütte at Sterkrade, so detailed data will be omitted in this preliminary report. These chambers were rectangular, about 20 ft. long, 6 ft. wide and 9 ft. high, and were filled with thin vertical steel plates parallel to each other and about ⅜ or ½ inch apart. Passing through these plates at right angles were numerous horizontal tubes about one inch in diameter, which served to carry the water, the vaporizing of which removed the exothermic heat of the hydrocarbon synthesis occurring in the chambers. Catalyst occupied all of the spaces between the steel plates and these plates acted as heat-transfer fins to carry the generated heat to the water tubes. The water tubes connected to tube sheets located at each end of the chambers, and the generated steam from every pair of two chambers united in a common header on which was an automatic pressure regulator so that the proper steam pressure (and therefore the temperature) could be maintained constant. Two headers (from four chambers) entered an overhead steam drum and from these drums the steam entered a common steam collecting main for use in the plant.

The tops of each chamber were removable so that fresh catalyst could be charged by gravity flow directly from the large "Kübel" containing it, by means of an overhead crane running the length of the catalyst chamber building. Spent catalyst was removed by means of a drag chain conveyor which could be installed in a trough at the bottom of the chamber and running its full length. Gas entered the chambers at the top and left at the bottom, after passing through the thin layers of catalyst lying between the heat dissipating plates.

The gas connections to each chamber were so arranged that any chamber could be connected into the first stage of synthesis or the second stage or could be isolated entirely. Other gas connections, presumably for hydrogen for regeneration, nitrogen or carbon dioxide for ~~blanketing, etc., were also provided, but it was~~ impossible to trace such lines because of bomb damage.

The above description of the normal-pressure chambers corresponds to that known before the war and apparently no change had been made since that time.

Both the first stage and the second stage outlet mains connected directly to their respective condensers, which were two tall towers situated outside the catalyst chamber house. These were the usual direct coolers with water sprayed into the top and gas passing countercurrent from bottom to top. The tower filling was not examined but it is presumably Raschig rings.

After the second stage condenser the gas passed to the active carbon absorbent chambers where light benzin and C_3-C_4 hydrocarbons (gasol) were removed from the gas. These absorbent chambers were vertical cylindrical tanks about 15 ft. in diameter and 10 ft. high. Since these operated on a definite time cycle of absorption, stripping, cooling, etc., automatic time cycle machines had been installed to automatically open and close the various valves.

Medium-Pressure Catalyst Chamber System.

These chambers which appeared to be about 72 in number were located in an extension of the same building that housed the normal-pressure chambers. The construction details of these chambers were not so well known as were those for normal-pressure, so a more detailed examination was made. This was greatly facilitated by the fact that one chamber was lying on its side outside the building and was apparently in the process of being re-tubed when the personnel evacuated the plant. This was examined and photographed (see Fig. 2). Also at a later date, drawings showing all construction details were obtained from Gutehoffnungshütte in Sterkrade and this information will be available in the final report.

These medium-pressure chambers were vertical cylinders, 2.7 m. internal diameter, containing 1984 tubes, placed vertically and uniformily throughout the interior of the cylindrical chamber. These tubes were approximately 48 mm. outside diameter and 44 mm. inside diameter and about 4½ m. long. At both the top and the bottom they were welded into tube sheets, the distance between tube centres being 54 mm. Inside each tube was another tube of almost the same length, concentrically placed and about 24 mm. outside diameter and closed at each end. Near each end, however, was a side connection so that the inner tube had free access to the space in the chamber that was outside of the large tubes. Water was kept in the chamber outside of the large outer tubes and this water also flowed through the inner tube by means of the side connections at each end. Between the outer and inner tubes, it is evident that an annular space about 10 mm. wide existed which connected directly to the space above the upper tube sheet and the space below the lower tube sheet, but was isolated entirely from the water system outside and inside of this annulus. This space was filled with the catalyst and the synthesis gas entered the chamber in the space above the upper tube sheet, then flowed down through these annular catalyst spaces and finally left the chamber below the bottom tube sheet. To insure the uniformity of the annular space, small spacing plugs had been welded to the tubes, thereby rigidly holding the inner tube concentric to the outer tube throughout its length. This design of catalyst chamber insures that the maximum distance of any particle of catalyst from a water-cooled surface will not be more than about 5 mm.

Directly beneath the bottom tube sheet is a heavy reinforced screen for the support of the catalyst particles. This screen is separated into eight pie-shaped segments, hinged at the outside so that the segments may be allowed to drop from the center, thereby discharging spent catalyst from the chamber. The sections of the screen are supported by a Y-shaped member resting on a jack screw which passes through the cone-shaped bottom of the catalyst chamber, which allows the catalyst to be discharged into a container under the chamber.

The top of the catalyst chamber is a large flanged and dished head. The gas inlet is not through this head, thereby allowing easy removal of the head for catalyst charging. Instead, the gas enters through a side nipple just below the head flange. The gas outlet is through a nipple welded onto a manhead located on the conical bottom of the catalyst chamber.

The 72 chambers are arranged in sets of four chambers, each set of four chambers being placed in the form of a square. The inlet gas connections of all four chambers join in a common header and this header is valved so that it may receive first stage, second stage, or third stage gas from the appropriate mains passing through the catalyst chamber house. This indicates that the rotation of catalyst chambers between the different stages and other operations such as regeneration proceed by units of four chambers rather than individual chambers. The only independent valve provided for each individual chamber is a shut-off valve, so that one or more chambers may be cut off from the unit header, if so desired. It follows as a natural consequence that the gas outlets from each set of four chambers also connect to a common header to go to the appropriate outlet main.

The steam from the water section of the chambers is also handled as a unit from each set of four chambers. Outlets from the top of the chamber steam section join in a common pipe for each set of four and this connects in turn to the bottom of a horizontal steam drum. A similar arrangement exists for the bottom of the chamber steam sections.

Experimental Catalyst Chambers.

At one end of the row of medium-pressure catalyst chambers there was discovered one chamber of a rather unusual design that had apparently been installed for purposes of experimentation. As judged from its external appearance, it apparently contained the thin steel plates and horizontal water tubes of the normal-pressure catalyst chambers, but the shell had been built of curved heavy steel plate sections welded together so as to give the outside a corrugated appearance (see Fig. 3) It seemed probable that this vessel was the 'Druck-lammellen Ofen' referred to in the S.I.C.S. correspondence, and was an attempt to construct an oven to stand the higher pressure (20 ats.) required for the iron catalyst process, based on the internal arrangement used for synthesis at atmospheric pressure.

Adjacent to the above vessel was a vertical, cylindrical medium pressure reactor which, it appeared, differed from the normal type only in being fitted with its own, self-contained steam drum which took the form of an annular space round the circumference of the vessel near the top. (see Fig. 4)

In addition to the usual system of condensing towers and active carbon absorbers, an extensive system of what appeared to be condensers, scrubbers, heat exchangers and boosters was found close to the medium-pressure end of the catalyst chamber house and connected to the catalyst chamber gas mains. It was quite impossible to determine the significance of this arrangement by unguided inspection.

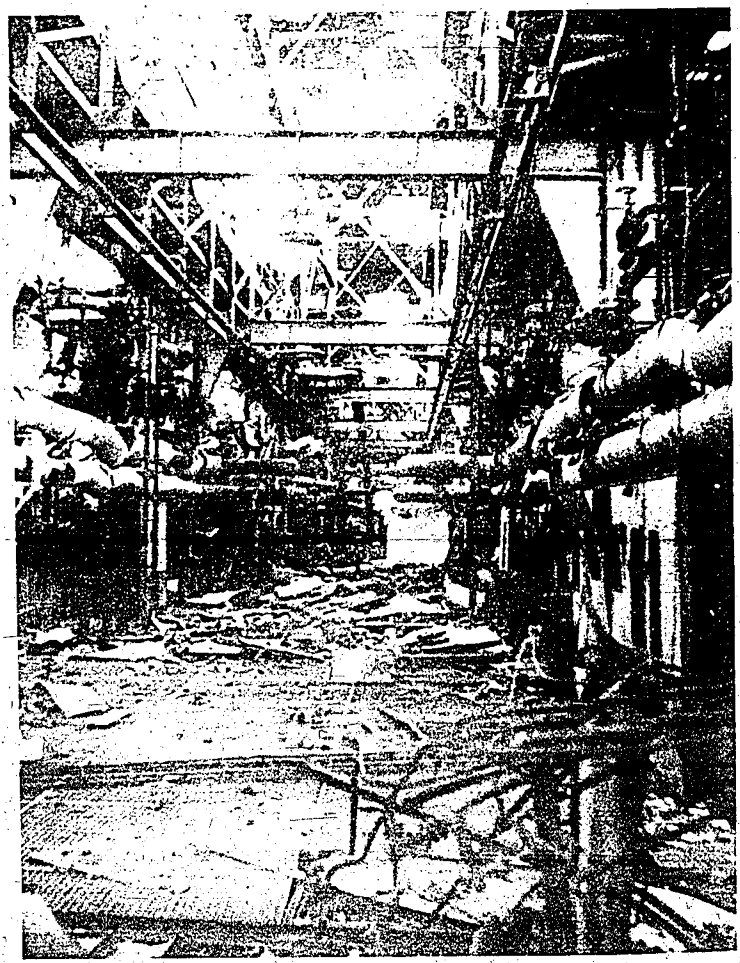


Fig.1. The control platform in the catalyst-chamber building.
(30/5.01, Ruhrchemie, A.G., Sterkrade-Holten)

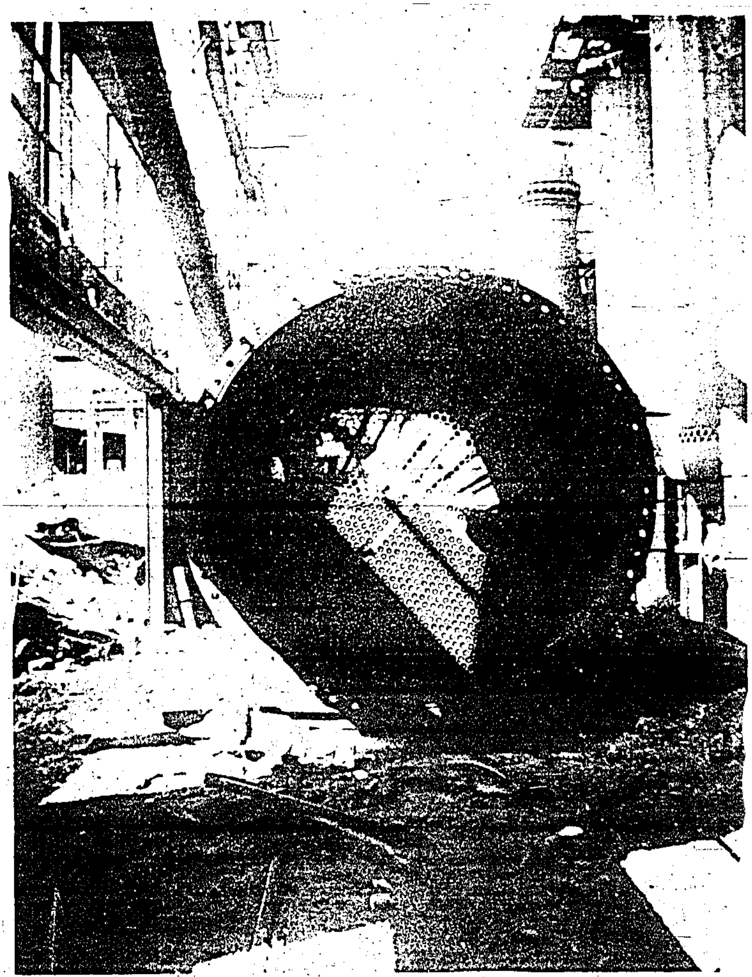


Fig. 2. End view of partly tubed medium-pressure catalyst chamber.

(30/5.01, Ruhrchemie A.G., Sterkrade-Holten)

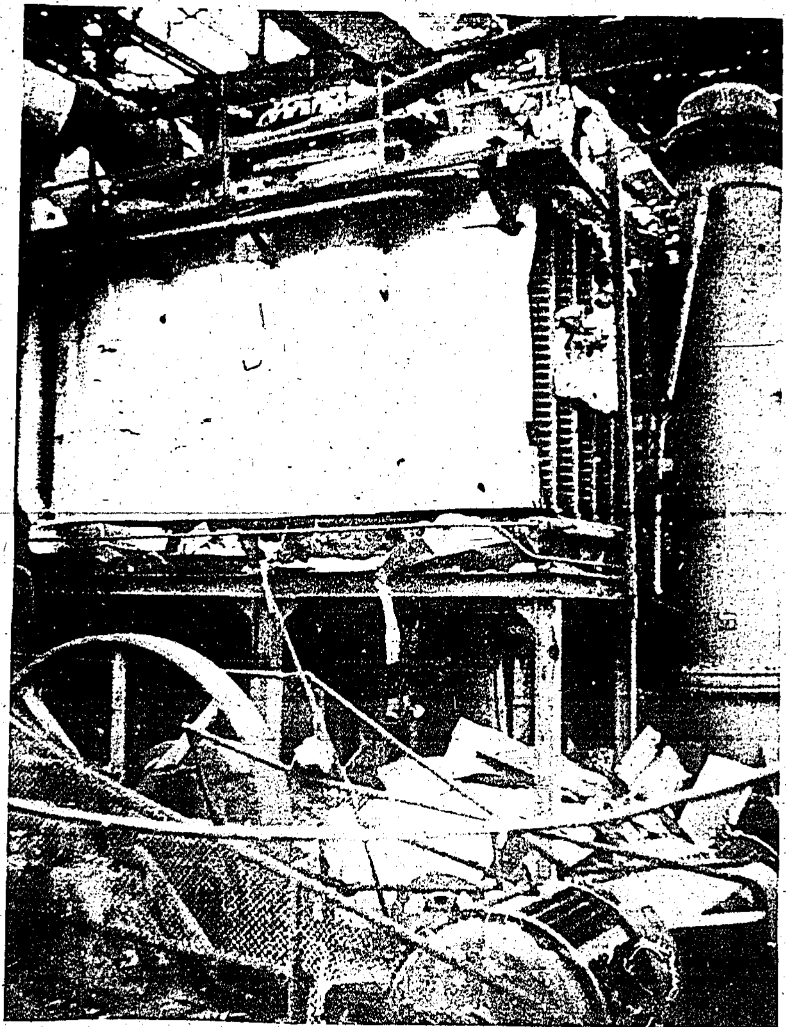


Fig. 3. Experimental medium-pressure catalyst chamber ("Drucklammellen Ofen")
(30/5.01, Ruhrchemie A.G., Sterkrade-Holten)

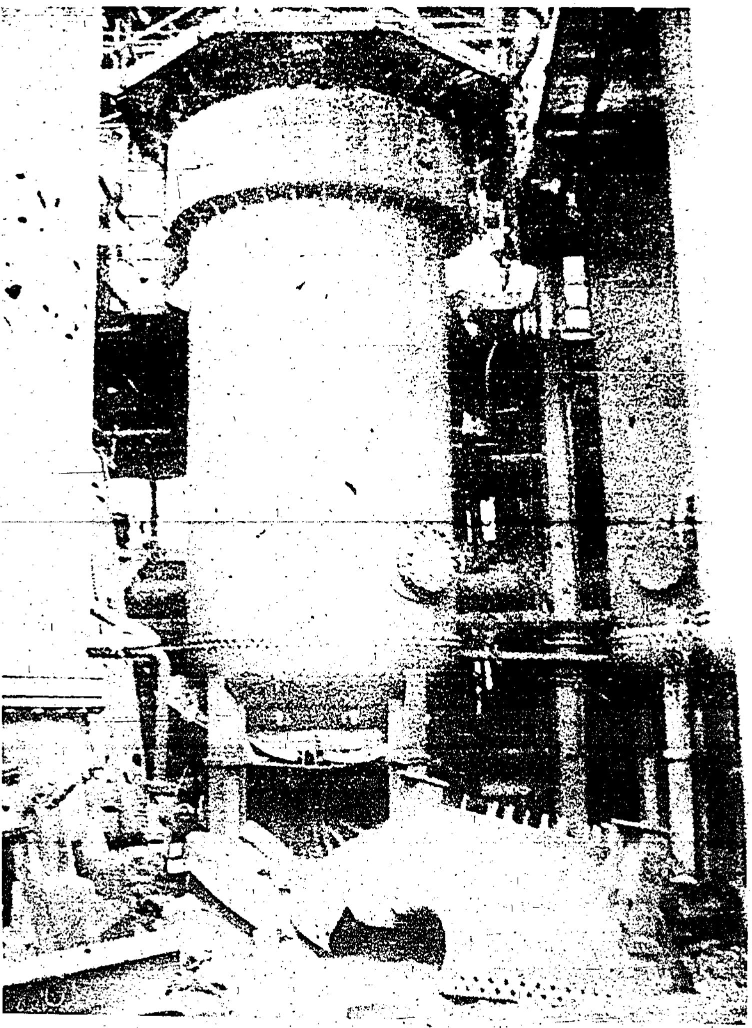


Fig. 4. Medium-pressure catalyst chamber with self-contained steam drum.
(30/5.01, Ruhrchemie A.G., Sterkrade-Holten)

Report 2. Interrogation of Dr. Spanier and Dr. Schrieber

Date of Interrogation: April 6th, 1945.

Personnel conducting interrogation:

Lt. Col. A. Parker, British, Ministry of Fuel and Power.
Col. J.A. Oriel, " " " " "

Reported by : Lt. Col. A. Parker

Interrogation of Dr. Spanier.

This man was left in charge of the works when the main body of technical personnel was evacuated following the destruction of the plant by bombing. He originally held some position of responsibility in the Ruhrchemie nitrogen factory but was unable to supply any useful information concerning the Fischer-Tropsch section. He was little more than a 'caretaker'.

Interrogation of Dr. Schrieber.

This man gave an account of his laboratory researches on dehydrogenation. Before the war he had worked on the dehydrogenation of C_3 and C_4 paraffins using an Al_2O_3 - Cr_2O_3 catalyst containing 0.2% of cobalt, prepared by heating aluminium hydroxide with chromium and cobalt nitrates. The catalyst was run for one hour at 590°C. and then reactivated with air at the same temperature. A 3 months' run had been carried out in this way with a n-butane feed, and an average conversion to butenes of 20% was obtained.

His more recent work was concerned with the dehydrogenation of C_{16}-C_{18} Fischer-Tropsch paraffins to produce olefines suitable for use as raw material in the OXO process. The main catalyst used in this work was prepared as follows. Carborundum granules (2-4 mm.) were washed with dilute nitric acid, dried and heated to 650°C. The granules were then placed in a vessel heated to 350°C. which was rotated in an inclined position while a 3% solution of the nitrates of thorium and chromium (21 gm. ThO_2 : 7 gm. Cr_2O_3 for 200 cc. granules) was sprayed in during the course of 4-5 hours, to form an even deposit on the granules. The resulting catalyst was then heated slowly to 520°C. and then to 850°C for 2 hours in a stainless-steel tray. The granules were then reduced in hydrogen at 200 l./hour for 5 minutes at 560°C., the hydrogen replaced by nitrogen and the reaction tube evacuated to 20 mm. Hg. The vapour of C_{16}-C_{18} paraffins was then passed over at a rate equivalent to 200 cc. liquid per 200 cc. of impregnated granules per hour. The catalyst was reactivated by oxidation with air. Its life was believed to be 3 months. The yields obtained were, 15% C_{16}-C_{18} olefines 6% lower (liquid) olefines, 2-3% gas and 0.5% carbon, deposited on the catalyst. The addition of 12 gm. of BaO as barium nitrate to the above quantities of thoria and chromia was tried with the object of reducing aromatisation. By recycling twice, a yield of 21% C_{16}-C_{18} olefines and 7% of lower olefines was obtained.

Schrieber had also carried out some work on the production of carboxylic acids by the oxidation of micronised coal.

Report 3. Investigation of Catalyst Manufacture and Recovery

Date of Investigation: April 6 and 7, 1945.

Personnel conducting Investigation:

Dr. V. Haensel, U.S., Petroleum Administration for War
Capt. J.H.G. Plant, British, Ministry of Fuel and Power
Capt. C.C. Hall, ...

Personnel Interrogated:

Dr. Blöchel
Dr. Herbke

Reported by: Capt. C.C. Hall, British, Ministry of Fuel and Power.

The Preparation and Reduction of Cobalt Catalyst.

Dr. Gehrke, who was in charge of the Ruhrchemie catalyst factory, was not available for interview but Dr. Blöchel who was in charge of cobalt catalyst manufacture and recovery and Dr. Herbke, in charge of catalyst reduction, were present and gave full information in their respective fields.

The composition of the standard cobalt catalyst prepared at Sterkrade and supplied to all Western-German Fischer-Tropsch plants was given as 100:5:8:180-200 cobalt:thoria:magnesia:kieselguhr. This catalyst had been in use since 1938 and replaced the former 100:15:200, cobalt; thoria:kieselguhr catalyst.

To be suitable for catalyst preparation, the kieselguhr must contain less than 1% of iron (as tested by refluxing a sample for 1 hour with 25% HNO_3) otherwise excessive methane production occurs during the synthesis. It must also contain less than 0.4% Al_2O_3 in the raw, uncalcined state, otherwise the catalyst tends to 'gel'. To avoid the necessity for acid-washing, the kieselguhr used at Sterkrade is selected to meet the above conditions. The present material is obtained from deposits near Hanover and is calcined before use, at Sterkrade, at 600-700°C. After this treatment the total volatile matter, including water, must not exceed 1%.

Due to slight variations in the density of various batches of kieselguhr, the proportion used in the catalyst is varied over the range indicated above in order to maintain a constant cobalt content of 80 gm./litre unreduced catalyst granules.

The various steps in the catalyst preparation are indicated in the diagram (fig. 5). 750 l. of a solution of the nitrates in the desired proportions, 100 Co : 5 ThO_2 : 10 MgO (2 parts MgO are left unprecipitated) containing 40/41 gm. Co./l. are heated to 100°C. in an overhead, stainless-steel tank (1). The contents are run into the precipitating tank (2) fitted with a direct-drive twin-screw stirrer and containing 750 l. of a solution containing 104 gm. Na_2CO_3/l. also maintained at 100°C. The mixture is stirred for $\frac{1}{2}$ minute and then dry kieselguhr is added through the hopper (3) and stirring continued for a further 1 minute. The slurry is pumped to a standard-type filter-press (4) and the cake washed with distilled water until the wash-water is neutral as tested by the addition of nitrophenol to 100 ml. wash water + 5 ml. 1/10 N.H_2SO_4. Catalyst equivalent to 64 Kg.Co requires ca. 10m^3 wash-water and the washing occupies 14-15 minutes.

The washed cake is then dropped into a "masher" (5) situated below the press and is mixed with dust from the screening plant. (64 kg. total Co gives 45 Kg. Co as dust). The resulting cream is then pumped to a rotating suction filter (6). The thin cake scraped off the filter drum contains approximately 70% water and falls into the extruder (7) where rotating arms force the paste through 3 mm. diameter holes whence it falls into the drying chamber (8). The dryer is a cylindrical vessel 7 m. in diameter and comprises 20 super-imposed stages 20 cm. apart. The catalyst is swept round each stage by rotating arms and falls down the vessel from stage to stage during a period of $1\frac{1}{2}$-2 hours. Drying is effected by steam heat and an air blast.

From the final stage of the dryer the rough granules containing 10% moisture are carried by a conveyor to the vibrating screens (9) and separated into over 3 mm., 1-3 mm. (the desired size), fines, and a dust which is sucked away in an air current. The air stream is filtered through a cloth filter (10) and then scrubbed with water and steam (11). The fine catalyst recovered from the scrubber is not returned to the masher for inclusion in the final catalyst because oxidation tends to convert carbonate to oxide which renders reduction more difficult and because dirt and dust are apt to become concentrated in this fraction. This material, which only represents 0.1 0.2% of the whole, is therefore sent to the catalyst regeneration plant and treated as spent catalyst.

The fines from the screens and cloth filters are returned to the masher.

The particles above 3 mm. pass to a further set of screens (12) where rotating arms force the granules through the 3 mm. screen. The dust and fines from this process are returned to the masher and the 1-3 mm. grade is blended with the stream from the original screens (9) and is bagged for transport to the adjacent reduction plant via a telfer conveyor.

The bulk density of the granules is 320-350 gm./l. The maximum daily output of the plant is equivalent to 4 tonnes of cobalt.

The flow-scheme for catalyst reduction is shown in Fig. 6, which is based on a diagram prepared by Dr. Herbke. The reduction vessel comprises a central compartment of square cross-section containing the catalyst in a bed 30-35 cm. deep and 2.1 m^2 in area, with top and bottom fittings in the form of truncated pyramids. A sheet-iron grille (15 cm. cubes) is placed on top of the catalyst bed and sinks into it to a depth of about 10 cm. This device serves to break up the gas stream entering the top of the reduction vessel. One charge of catalyst weighs 200-250 kg. and occupies 800 l. There are 6 of these reduction vessels. (See Fig. 7)

The reduction is effected by passing downwards through the catalyst a rapid stream of ammonia synthesis gas (75% H_2 + 25% N_2) which is preheated to 460°C. in a tubular heater fired with coke-oven gas. The effluent gas is re-heated to 300°C. and the CO_2 present (ca. 2 gm./m^3) is converted to methane by passage through a bed of synthesis catalyst in another reduction vessel. The gas is then cooled, dried by refrigeration and passage through silica gel and is returned to the preheater for the reduction where it meets fresh make-up gas.

The recycle and fresh gas enter the reducer at about 7000 m^3/hr. (S.V. 8800). The period of reduction varies from 40 to 60 minutes, depending on the exact gas velocity which varies according to the number of reduction vessels in use. The temperature is varied according to the time and gas velocity as shown below :

Time	Temperature at inlet to reducer	Gas Velocity
40 mins.	435°C	8000 m^3/hr.
60 mins.	428°C	6000 m^3/hr.

The temperature is controlled to within ± 2°C. After reduction is complete the catalyst is cooled to room temperature in a stream of nitrogen, the nitrogen then displaced by CO_2 and the contents of the reduction vessel discharged into a kübel by removing the top cover plate and inverting the vessel. The vessels were so balanced that this inversion could be accomplished by a hand-operated mechanism.

A total of 16 reduction charges are required to fill one kübel.

In the reduction process 50-60% of the cobalt is reduced to metal. If over 60% is so reduced a less suitable catalyst results. The extent of the reduction is determined by measuring the volume of hydrogen evolved when the reduced catalyst is treated with acid.

The exact reduction conditions were said to depend on the nature of the kieselguhr used in the catalyst preparation. Dense catalysts caused difficulties in the reduction.

Regeneration of Spent Cobalt Catalysts

This subject was not discussed in detail but Dr. Blöchel prepared a diagrammatic flow sheet (Fig. 8) for the recovery of cobalt and thorium. The regeneration plant had been almost entirely destroyed by bombing.

The Preparation of Other Catalysts

Nickel catalyst for the methanisation of coke-oven gas, chromium-aluminium catalysts for dehydrocyclisation of heptane, water-gas shift catalyst and Feinreinigungsmasse were also prepared in the catalyst factory, but as these did not come under Blöchel's control no further information was obtained.

Plant similar in general design to the cobalt catalyst plant was being erected for large-scale manufacture of iron catalysts. So far these catalysts had only been prepared on pilot-plant scale.

The iron catalyst preparation was carried out directly under Dr. Gehrke's supervision but Blöchel understood that the catalyst which was to have been prepared on a large scale had the composition :-

100 Fe : 2.5 Cu : 10 CaO : 15 kieselguhr

The precipitation was carried out with KOH and the nitrates under conditions generally similar to those used for cobalt. Blöchel believed that the precise details of the precipitation were most important but he was not acquainted with them. He understood that the best reduction conditions were not fully established, but believed that H_2 was used at 300°C. under conditions generally similar to those used for cobalt.

Samples

Small samples (2-5 lb.) of tested and approved unreduced and reduced cobalt catalyst and kieselguhr were obtained ~~(under Blöchel's guidance)~~ from the sample room. A bulk sample (28 lb.) of kieselguhr was taken from the store adjacent to the feed hopper on the top floor of the cobalt-catalyst plant.

Samples of reduced and unreduced iron catalyst were removed from Dr. Gehrke's laboratory.

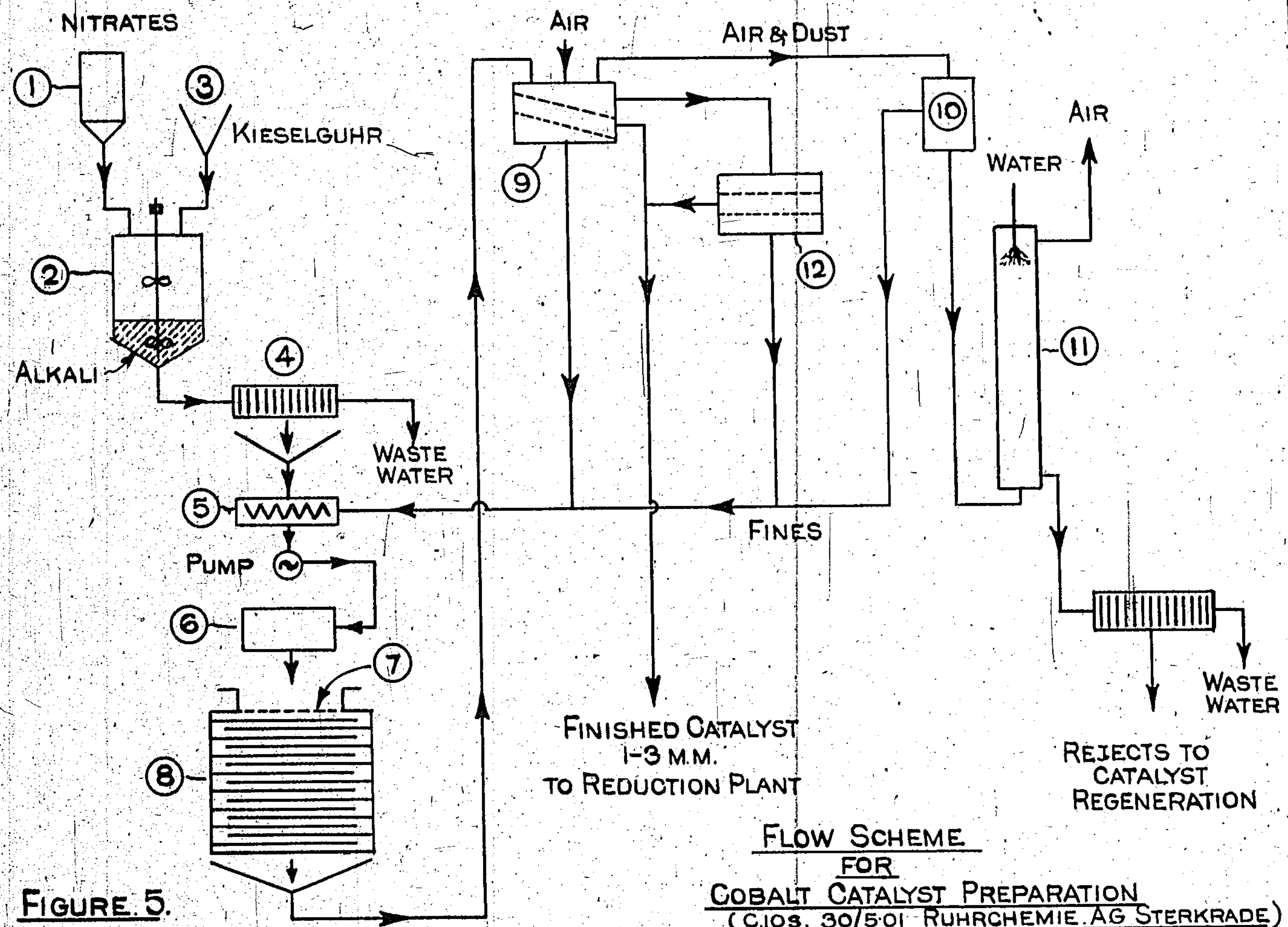


FIGURE. 5.

FLOW SCHEME
FOR
COBALT CATALYST PREPARATION
(C.I.O.S. 30/5.01 RUHRCHEMIE. AG STERKRADE)

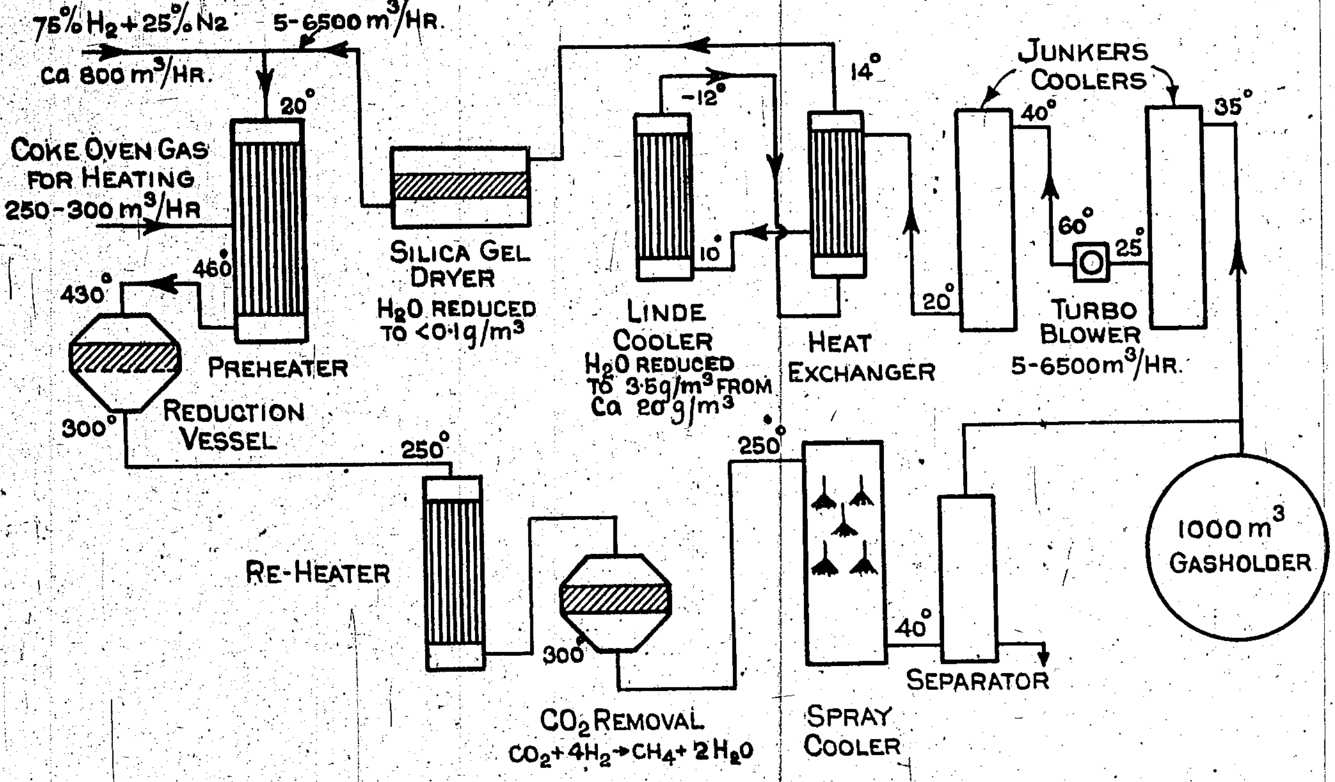


FIGURE 6. FLOW-SCHEME FOR COBALT CATALYST REDUCTION
(C.I.O.S. 30/5·01 RUHRCHEMIE A.G. STERKRADE)

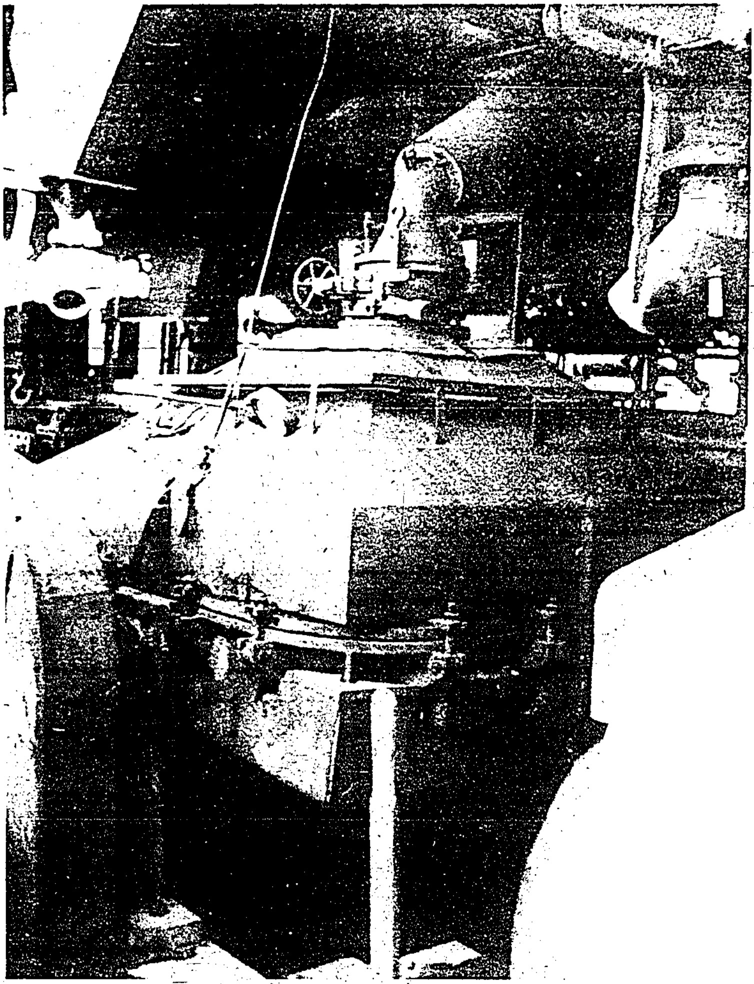


Fig. 7. Catalyst reduction vessel.
(30/5.01, Ruhrchemie A.G., Sterkrade-Holten)

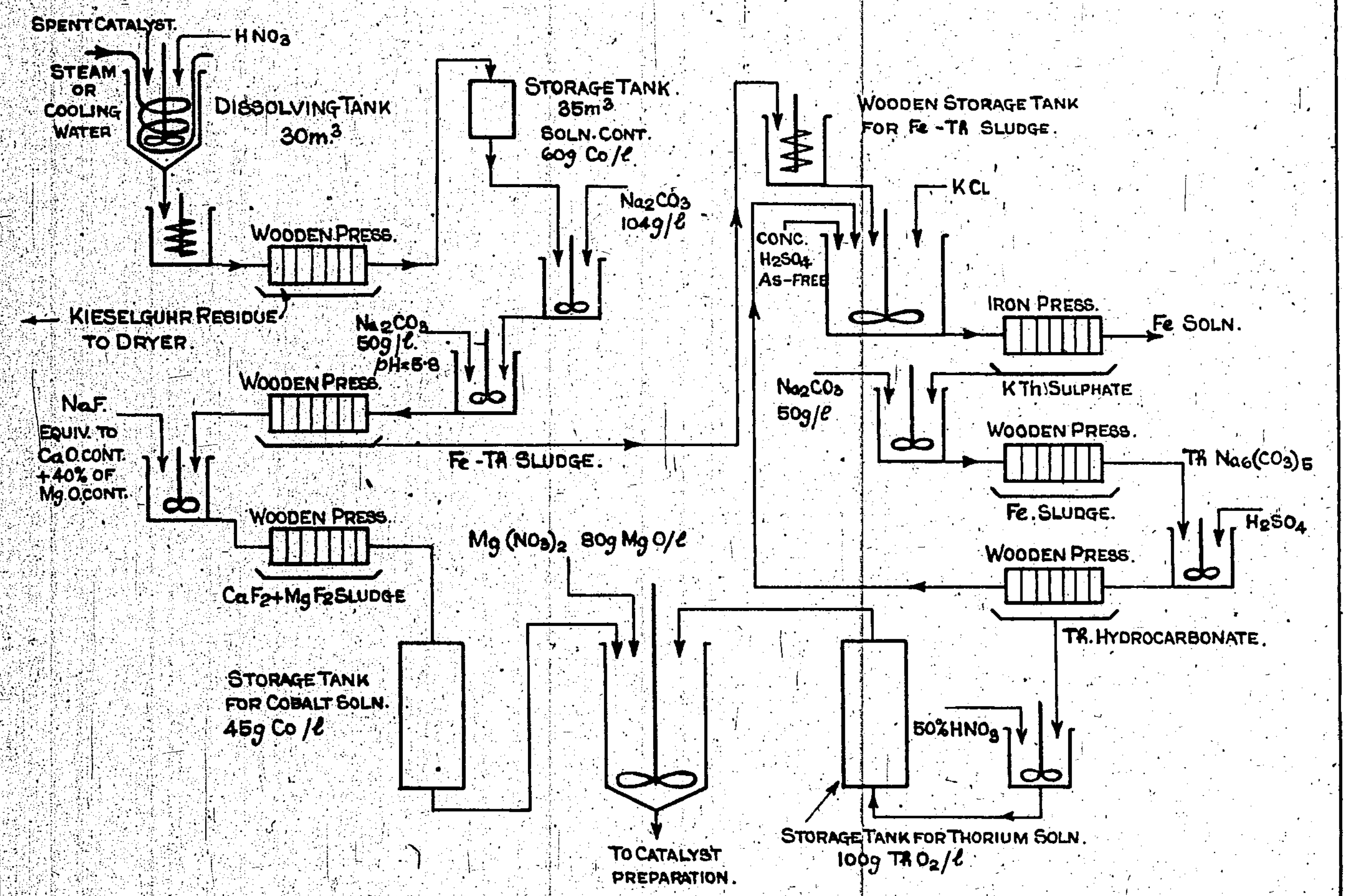


FIG.8. FLOW SCHEME FOR RECOVERY OF COBALT AND THORIUM.

C.I.O.S. 30/5·01 RUHRCHEMIE A.G. STERKRADE.

Report 4. Investigation of the OXO Process

Date of Investigation : April 7, 1945

Investigator: Dr. E.B. Peck, U.S., Petroleum
Administration for War

Personnel Interrogated : Dr. Landgraff, Manager of the
OXO Plant.

Reported by : Dr. E.B. Peck.

Introduction.

A joint company known as the OXO Gesellschaft had been formed by Ruhrchemie A.G., I.G. Farbenindustrie A.G. and Henkel et Cie to manufacture C_{12} to C_{18} alcohols by a process based on the reaction between aliphatic ~~olefines and carbon monoxide and hydrogen. The object of~~ the project was the production of detergents by sulphonation of the alcohols.

The basic reaction was discovered in the Ruhrchemie research laboratories under Dr. Roelen. In view of the great experience of I.G. in large-scale operations at high pressure they were brought in to assist with the commercial development of the process, and the Henkel concern were to carry out the preparation of the detergents. The latter were said to be very efficient but there appeared to be some doubt about their physiological properties as they were reported to have a strong de-fatting action on the skin.

The company had built a plant with a nominal annual capacity of 8-10,000 tonnes of alcohols on the Ruhrchemie site at Sterkrade-Holten, but apart from a few test runs on parts of the equipment, the plant had not been operated. The main part of the plant had almost completely escaped bomb damage. (See Figs. 9 & 10)

The information given in this report is based partly on material supplied by Dr. Landgraff and partly on the results of a preliminary examination of documents found at Sterkrade.

THE OXO REACTION

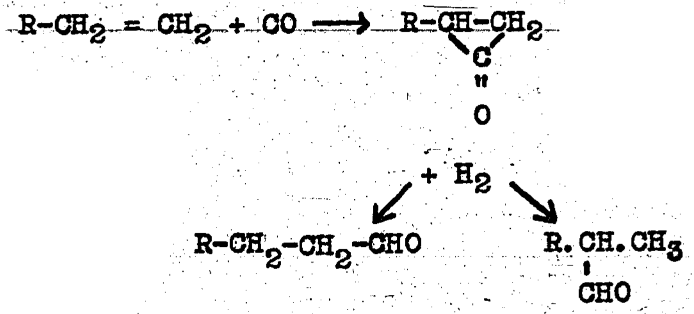
The main reaction is the addition of synthesis gas ($CO + H_2$) to olefines to form aldehydes.

$$R-CH=CH_2 + CO + H_2 \longrightarrow R-CH_2CH_2CHO$$

This reaction takes place at 100-200°C. and 100-200 ats. pressure in the liquid phase with the Fischer-Tropsch catalyst ($Co-ThO_2-MgO$-Kieselguhr). The aldehyde is then hydrogenated at 180°C. and 100-200 ats. with pure hydrogen and the same catalyst.

This reaction produces a variety of isomeric primary alcohols and 5-15% of heavy products consisting of ketones, condensed aldehydes, secondary alcohols and hydrocarbons.

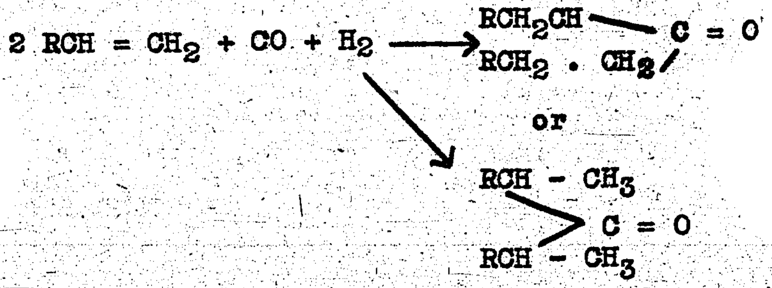
The main reaction produces two isomeric aldehydes in about equal amounts. This is explained by the addition of CO to the olefine to form the unstable cyclopropanone linkage which is then hydrogenated to the aldehydes as follows :



$$R-CH_2=CH_2 + CO \longrightarrow R-\underset{\underset{O}{\overset{\|}{C}}}{CH-CH_2} \xrightarrow{+H_2} R-CH_2-CH_2-CHO \ \text{or}\ R.\underset{CHO}{CH}.CH_3$$

Other isomers are formed due to displacement of the olefine linkage toward the middle of the molecule.

Other side reactions take place as follows (1) the condensation of aldehydes and (2) the reaction between two olefines and CO to form ketones :-



$$2\,RCH=CH_2 + CO + H_2 \longrightarrow \begin{matrix} RCH_2CH \\ RCH_2 \cdot CH_2 \end{matrix} \!\!> C=O \quad \text{or} \quad \begin{matrix} RCH-CH_3 \\ RCH-CH_3 \end{matrix} \!\!> C=O$$

Under proper reaction conditions these side reactions can be held down to 5-15% of the olefines reacted. These conditions appear to be 130-140°C and 150 ats. for the $C_{11}-C_{17}$ monoolefines.

The OXO reaction is quite general and a wide variety of olefines and other compounds have been tested including the following :-

Ethylene (to produce propionic acid or, n-propyl alcohol)
Acetylene (to produce acrylic acid)
Propylene (see below)
α-Butene
N-α-Octylene
Diisobutylene
Decylene
Cetene
Mixed polymers
Cyclohexene
Octadiene
Styrene
Butadiene
~~Olefinic lubricating Oil~~
Oleic alcohol
Linseed Oil
Terpenes
Rubber
And certain other compounds including -
Vinyl ether
Acrylic acid ethylester
Tetrahydrofuran (cyclobutylene oxide)

OXO REACTION WITH PROPYLENE

The reaction is not clean cut as shown by the reaction products produced from propylene :

Input

I.	Propylene	2,500 gms.
	Catalyst R.B.V.[1] (Fischer Catalyst 30% Cobalt)	100 "
	Reaction conditions 1st stage 110°C. 120 ats. ($CO + H_2$)	
OXO Product yield		2,560 liters
	Theoretical yield as aldehyde	2,688 liters

II. Hydrogenation with same catalyst at
180°C. and 200 ats. H_2

Hydrogen absorbed	917 liters
Theory	1,344 liters
Hydro product	3,946 gms.
Theoretical yield	4,400 gms.

The product corresponds in weight to 89.7% absorbtion or 1 mol CO + 2 Mols H_2 per mol of C_3H_6.

PRODUCT INSPECTION

(a) Distillation

Fraction	Pressure mm	Temperature °C	Gms.
1	760	90-103	270
2	"	103-120	1472
3	25	55-90	175
4	"	90-107	295
5	"	107-120	75
6	"	120-140	554
7	"	140-150	438
8	"	150-160	48
9	"	160-200	92
10	"	200-218	125
11	"	218-226	65
			3,609

The first fraction was a butanol-water mixture with 30% H_2O. The second fraction was a mixture of butyl alcohols (isopropylcarbinol, B.P. 108° and n-butanol, B.P. 116°C.) The fourth fraction was composed mostly of secondary alcohol, dipropylcarbinol and the fifth fraction contained alpha ethyl-hexanol ($C_8H_{18}O$). This last is explained by earlier researches of J.V. Braun by the reaction of two molecules of butyraldehyde in the presence of finely divided metals in the presence of hydrogen.

The sixth and seventh fractions contained the butyric acid monoester of ethylhexenediols which is explained by the Cannizarro reaction. The components of the higher fractions were not easily identified but are believed to be condensation products of normal and isobutyraldehydes.

The yield of butanol was 38% based on propylene with 12% of C_7 - C_8 alcohols and 23% as ethylhexandiolmonobutyrate. It is pointed out that better yields of undivided alcohols might be expected with a better choice of reaction conditions. This is in fact achieved in the reaction with C_{11} - C_{17} olefines where some 85% yield of corresponding alcohols are claimed for pilot plant operation. The alcohols in this case are branched and of various structures, though all primary alcohols.

The I.G. have developed the basic reaction with a variety of new catalysts, particularly with nickel carbonyl or the nickel halides. ($Ni\ Cl_2$ activated with iodine). This is the subject of a separate report. (Reppe Chemistry). The I.G. have also developed their hydrocarbon syntheses to make a product directly from synthesis gas ($CO + H_2$) which is about half primary alcohols and half hydrocarbons. This is separately reported in the report on the Leuna plant (30/4.02) under the title "Synol Process".

THE OXO PROCESS

The OXO Process has been directed primarily to the production of C_{12} - C_{18} primary alcohols from C_{11} - C_{17} acyclic olefines. These olefines are derived in 30 - 50% concentration either from the 180 - 320°C cut of the Fischer-Tropsch product or from cracking heavier fractions (gatsch). The olefines from cracking petroleum may also be used but it appears to be preferable to separate these olefines by solvent extraction. A pilot plant was sent to the Bombini Company in Italy for the production of alcohols or acids from ethylene but no information on this work is available.

The process is carried out with narrow fractions of olefines in order to simplify the separation of the resulting alcohols from unreacted fractions and byproducts. The Henkel Company requires alcohols of 97-98% purity for sulphonation to detergents.

For the production of detergent alcohols the 180-320°C fraction is cut in four fractions by atmospheric and vacuum distillation as follows :

Cut	Boiling Points at 760 mm of Hg.	At / mm of Hg
C_{11} - C_{12}	180-220	70-110/20
C_{13} - C_{14}	225-260	100-140/20
C_{15} - C_{16}	260-295	100-140/5
C_{17}	295-310	140-160/5

Steam at 80 ats. pressure is used for heating and the last two cuts are separated by batch vacuum distillation. Each cut is reacted separately.

The main reaction is carried out in the liquid phase with finely suspended Fischer-Tropsch catalyst (30% Co) at 130-140°C. and 150 atmospheres under which ~~conditions the reaction is completed in 20-30 minutes.~~ Some of the cobalt is converted to the carbonyl ($Co(CO)_4$), and this is reduced to metal in the next stage where the aldehydes are hydrogenated to primary alcohols with the same catalyst at 180°C. and 150 ats. with pure hydrogen. It appears that the carbonyl and CO brought over to the hydrogenation stage poisons the hydrogenation reaction and the CO must be removed by conversion to methane with iron catalyst in the cycle gas.

The catalyst and reduced cobalt are separated from the product by filtration under mild pressure thru ceramic thimbles.

The alcohols are then separated with 98% purity from unreacted oil and heavy oil byproducts by distillation. The distillation is carried out in vacuum stills with packed columns heated by steam at 8 ats. to prevent decomposition.

The OXO plant at Holten was built for batch operation but the I.G. at Leuna have developed a continuous process that appears to be a great improvement. (See Report on 30/4.02).

The batch plant consists of nine reactor units, each with two reactors of 1.2 cubic meters volume, one for the reaction of olefines with synthesis gas and one for hydrogenation of the aldehydes to alcohols. These reactors are 570 mm. o.d.; 400 mm i.d. and 12 meters high and contain a bundle of cooling tubes connected to a steam chest and a leg for thermosyphon circulation of cooling water. (See Fig. 11) The reaction heat is substantial, (35 Kcal. per gm. mol of olefine reacted) and there are 31 tubes 38 mm. o.d. x 8 meters with a cooling surface of about 30 square meters for removing this heat. The temperature of reaction is controlled by the pressure on the steam and the rate of circulating the synthesis gas. The reactor is charged with 700-720 liters of liquid feed containing 3-5% (15 Kgs.) of finely ground Fischer catalyst. The concentration of olefines in the feed is not critical but this plant is designed for handling a feed with 40-50% olefines. The feed is heated to 130°C. and the synthesis gas recycled thru the reactor with a compressor having a capacity of 200 N M^3/hour (1.3 cu.m. of gas at 150 ats.).

The OXO reaction is completed in 20-30 minutes when the liquid feed with suspended catalyst is pumped into the hydro-reactor where the aldehydes are hydrogenated at 180° and 150 ats. with pure hydrogen. As noted above, it is believed to be necessary to remove the carbon monoxide that comes over to the hydrogenation stage by converting it to methane over an iron catalyst in a converter in the recycle hydrogen line. This reduces the CO from 2.0 to 0.05%.

The product is filtered under moderate pressure thru a battery of ceramic thimbles (manufactured by Meisner Filterwerk, Dresden). The filters are washed with fresh oil feed which is fed with recovered catalyst and make up to the process. These filters are reported to be good for 5000 filtrations before replacement.

The filtered product is then distilled under vacuum to separate (1) alcohols in 98% purity, (2) unreacted oil and (3) thick oil bottoms which amount to 15% on alcohols and consists of a mixture of aldehydes, ketones, esters, and hydrocarbons.

The over all yield of alcohols is probably around 65-70% but firm information is not available for lack of full-scale operating data. There are undoubtedly losses of alcohol in the unreacted oil fraction aside from reaction losses. There are references to work on alcohol recovery by solvent extraction with methanol, etc., and the I.G. (Leuna) have a recovery process for the Synol Process based on esterification with anhydrous boric acid. (See Synol Process, 30/4.02).

The continuous process developed by I.G. is shown schematically in Fig. 12 and consists of two reactors in series with synthesis gas recycle, seperator and scrubbing tower for the gas that is bled off. The first reactor is identical with that used in the batch process (with inner coolers) while the second reactor of the same size does not require coolers but has 'disc and doughnut' baffles. The hydrogenation section is the same except for a converter in the gas recycle line for converting CO to methane. This is claimed to reduce the CO from 2.0 to 0.5%, and is essential for avoiding poisoning of the catalyst for hydrogenation. No release gas scrubber is required. The release gas in the first stage uses fresh feed for scrubbing which is then fed to the processes without stripping.

The continuous process was worked out at Leuna in a water-jacketed reactor of 250 liters capacity and divided into concentric sections. In this reactor the oil is fed upflow into the outer ring and down flow thru the inner section. The gas flows upward thru both sections in separate streams. The inner section is baffled. From the results in this pilot plant it is estimated that the thruput for 95% reaction would be 3 v./v./hr. which is 9-10 times as much as for the batch equipment. (See 30/4.02).

ECONOMICS

The economics of the process as calculated by Ruhrchemie is shown below and indicates a cost of alcohols of 71 pfg./kg. I.G. corrected this estimate as shown to 77 pfg./kg. These costs are based on an olefine cost of 38 pfg./kg. and a capital cost of 6 million RM. There is now 11 million RM. invested in this plant by OXO Gesellschaft. The I.G., on the other hand, estimated a cost of 60 pfg./kg. for the continuous process. Within the above limits the cost of these alcohols lies between 60 and 100 pfg./kg. which, with exchange at 5.2 RM. per dollar, would be 5 to 9 cents per pound.

Estimated Cost of Primary Fatty Alcohols by the OXO Process

	Ruhrchemie pfg./kg.	I.G. Corrections
100 Kg. Olefines (for 95% yield)	38.00	--
Gases: (CO/H_2 & H_2)	1.30	--
Catalyst	0.60	--

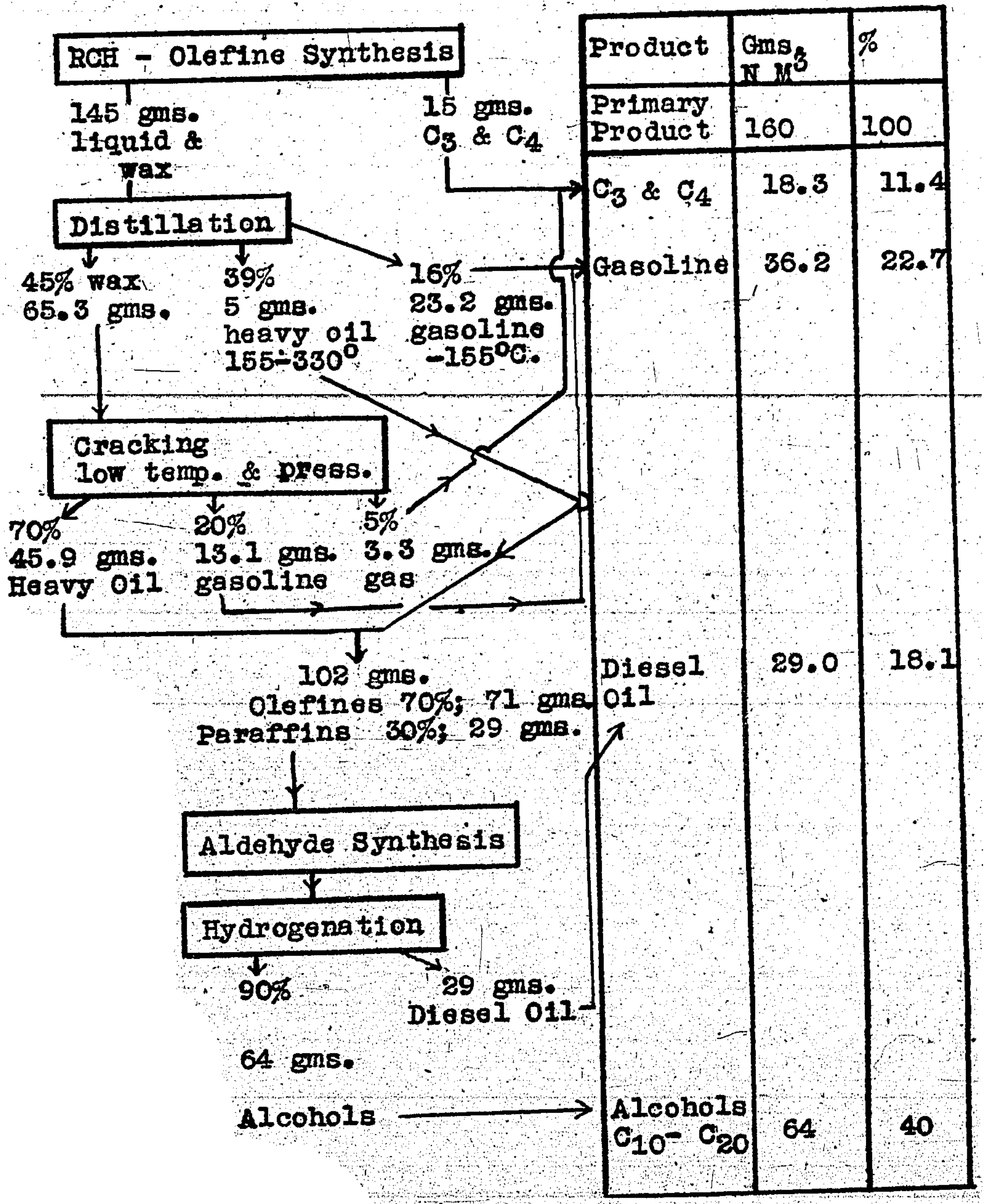
	Ruhrchemie pfg./kg.	I.G. Corrections
Distillation (Feed & Product)	6.00	10.00
Water	1.50	3.00
Power for compression, etc.	2.30	--
Charges	1.60	--
Wages & Salaries	4.80	--
Amortization & Interest 15% on RMG million	15.00	
	71.10	76.60

The overall picture of OXO alcohol production from synthesis gas is presented by Ruhrchemie in the following schematic diagram. This shows the Fischer conversion with the iron catalyst developed by Michael of I.G. and shows an overall production per N M^3 of synthesis gas ($CO/H_2 = 1/1.2$) of hydrocarbon products, 84 gms. and $C_{10} - C_{20}$ alcohols, 64 gms. The 155-330° fraction of oil with 70% olefines is processed as is also the olefines from cracking the heavier oils (gatsch). A special low temperature and pressure cracking procedure has been worked out with U.O.P. for the production of maximum olefines in the $C_{10} - C_{20}$ range.

SCHEME FOR FISCHER PROCESS WITH OXO

Using Iron Catalyst at 20 ats.
280-300°C. in M^3 Synthesis gas.

(Prepared by Ruhrchemie 7 Feb. 1940)



Product	Gms. $N M^3$	%
Primary Product	160	100
C_3 & C_4	18.3	11.4
Gasoline	36.2	22.7
Diesel Oil	29.0	18.1
Alcohols C_{10}- C_{20}	64	40

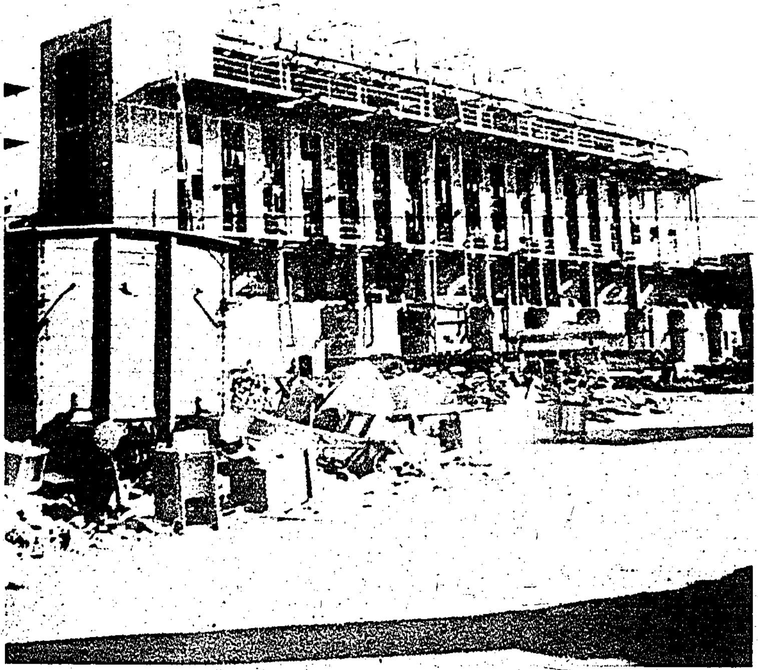


Fig.9. The OXO plant reactor building.
(30/5.01, Ruhrchemie A.G., Sterkrade-Holten)

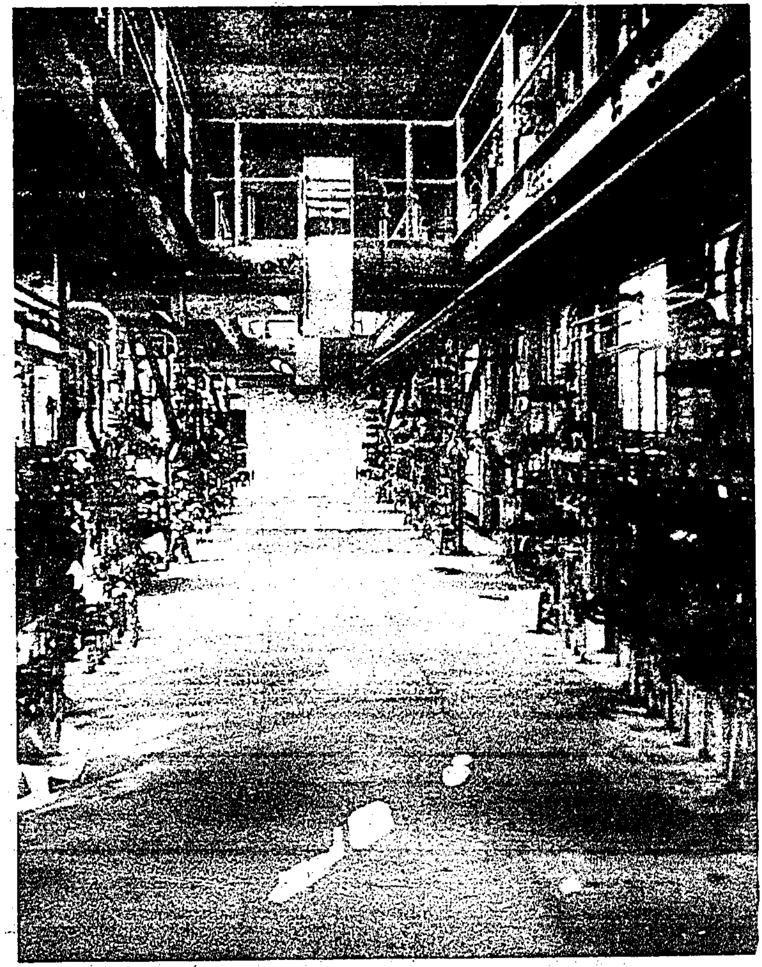


Fig.10. The control platform in the OXO reactor building.
(30/5.01, Ruhrchemie A.G., Sterkrade-Holten)

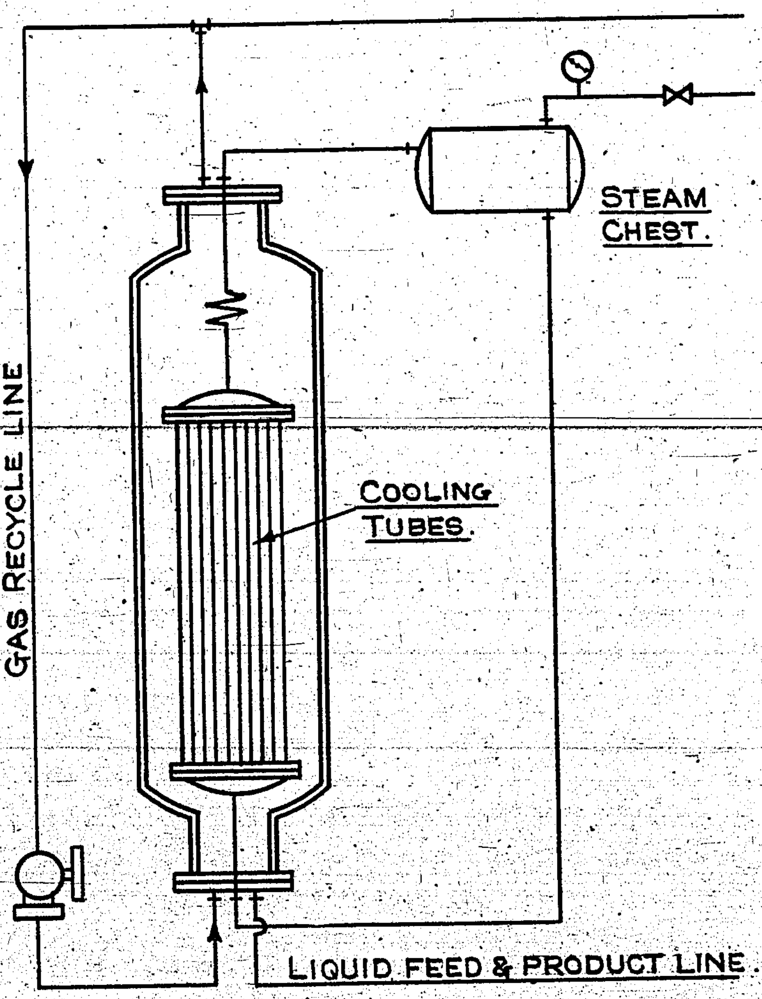


FIG. 11. OXO REACTOR UNIT.

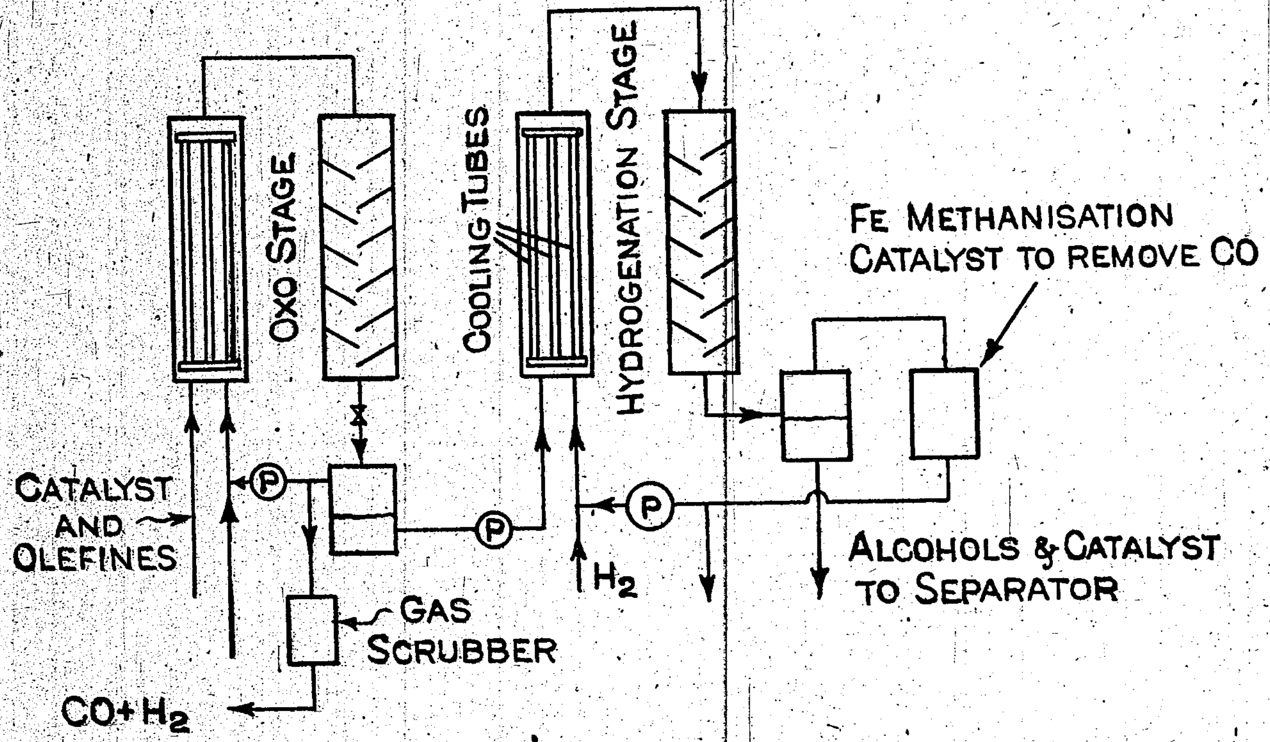


FIG. 12 FLOW SCHEME FOR I.G. CONTINUOUS OXO PROCESS

Report 5. Interrogation of Director Alberts.

Date of Interrogation : April 13, 1945

Location : Herr Alberts' house, "An der Muhle",
Waltrop, nr. Castrop-Rauxel.

Personnel conducting Interrogation :

Dr. V. Haensel, U.S., Petroleum Administration for War.
Capt. C.C. Hall, British, Ministry of Fuel and Power

Reported by : Capt. C.C. Hall.

Object of Interrogation

Herr Alberts' present position is that of ~~Director of the Castrop-Rauxel plant (Target 30/5.03),~~ but up to late in 1943, he had been manager at Sterkrade-Holten, and the object of the interrogation was to obtain information concerning this latter plant and the work of Ruhrchemie.

The Synthesis Cycle at Sterkrade. According to Herr Alberts, the system employed by Ruhrbenzin during recent years is as outlined in the flow scheme Fig. 13. It comprises two independent systems, one operating in two stages at normal pressure and using $H_2 : CO = 2 : 1$ as raw material and the other operating in three stages at 11 atmospheres pressure, the $H_2 : CO$ ratio of the inlet gas to the three stages being adjusted to 1.4 : 1, 1.6 : 1 and 1.8 : 1 respectively, by introducing the requisite amount of "converted" water-gas before each stage.

For Stage 1 on the medium-pressure side the inlet gas rate is 1000 m^3/oven/hour, the temperature 180-200°C. and the gas contraction, 50%. Similar conditions obtain for Stage 2. In Stage 3, where all newly-charged ovens are started, higher rates (2,000 m^3/oven/hour) and lower temperatures (165-185°C.) can be employed. The overall contraction is about 75% and the yield, 150 gm. C_3 and higher hydrocarbons/m^3 ideal gas.

The history of a freshly-charged oven was as follows. It is started in Stage 3 and run for 10-14 days. It is then put on Stage 2 where it may remain for the rest of the catalyst's life or it may be transferred after a period to Stage 1. Alternatively it may go direct from Stage 3 to Stage 1. The precise history depends on the demands of Stages 1 and 2 for new ovens but the charge of catalyst always remains on stream for approximately the same total time i.e. 9 to 11 months, depending on smoothness of operation, lack of interruptions etc. No solvent-extractions or other reactivation treatments are carried out in the medium pressure section.

The advantage of the scheme of commencing with a gas relatively deficient in hydrogen and then increasing the proportion of hydrogen in later stages lies in combining the beneficial effects of low hydrogen proportion on olefine content and methane production with the efficient utilisation of the carbon monoxide achieved with normal synthesis gas (H_2 : CO = 2:1).

Using normal synthesis gas throughout, 14% of the total hydrocarbons produced is methane but with the above scheme the proportion is reduced to 10%.

The products produced by this method of working are as follows :-

$C_3 + C_4$	: 10%	(Olefines 40%) (13% of C_4H_8 is iso)
C_5-170°C.	: 25%	(" 24%) O.N. (Motor) ca. 45.
170 - 280°C.	: 30%	(" 9%)
280 - 340°C.	: 20%	Soft Wax
Residue*	: 15%	Hard Wax M.P. ca. 90°C.

(*This includes 3% of wax extracted from the catalyst at the end of its life.)

It would appear that the total annual output of primary products from the whole system was of the order of 70,000 tonnes.

<u>The Water-Gas Recycle Project</u>. One of the reasons why it was found difficult, from an inspection of the contact oven house and the adjacent plant, to determine the nature of the cycle employed was that although the scheme outlined above was actually being used, most of the plant and pipe connections necessary for an entirely different scheme had been installed. This scheme involved the use of all the medium-pressure ovens in one stage with water-gas as the feed material and a 3:1 recycle gas-fresh gas ratio, the unrecycled residual gas being passed to a

normal 2-stage atmospheric-pressure section after adjustment of the H_2:CO ratio to 2:1 in a CO-conversion unit. The system is illustrated by the flow diagram, Fig. 14. It had only been tried out on an experimental scale, the full-scale trials having been held up due to difficulties in obtaining certain items of equipment such as heat exchangers and expansion joints. As stated above, most of the equipment was already installed, and a series of towers found at Sterkrade were identified by Alberts as the system of heat exchangers, direct condensers and charcoal absorbers for the recycle gas stream.

The object of this method of working was the production of olefines by maintaining a high concentration of CO in the gas mixture. If this is attempted by, for example, using an undiluted synthesis gas of composition $2CO + H_2$ there is a tendency to get carbon deposition. Alberts stated that the use of water gas with recycling was the best method of achieving the desirable effects of high CO concentration while avoiding carbon deposition. The principle of the process was illustrated by Alberts as follows :-

	Parts H_2	Parts CO
Fresh water gas	1.25	1.00
Consumed in reaction ..	1.00	0.50
Residual gas	0.25	0.5
3 volumes recycle gas .	0.75	1.5
1 " fresh water gas	1.25	1.0
Total	2.0	2.5

i.e. total inlet gas has the inverse H_2 : CO ratio to that of water gas.

The reaction temperature for the process was higher than usual viz. 220-225°C. The gas contraction in the process was 50% and the yield 100-110 gm. C_3 and higher hydrocarbons/m^3 ideal gas. In the pilot plant experiments a catalyst life of 6-7 months had been obtained. The products were as follows :-

$C_3 + C_4$ = 8% (olefines 60-65%)
Benzin $C_5 - C_{10}$ = 30% (" 60 ")
Middle oil $C_{10} - C_{17/18}$ = 28% (" 40 ")
Wax $> C_{18}$ = 34% (" small %)

The gasol fraction formed an excellent raw material for polymer gasoline production. The benzin had an octane of 50-55 but this could be increased to 70 by an isomerisation process involving no gas formation or change in boiling range and olefine content. It consisted of treatment at atmospheric pressure and 300°C. in the vapour phase over Floridin activated by treatment with HCl. The space velocity and clay life were the same as for normal clay refining. Alternatively the benzin could be polymerised with aluminium chloride to give a lubricating oil of viscosity-pole-height 1.7.

The unsaturated middle oil would have formed the main raw material for the OXO plant. The paraffinic residue, after the latter process had removed the olefines, would be sold as diesel oil.

Alberts considered that this recycle process was the best method of conducting the synthesis with a cobalt catalyst.

Composition of Cobalt Catalysts

Alberts stated that in his view the most important effect of replacing thoria with magnesia was the increased hardness of the resulting catalyst and consequent reduction of dust formation in the ovens which causes bad gas distribution leading to "hot spots". Other advantages were ease of initiating synthesis, less tendency to form methane and carbon and increased life. It was only since magnesia-containing catalysts had come into use that lives up to 8 months had been achieved at normal pressure.

Alberts stressed very strongly the necessity for trials on the full-scale as early as possible in the development of new catalysts. On the laboratory scale, comparatively small differences were detected between ThO_2, MgO, and ThO_2 + MgO promoted catalysts. In the full-scale ovens, however, very important differences appeared. He considered that Co-MgO-Ksgr. catalysts were best for large-scale operation. The most suitable catalyst for normal-pressure operation is also most suitable for medium-pressure operation.

Oven Charge. Originally the charge per N.P. oven was 1000 kg. Co but in the last few years the charge had been successively reduced to 900, 850 and 820 kg. without reduction in the gas throughput or yield. The oven charge used in the normal-pressure oven in the cycle shown in Fig. 13 was 820-850 kg.), and for the medium-pressure ovens about 10% less. Alberts stressed that the maximum gas rate which could safely be employed in Stage 1 was 1000 m^3/oven/hour.

Iron Catalysts. There had been no full-scale trial of iron catalysts but a considerable number of tests on a 1/10th full scale (100 m^3/hr.). Ruhrchemie, Rheinpreussen, Ruhland and Lurgi had all developed iron catalysts and a trial of all four types had been staged at Ruhland on the 100 m^3/hr. scale. The results were inconclusive. Alberts claimed to have no information about the Kaiser Wilhelm Institute iron catalyst.

Concerning the work of RCH on iron catalysts, Alberts said that further progress had been made since the S.I.C.S. contract. At the time of this contract the development was in quite an early stage. There were difficulties in reproducing batches of catalyst and the trials had not reached the 100 m^3/hr. scale. The yields guaranteed to S.I.C.S. were calculated from small-scale single-stage results! It was anticipated that it would take 2 years to build the S.I.C.S. plant and that during this period RCH would be able to straighten-out all the difficulties.

When Alberts left Sterkrade in 1943, the proved life of the iron catalyst was only 3 months. On this basis, in a period of 1½ years the cost of replacement would be greater than that of cobalt. He believed that the RCH catalyst contained copper but no alkali and was prepared by precipitation from the nitrates on to kieselguhr. The catalyst was designed to give a balance between CO_2 and H_2O as oxygen end-products. The temperatures and pressures employed in the synthesis control the proportion of organic oxygen compounds formed. Alberts believes that iron is the catalyst of the future.

Alberts was then questioned on a number of miscellaneous topics :-

The Fischer Iso-Synthesis. He believed that it operates at temperatures in the region of 400°C. and pressures of the order of 150 atmospheres with catalysts other than Ni, CO or Fe. He doubted whether it had any practical value; it was probably cheaper to use catalytic cracking.

Nickel synthesis catalysts were of no value; they produced excessive methane.

I.G. Developments. I.G. were supposed to have three lines of development :-

1. Use of sintered iron catalysts in a fixed bed.
2. Use of other types of iron catalysts in the liquid phase.
3. Use of iron catalysts with a high rate of recirculation.

All three processes gave low yields and gave rise to complex mixtures of hydrocarbons and oxygen compounds which were only of value as fuel. The octane number of the benzin produced was in the region of 70. So far as he knew none of the processes had been applied on the large scale.

New Types of Synthesis Ovens. Alberts did not believe that cobalt catalysts could be operated successfully other than in the conventional German type of oven. Iron catalysts might possibly be employed in other types of apparatus. Their own experience with liquid-phase operation, which had been tried out several times at different plants, was most discouraging.

The experimental oven at Sterkrade had been constructed for the S.I.C.S. project. It was not a success.

Cobalt-Silver Catalysts. These had not been tested outside the laboratory. The catalysts were soft and of short life.

Cobalt Catalyst Reduction. The optimum conditions were very difficult to establish. Generally speaking, the lower the reduction temperature, the better, but lower temperatures required longer times. A 10°C. difference in the temperature of reduction made an important difference in the activity and life of the catalyst in the oven - a difference visible during the first three days of operation.

The Slow Precipitation of Cobalt Catalysts was dismissed as a 'patent racket'.

Metallgesellschaft developments such as the use of diluted catalysts and of 'porous rods' in the catalyst space were dismissed as 'patent rackets'.

Reactivation of Cobalt Catalysts. Reactivation with solvent or hydrogen is never used in medium-pressure synthesis and only in the first stage of atmospheric-pressure synthesis. In the second stage it is unnecessary as little or no wax is formed. Originally hydrogen was used, for the first time after 4 weeks operation then at 14-day intervals. Then, to save hydrogen, solvent treatment was substituted, but this was not so effective as hydrogen treatment. Finally solvent treatment followed by hydrogen treatment was used and this was the most successful method of all. The time intervals used are the same as those given above.

The high-temperature re-reduction treatment was a Roelen invention. It has never been tried on the full-scale but Alberts is convinced it will work and was preparing to try it at Castrop-Rauxel just before the bombing started. The process consists in treating the oven contents at 400°C. for 3 hours in pure hydrogen at 2000 m^3/hour. The object of the treatment is the removal of persistent carbonaceous deposits.

Kieselguhr for Cobalt Catalyst Preparation. Iron and calcium should be as low as possible. Physical structure is of particular importance and there is a risk of ruining this by acid treatment. The only real test is to "try it and see".

Total Recycle of Products. This had been tried-out on the full scale, but was found to lead to lower conversions and an increase in saturated hydrocarbons.

Catalyst density. Use of dense catalysts (i.e. weighing more than 350 gm./litre) led to excessive reaction in the top layers of catalyst with formation of methane and carbon.

Synthesis of Lubricating Oils. The best oils were obtained by aluminium chloride polymerisation of cracked primary product. The normal procedure was to crack the total primary product after removal of benzin (e.p. 170°) in a Dubbs unit operated at as low a pressure as possible in order to ensure reaction in the vapour phase. The pressure was ca. 8-10 ats. and the temperature 480-500°C. The yields were as follows :-

Spirit to 180°C. : 70% (olefines 70-75%)
Gas : 30% ($C_3 + C_4$: 25%
C_2H_4 : 14%
C_2H_6 : 12%
Rest: H_2, CH_4, etc.)
Residue ca. 1%

The soft wax fraction alone forms a better cracking stock giving 80% yields of benzin to 180° containing 80% olefines.

The polymerisation is carried out in batches in vessels 3 m. in diameter and 6 m. high fitted with agitators and heating and cooling coils. The charge is 24-30 m³ stock + 1.5% $AlCl_3$. At the start the temperature is maintained at 40°C. and is subsequently raiced to 80° and finally to 100°C. The total reaction time is 6 hours. The sludge settles to the bottom and the upper layer still containing sludge in suspension is run into a settling tank. The sludge remaining in the polymeriser is used for the subsequent batch. After settling the clear upper layer is mixed with clay and zinc oxide and then passed through a filter press. The filtrate is topped at atmospheric pressure and then distilled in vacuum, 5 cuts being made. The viscosity pole height of the best cut is 1.85.

Using soft wax as cracking stock an oil of v.p.h. 1.6 can be prepared. In this case the olefines boiling up to 250°C. can be polymerised.

When using primary product (less benzin) as raw material, the over 180° portion can either be recycled or disposed of as diesel oil.

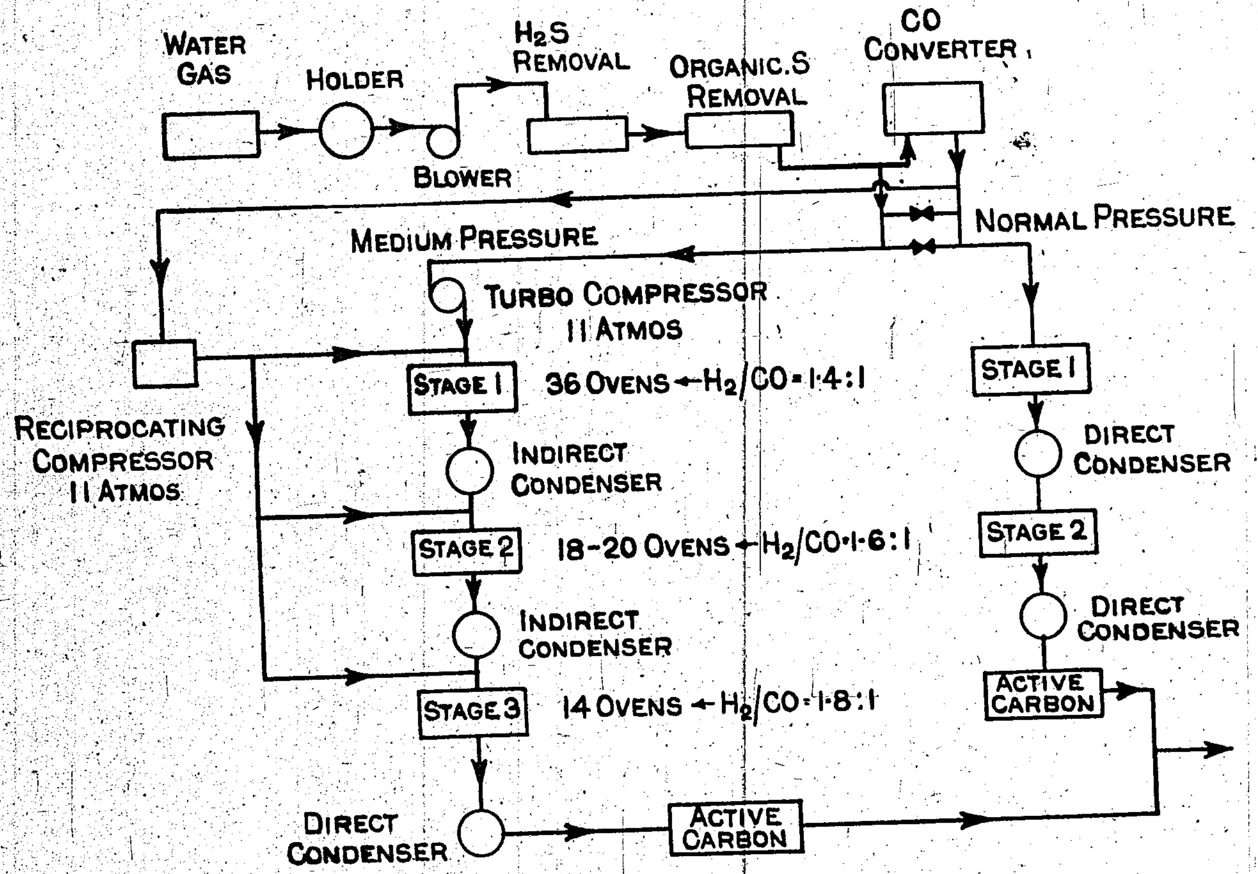


FIGURE 13. FLOW SCHEME FOR SYNTHESIS CYCLE USED AT STERKRADE
(C.I.OS. 30/5·01, 5·02, RUHRCHEMIE AG-RUHRBENZIN AG, STERKRADE.)

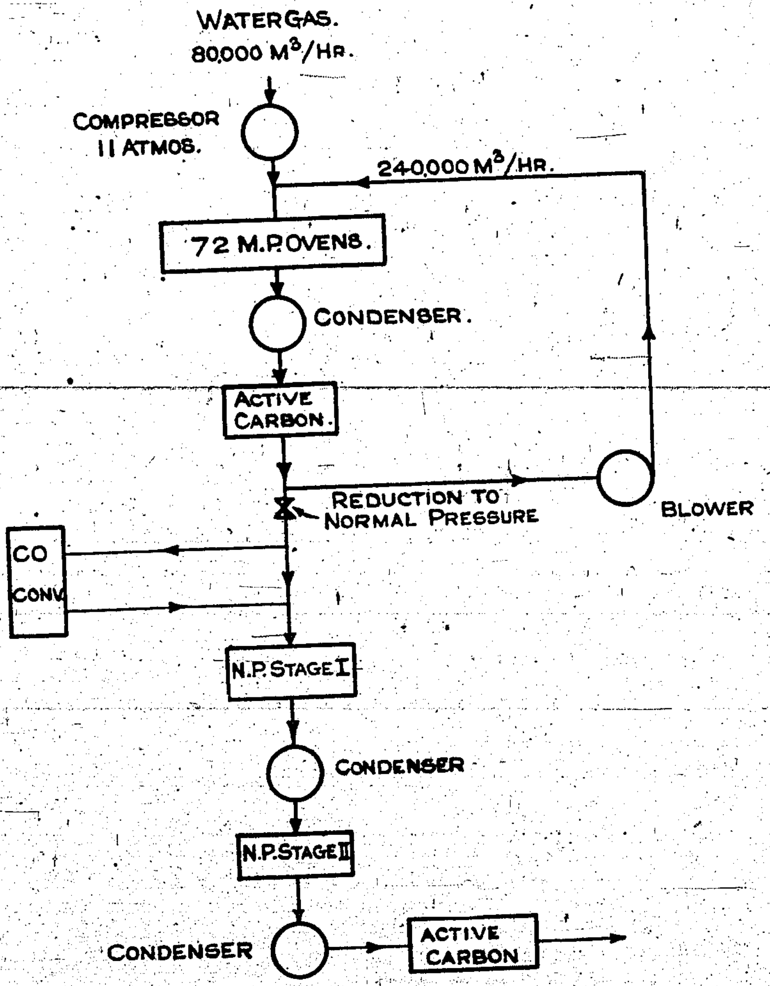


FIG. 14. FLOW SCHEME FOR RECYCLE PROJECT.
(C.I.O.S. 30/5-01, 5-02 RUHRCHEMIE A.G.
- RUHRBENZIN A.G. STERKRADE.)

Report 6. Interrogation of Prof. Dr. F. Martin.

Introduction.

Prof. Martin was President of the Vorstand (Directorate) of the Ruhrchemie A.G., the other members being Dr. Hagemann (chemist) Herr von Asboth (engineer) and Herr Waibel (financier).

Martin, therefore, headed the list of key men relating to the Target under investigation and his interrogation was of particular importance. He was located at a farm near Gebhartshagen in the Braunschweig area by 30 A.U., R.N. and, together with Dr. Hagemann, was brought by them to Brussels en route for London.

In Brussels, members of the C.I.O.S. Item 30 Ruhr team were able to interview Martin before his departure for London. The report of this interview is given below followed by a record of additional information obtained as a result of subsequent interviews held in London.

Interview in Brussels on April 22nd, 1945.

Personnel conducting Interrogation:

Lt. Col. A. Parker, British, Ministry of Fuel and Power
Dr. A.R. Powell, U.S., Petroleum Administration for War
Capt. C.C. Hall, British, Ministry of Fuel and Power.

Reported by: Dr. A.R. Powell, U.S., Petroleum Administration for War.

General Assessment of Fischer-Tropsch Process:

Martin stated that he believed the Fischer-Tropsch process would be of no present value for production only of motor fuel in a free world economy. Under such conditions, he believes the process is of value only for manufacture of special chemicals or upgraded products commanding a considerably higher unit sales value than does motor fuel. He stated that some of these special applications of the Fischer-Tropsch process had been described by a Dr. Asinger in Zeitschrift für (angewandte) Chemie about five months prior. Some of these special applications were mentioned by Martin later in the interview.

Synthesis Gas:

Martin said that he favored the production of the synthesis gas for Fischer-Tropsch plants by the original process of using coke as fuel in water-gas generators, followed by partial conversion of the carbon monoxide to obtain the correct hydrogen-carbon monoxide ratio. This method of synthesis gas manufacture had always been used at the Sterkrade plant of Ruhrchemie, and for the most part had been used in the other Fischer-Tropsch plants located in the Ruhr area. At the time these plants were started, coke manufacturers in the Ruhr were seeking sales outlets for coke other than the usual consumption in blast furnaces and this situation largely determined the fuel policy at that time. However, Martin said that he still preferred coke as the raw material instead of the somewhat cheaper raw coal or brown coal since coke was clean, free of tarry matter, could be gasified with relatively simple and trouble-proof equipment, and allowed easier and more accurate control of the composition of the synthesis gas.

Martin stated that the various processes for making synthesis gas from brown coal or by the cracking or reforming of coke-oven gas always gave operating troubles due to the presence or deposition of tar, carbon, resins and other disturbing substances. The presence of resin-formers in such gas led to the fouling of the catalyst for removal of organic sulphur, and the necessity in such cases of installing active carbon chambers before the organic-sulphur-removal equipment to free the gas of these harmful compounds.

Despite his preference for the coke water gas method of making synthesis gas, Martin believed much could be done to improve the process. Specifically, he thought water gas generators, using coke as fuel, should get away from the usual cyclic manner of operation and should operate continuously, for example by using oxygen and steam. This would avoid some difficulties encountered at the Sterkrade plant, such as mechanical troubles, dilution of the gas with nitrogen etc. He admitted that this was an unsolved problem at present.

Martin was asked about the present status of the Wintershall-Schmalfeldt process for making synthesis gas from finely pulverized coal. He stated that the process was in experimental full-scale operation, but that the process now uses some oxygen in its operation, which was not true of the original Wintershall-Schmalfeldt process as described in the literature.

Martin also briefly commented on the production of synthesis gas from coke oven gas, which had been experimented with by Bamag. He mentioned that they used steam rather than carbon dioxide as the reaction between methane and carbon dioxide was too slow.

Martin was asked about the possibilities of using coke-oven gas directly as a synthesis gas in the catalyst chambers. He said that this had been tried but one of the chief difficulties had been the complete removal of the organic sulphur from the gas since coke-oven gas contains thiophenes which are difficult to remove and also even the carbon bisulphide and carbon oxysulphide had been difficult to destroy, due to the bad effect of coke-oven gas hydrocarbons on the organic sulphur catalyst. For a reasonable life of the Fischer-Tropsch catalyst, it would be necessary to remove all sulphur and cyanogen compounds from the gas. In this connection he mentioned that Ruhrgas had erected a plant near Essen (based on Ruhrchemie research work) to catalytically treat coke-oven gas over a nickel catalyst so as to increase the methane content by interaction of hydrogen and carbon monoxide. By this scheme, they increased the heating value of the gas from 4,000 K cal/m^3 to 6,000 K cal/m^3. The object was the production of "Treibgaz" for motor transport.

Catalysts:

Martin stated that the cobalt catalyst is still the favorite for most purposes, and had not been displaced by the iron catalyst by any means. Cobalt catalysts were easy to make and were reliable in operation. The iron catalyst had been proposed largely as a war-time substitute for cobalt which was in short supply in Germany, due to the war. If the Ruhrchemie were to project a Fischer-Tropsch plant today, with free access to world market metals, they would recommend the cobalt catalyst.

Martin stated that they had discovered that the life of the cobalt catalyst could be materially lengthened by strict attention to thoroughness of purification of gas from sulphur, and that this life would now average 5 to 6 months. Regarding regeneration of the cobalt catalyst, Martin said there was a loss of four per cent per regeneration, but he felt confident this could be decreased to two per cent.

Asked about the most important factor involved in the manufacture of catalyst, Martin stated that the reduction step was the most critical and that the washing step was second in importance.

Martin was then asked about the known policy of Ruhrchemie in substituting magnesia for a part of the thoria in the cobalt catalyst. He stated that the full amount of thoria in the catalyst produced more paraffin and that any substitution of thoria by magnesia decreased this production. The magnesia was added solely to improve the physical characteristics of the catalyst. It had the effect of making the catalyst particle harder and less subject to disintegration to a dust. It was necessary to reach a compromise between the relative proportion of thoria and magnesia in order to obtain both a reasonably high production and good physical quality in the catalyst.

Martin stated that Dr. Gehrke, formerly in charge of catalyst manufacture at Sterkrade, had left and that he did not know his present location.

Martin stated that they had about 100 small, catalyst testing units in the laboratories at Sterkrade. These were constructed on the 'aluminium-block' principle and had a catalyst capacity of 50-100 ml. Each large-scale batch of catalyst was tested in these units using a standard temperature* and fixed gas rate (1 litre /g.Co /hour) at atmospheric pressure. If the yield of products remained approximately constant for about 14 days under the conditions of this test, then they could confidently predict from their experience that the batch under test would give a satisfactory performance in the full-scale ovens.

However, the test could be applied only to catalysts of similar composition and would not be applicable to any radically different catalyst on which there was no plant data.

In another phase of the interrogation, Martin

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* Martin gave this temperature as 'about 190°C.,' but documents found in the laboratories at Sterkrade indicated a figure of 185°C., which is much more probable.

was asked about iron catalysts. Martin reviewed the statement of Dr. Franz Fischer that a temperature of 240° was necessary for successful operation with the iron catalyst. Such a temperature required a water pressure in the cooling system of the catalyst chamber of 30 atmospheres. Since such a pressure presented many construction problems, it was most desirable to obtain an iron catalyst that would operate at a lower temperature. By a special process developed by Ruhr-chemie, an iron catalyst was produced that could operate at 215-225° (average 220°) and the pressure then was such that the concentric double tube catalyst chambers of the medium-pressure process could be used.

This catalyst contained for every 100 parts of iron, 30 parts of kieselguhr, about 3-4 parts of copper (Cu) and 10 parts lime (CaO). Increase in the proportion of copper gives harder catalysts which yield more wax but also more alcohols. For the preparation, the metals are dissolved in nitric acid and precipitated rapidly from hot solutions using potassium carbonate. Martin stressed the necessity for using potassium and not sodium as the alkali. After precipitation the precipitate is washed until samples taken from the filter show a pH of 8.0. If this point is over-shot, the pH is brought back by the addition of a weak potassium carbonate solution.

The amount of nitric acid involved in the preparation and the necessity for using potassium for the precipitation, makes the iron catalyst more expensive to prepare than cobalt. The difference in cost can be somewhat reduced by recovering potassium nitrate from the filtrate and wash waters.

The reduction of this material is less critical than that of the cobalt catalyst and is carried out at 325-350° for a somewhat longer time than the cobalt reduction. As in the case of cobalt, the iron catalyst must be only partially reduced, about 60 to 70%, since the presence of some iron oxide seems to be essential to the efficient working of the catalyst.

Martin believes that the use of potassium carbonate causes a metamorphism of the iron oxides and hydroxides into a form that makes the catalyst more effective at lower temperature. Ruhrchemie had operated a pilot plant with the iron catalyst, using 100 m^3/hr. synthesis gas for about a year. Experience with this pilot plant had furnished the data for the Italian project which had been set up for use of iron catalyst.

Martin stated at this juncture that results obtained on the 100m^3 /hr. scale were closely comparable with the full scale, but added that this was the minimum scale which gave fully reliable prediction of full-scale performance.

Martin was asked about the sintered iron catalyst of I.G. He said that I.G. had used this sintered iron catalyst exclusively for the manufacture of C_9 alcohols for plasticizers etc. and that this had no relation to the Fischer-Tropsch process as ordinarily conducted. As an aside at this point, Martin said that the Fischer-Tropsch process had been offered to I.G. in 1930 for about 500,000 marks, but that they had refused it.

Operation of Catalyst Chambers:

Martin was interrogated on capacity of catalyst chambers and yield of primary products and the relationship between yield and rate of gas throughput. He said that each chamber contains one metric ton of cobalt and produces 1.5 metric ton of primary product per day on the average, including chambers in all stages. The main objective is to utilize the synthesis gas at the highest efficiency consistent with reasonable capacity per chamber since synthesis gas is expensive. The normal operating rate will produce a yield of 150 g. primary product per m^3 of ideal synthesis gas. Some plants use a lower operating rate and thereby attain yields as high as 165 g. per m^3. In each case, a proper balance must be maintained between fuel cost and capital charges on equipment. For the 150 g. per m^3 yield noted above, synthesis gas flow is 1000 m^3 per metric ton of cobalt per hour in the first stage chambers, but as the catalyst becomes older, this rate is lowered until it is 800 m^3 per ton per hour just before regeneration of the catalyst. When operating to the higher yield, the initial rate is 900 m^3 and the final rate 700 m^3 per hour. The general policy of chamber rotation is to put fresh catalyst in the last stage in contact with older gas while older catalyst is put into the first stage in contact with fresh synthesis gas.

Martin was then asked whether normal-pressure or medium-pressure operation was best. He explained that each plant had been given a free choice as to which system it desired. The medium-pressure system has the advantage of giving three times as much hard paraffin as does the normal-pressure, and hard paraffin can be used for the manufacture of higher alcohols, such as C_{25}, which form valuable neutral emulsifying agents and can be made by no other process. Also the medium-pressure operation gives a somewhat longer catalyst life (about 2 months). The normal-pressure process gives a high yield of benzin (gasoline or petrol), but under peace conditions and a free world economy such benzin could not compete with that made from natural petroleum, so this is no advantage. Summing up, Martin said that the medium-pressure process should be chosen for any post-war project.

Martin was then asked about the use of recirculation with the cobalt catalyst and he gave information fully corroborating that previously obtained from Herr Alberts.

On the method of operating with the iron catalyst, Martin said that water gas was used as the raw material with a recirculation of two parts residual gas to one part fresh gas. The gas rate was the same as that used for cobalt on an oven basis, i.e., 1000m^3 /oven /hr. of fresh gas. The average working temperature was 220°C.. The use of recirculation entirely suppressed the deposition of carbon on the catalyst which otherwise tended to occur when water-gas was used as raw material. Both water and carbon dioxide are oxygen products of the reaction.

For one stage with recirculation, the yield of products is about 110 g./m^3, and for two stages, about 150 g./m^3.

The steam drums in the Ruhrchemie catalyst chamber system limit the top temperature of operation to 225°C., and with this limiting temperature the life of the iron catalyst is 5-6 months. If a new plant was constructed without this limitation, a higher final temperature could be reached and a longer life be obtained.

The Ruhrchemie iron catalyst gives a high yield of wax, i.e., 40-50% of the primary product.

Iron catalysts suffer from the disadvantage of producing carbon dioxide which must be scrubbed out of the gas between the stages if excessive dilution of the stage 2 inlet gas is to be avoided, whereas with cobalt, the water, which is practically the sole oxygen product, can be removed simply by condensation.

Diesel Oil

Despite the excellent quality of the diesel oil recovered from Fischer-Tropsch primary products, Martin considered this a low-grade use of the product, emphasizing again Martin's opinion that Fischer-Tropsch primary products should be converted into more valuable materials, such as special chemicals. For example, he mentioned that I.G. had purchased the diesel oil fraction (B.P. 230°-320°) for the purpose of manufacturing detergents. The fact that this had been done in war time, when diesel oil was in critical demand, illustrated his point.

Questioned as to the possible increase in yield of the diesel oil fraction by some modification of the normal Fischer-Tropsch process, Martin said every effort to accomplish this had failed. In general, the maximum yield of this fraction by any type of operation was about 35 per cent.

High-Melting-Point Wax:

Martin was asked about the possible commercial production of high-melting-point wax by a ruthenium catalyst as proposed by Pichler. He said that he did not consider this commercially feasible because of the extreme scarcity of ruthenium. Martin said that such waxes could be produced more economically by means of the usual cobalt catalyst, although, of course, not in 100% yield as had been claimed by Pichler for the ruthenium catalyst. Martin repeated the known claim that waxes with melting points as high as 90° or 95° could be recovered in a relatively small percentage from the primary products of the usual cobalt catalyst.

Martin stated that a method for increasing the yield of hard wax by means of the usual cobalt catalyst was to pass synthesis gas through the catalyst chambers at a considerably lower rate of flow and at a lower temperature. Following this, the hard wax could be extracted from the catalyst by means of benzin. Martin stated that the commercial demand for this special hard wax had been extremely small and was only of the order of one metric ton per month, so that it would not be a very important product unless new uses were discovered.

Synthetic Lubricating Oil:

Martin said that the quality of the lubricating oil made from Fischer-Tropsch primary products had been much improved since the beginning of the war. The oxidation test had been improved by the addition of inhibitors, the best one being phenathiazine (0.1 - 0.2%), or by treating the oil with elemental sulphur and aluminium chloride.

The best stock for lubricating oil was cracked material made from those fractions of the primary product boiling between 220° and 320° and wax with a melting point up to 30°. All material intended for this cracking step was filtered to remove the small amount of cobalt that had entered the oil from the catalyst, since it had been found that even the small amounts of cobalt caused undesirable side reactions during cracking. The cracking was carried out in a Dubbs unit in the presence of steam at a temperature under 500°C. This unit would operate for periods of 90 days before it was necessary to remove carbon. Martin said that all details of their synthetic lubricating oil process would be found in their documents, such as projects and correspondence, dealing with proposed Japanese plants.

The production of synthetic lubricating oil at the Sterkrade-Holten plant of Ruhrchemie had averaged 1400 metric tons per month. The yield of lubricating oil from the cracked product was about 55%, with about 25% going to gas. Most of the lubricating oil made had a viscosity of 6 to 7 degrees Engler and a viscosity pole height of 1.7, although attempts had been made to make higher viscosity oils by operating at lower temperature.

Martin stated that oil obtained by use of the iron catalyst had been considered good stock for production of lubricating oil without any preliminary cracking as was required for the product from normal Fischer-Tropsch operation. However, before the iron catalyst oil can be so used, it is necessary to remove all oxygen compounds. In the first laboratory tests, metallic sodium was used for this purpose. Later a catalytic process was developed that was considered to be more commercially feasible than use of sodium. The catalyst was clay that had been treated with sulphuric acid and then heated. By passing the vapor of the lubricating oil stock over this catalyst at a temperature which never exceeded 350°, the oxygen compounds were destroyed without any undesirable shifting of double bonds that might have affected the usefulness of this oil for lubricating oil manufacture.

A man by the name of Clar had been in charge of lubricating oil manufacture at Sterkrade, but Martin did not know his present location. (See Report 9, p.94).

OXO Process:

Martin was not interrogated on technical details of the OXO process. He was, however, interrogated regarding the conception of the process and his opinion of its commercial possibilities.

Martin explained the initiation of the OXO process as follows: In the gasol fraction, they had large amounts of propene and butene for which they had no use, so Martin instructed his chemists to find some new use for these compounds, other than direct conversion to propyl and butyl alcohols. At first, experiments were made on adding these olefines to water gas, then passing the mixture through the normal Fischer-Tropsch catalyst chamber with the objective of producing high-octane motor fuel. This objective was not attained, since substantially, only aldehydes were produced. Results indicated that such a process might be most desirable for production of aldehydes with possible later reduction to alcohols, so from this start, the OXO process was developed.

Martin said that he considered the OXO process the best one available for production of aldehydes and alcohols with an upper limit of about C_{18}. From the hard paraffins of the Fischer-Tropsch process, alcohols and acids up to C_{25} could be produced by first chlorinating the wax, but aside from this production of very high molecular weight compounds, the OXO process was considered the best, both technically and economically, for manufacture of compounds, especially aldehydes and alcohols, to an upper limit of about C_{18}.

Research on Direct Production of Higher Alcohols by Fischer-Tropsch Synthesis:

Martin said that small scale experiments conducted at a pressure of 200 atmospheres and a temperature of 200° showed a production of higher alcohols with excellent yields.

Martin was somewhat indefinite on the catalyst used but he believed that both cobalt, possibly containing a little zinc oxide, and an iron catalyst had been used in these experiments. The ratio of hydrogen to carbon monoxide in the synthesis gas used was 1.8 The product resulting contained as much as 80% alcohols, with the remaining 20% largely hydrocarbons and a small amount of fatty acids. The alcohols obtained were mainly in the range from C_7 to C_{12}, with smaller quantities of lower alcohols such as propanol and butanol and of higher alcohols above C_{12}. For the most part the alcohols were primary. By changing temperature, pressure, catalyst, etc., Martin is convinced that other proportions and types of alcohols could be made.

In this connection Martin mentioned that alcohols (mostly lower alcohols) were produced to some extent in the normal synthesis of hydrocarbons, and had been recovered from the reaction water. This had had much to do with initiating the above research.

Research on Direct Production of Fatty Acids by Fischer-Tropsch Synthesis:

The medium-pressure synthesis yields about 1% of directly synthesised fatty acids. About half of these are present in the diesel oil fraction and at Sterkrade-Holten about 3 tons per month of C_{11}- C_{18} acids had been recovered from the heavy diesel oil. Martin claimed that soap made from these acids was superior to that made by the Witten oxidation process in being free from objectionable odour. This claim, however, was certainly not substantiated by examination of a small sample of this soap which Martin had with him!

The value of these recovered acids had led to attempts to increase the yield, and some success had been achieved by the addition of small quantities of acetic acid to the synthesis gas. A 10% yield of acids had been obtained in this way.

Production of Fatty Acids by Oxidation of Wax:

Martin then gave an account of their process for producing higher fatty acids by the oxidation of wax using nitrosyl sulphuric acid, of which full details were subsequently obtained from Dr. Velde (See Report 8). He claimed that among the advantages of this process over that used at Witten, was the successful treatment of hard wax to produce the higher acids and the absence from the product of hydroxy acids and esters. The process appealed to the Ruhrchemie, furthermore, because it represented a 'cross-link' with their synthetic nitrogen plant. They had carried out research on other 'cross-links' such as the nitration of the Fischer-Tropsch paraffins.

Reaction of Water Gas and Acetylene using Cobalt Catalyst

Some tests were started on a pilot plant scale to find out what this reaction would produce. Possibly it was expected that acrylic aldehyde or its homologs might result. The total pressure was 20 atmospheres and, of this, acetylene accounted for about one atmosphere partial pressure. Water gas was present in about stoichimetrical quantity, while the remainder was inert gas. A cobalt catalyst had been used at a temperature of 100°C.. It was understood that this investigation was still in progress when the bombing stopped all research and that the results are far from complete. Definite evidence was obtained, however, that acetylene entered into the reaction.

Design of Fischer-Tropsch Catalyst Chambers:

Martin was asked why this had not made further progress in view of the fact that the present two standard designs (plate type and concentric-double-tube type) had been known before the war. He said that the construction companies making catalyst chambers (Gutehoffnungshutte, Mannesmann, Krupp, etc.) had decided to freeze the design in order to avoid changes in tools, patterns, etc. He said that Ruhrchemie itself had considered other designs, such as cooling liquids flowing over the catalyst, catalyst suspended in liquids, etc., but after consideration they always came back to present designs as preferable.

Martin said that Schaffgotsch Benzin had tried to do without the inner tube of the double-tube reactor and had experimented with the use of single tubes 20mm. i.d. The result, however, had been carbon deposition and excessive methane formation.

Recent Research:

Martin stated that practically no research work had been carried on by Ruhrchemie over the last 15 months because of the almost constant bombings. Not only was research personnel needed for other work in the plant, but they did not get sufficient sleep to carry on effective research work.

German Government Subsidy:

Martin said that only the primary products were protected by Government subsidy - not the various secondary products made.

Fischer-Tropsch Patents:

Martin said that the basic patents had expired, but many others had been in force that covered many details, modifications, and the working up of primary products.

Lurgi Patents Related to Fischer-Tropsch:

Martin said that the many Lurgi (Metallgesellschaft) patents related to Fischer-Tropsch process were mostly paper patents. The initiation of many of these patents resulted from the frequent visits of Lurgi engineers to the Fischer-Tropsch plants, where Lurgi had installed most of the active carbon units.

Personnel:

Martin stated that Dr. Roelen, Director of Research of Ruhrchemie, was at present ill and living on a farm near Salzwedle. His staff were in the vicinity of Salzgitte.

Interviews In London.

April 25th., 1945 **Interrogation conducted by:**

Major A.J.V.Underwood, British, Ministry of Fuel and Power

May 1st., 1945 **Interrogation conducted by:**

Mr. G. S. Bays, Jr., Dr. W.A. Horne, Mr. J. P. Jones, Mr. B. L. MacKusick,	U.S., Petroleum Administration for War
Col. J. A. Oriel, Lt. Col. R. N. Quirk, Major. A. J. V. Underwood, Mr. A. R. M. Murray,	British Ministry of Fuel and Power

(Note. The following information, which is additional to that given in previous sections of this Report, has been compiled from notes supplied by Major Underwood and from a report prepared by Messrs. Bays, Horne, Jones and MacKusick.)

Production of Fischer-Tropsch Plants.

Figures given by Martin and Hagemann for capacity of F.-T. plants are shown below, together with figures given in M.E.W. report on "The German Oil Industry" of October 1944.

Plant		Martin & Hagemann's figure Tons per year	M.E.W. Estimate, Tons per year.
Deschowitz	30/5.09	60,000	110,000
Dortmund	30/5.04	60,000	90,000
Sterkrade - Holten	30/5.01	70,000	125,000
Homberg	30/5.05	75,000	190,000
Kamen - Dortmund	30/5.06	75,000	100,000
Lützkendorf-Mücheln	30/5.08	*80,000	150,000
Castrop-Rauxel	30/5.03	50,000	100,000
Ruhland -Schwarzheide	30/5.07	210,000	350,000
Wanne - Eickel	30/5.02	60,000	130,000
		740,000	1,345,000

* Nominal capacity - actually production was only about 30,000 t/yr., owing to difficulties with Schmalfeldt gasification process.

Production and Purification of Synthesis Gas.

Martin said that there had been no new developments in synthesis gas production during the war; there was no direct gasification of coal except of brown coal at Lützkendorf and Ruhland. At Ruhland, the Didier plant had been found to be heavy on repair costs and the Koppers plant was the main source of gas.

At Lützkendorf the Schmalfeldt process was not very successful. There was much trouble with cracked products and sulphur compounds and arrangements had to be made with I.G. to borrow an expert. In order to make the process workable and to achieve the desired output, oxygen (0,25m^3 per m^3 synthesis gas) had to be employed. The gas still required oil washing followed by active charcoal to remove compounds which upset the Feinreinigung process.

The Lurgi pressure gasification process using oxygen operates best (from the point of view of synthesis gas production) with low-temperature, brown-coal coke. When using coal difficulties arise due to incompletely cracked tar.

Martin stated that Krupp had tried out the Thyssen-Galocsy gasification process on the large scale. He did not know what results had been obtained but they were believed to be good.

In the medium-pressure synthesis, removal of H_2S is always carried out before compression.

If coal or coke oven gas is used for synthesis gas production, oil washing or active carbon seems to be necessary to remove resin-forming compounds which affect adversely the life of the sulphur purification catalyst and synthesis catalyst. Essener Steinkohle had an active carbon plant before the organic sulphur purification and extended the life of the cobalt catalyst to 8 months from 5-6 months. Use of active carbon reduces the size of sulphur purification plant and generally seems desirable. Synthesis gas at Essener Steinkohle was bad, although made from coke. Possibly this was due to the use of lower temperatures in the water gas generator with coke of low melting point ash. No change had been made in the catalyst for sulphur purification.

Synthesis with Cobalt Catalysts.

Martin gave the composition of the cobalt catalyst used for both normal and medium pressure in all plants as: 100Co, 1 ThO_2, 10MgO, with the keiselguhr proportion adjusted to maintain 800kg. cobalt per oven charge of 10m³ of catalyst. (This ratio of thoria to magnesia conflicts with that given in Germany).

To ensure receipt of keiselguhr of the quality required for catalyst preparation, Ruhrchemie had installed a chemist at the mine (near Münster) who supervised the selection of the material and checked each consignment.

Pure hydrogen is considered preferable to the hydrogen-nitrogen mixtures used by Ruhrchemie for catalyst reduction. The reduction is more rapid and takes place at lower temperatures.

Martin gave the life of the cobalt catalyst as 5-6 months in the normal-pressure and 7-8 months in the medium-pressure process. The life depends greatly on the skill of the operator, particularly when starting-up a fresh catalyst. Starting conditions have to be varied according to the time the catalyst has been in storage or transit since its reduction.

Martin thought it was possible to increase the overall life of the catalyst by operating the first stage at a low conversion (e.g. 50% gas contraction) and a low temperature.

Various patented processes for the continuous extraction of the catalyst by reflux washing have not been adopted as they appear to cause some cracking.

There is usually no difficulty in removing spent catalyst from the ovens if solvent extraction and hydrogenation has been carried out. If the temperature has been too high, particularly at the start, carbon may have been formed and this makes the cleaning of the catalyst spaces in the oven difficult.

Experiments had been carried out at Sterkrade and at Castrop-Rauxel on the use of catalyst suspended in oil. During the process, the lighter products distill off and the proportion of heavy products in the oil increases. The throughput obtained was not high, the conversion was low and the methane formation was not reduced.

Difficulties had been encountered in the complete removal of catalyst from the oil. This was essential if the oil was subsequently to be cracked, as traces of cobalt cause excessive production of methane in the cracking process. The power cost of the process also proved to be high.

Use of Iron Catalysts.

Martin considered that the iron catalyst was mainly of interest for hard wax production. It was this aspect of the process which had attracted the Italian concern (S.I.C.S.). There was little to choose between cobalt and iron in sensitivity to poisoning by sulphur.

Martin stated that the I.G. sintered iron catalyst was very heavy and would cause structural difficulties on the large scale.

Condensation and Product Recovery.

Direct condensation was used for the atmospheric pressure process and indirect condensation for the medium-pressure process. Indirect condensation permits the recovery of alcohols and fatty acids formed in the synthesis. Schaffgotsch Benzin recovered 8-10 tonnes /month of C_2- C_4 alcohols (about 0.02% of the primary products) by distillation of the condensed water.

In the medium-pressure process it is usual to carry out the active carbon scrubbing after expansion, i.e., at atmospheric pressure. Oil scrubbing is not considered so satisfactory owing to the incomplete recovery of gasol.

A pre-war Linde project for the recovery of all products including gasol, by cooling under pressure had not been tried out.

Carbon dioxide was extracted from the residual gas after the active carbon plant by the Alkazid process and used for catalyst protection. The residual gas was used as fuel.

Product Utilisation.

The petrol fraction was blended with benzole for motor fuel and certain light fractions also found use as solvents, paint thinners. etc.

The fraction 180-230°C. was employed as a high-grade diesel fuel blending agent.

The I.G. had taken 8000 tonnes per month of the heavy diesel oil for conversion to Mersol detergents.

The hard wax of m.p. 90/95°C. had a good market for use in polishes, candles and explosives. The Ruhrchemie production of this hard wax from the medium-pressure process was about 500 tonnes/ month.

Martin stated that I.G. had a lubricating oil ~~plant which utilised Fischer-Tropsch products in con~~junction with the low-temperature hydrogenation of brown coal.

Special Products.

Fatty Acids. The addition of 0.2- 0.5% of acetic acid (based on the liquid products) to the synthesis gas in the medium-pressure, cobalt-catalyst process increased the yield of directly synthesised acids.

The OXO aldehydes could be readily converted into acids by the addition of sodium carbonate and air blowing.

Soaps prepared from the C_{13} and C_{14} acids were better detergents than those prepared from natural oils.

Alcohols. In this interview Martin stated that an iron catalyst containing up to 10% copper was employed in their laboratory synthesis of alcohols at 180°C. and 200 atmos. pressure.

Catalytic Cracking.

Martin said that Ruhrchemie were building a catalytic cracking plant to produce C_3, C_4, and C_5 olefines from the heavy fractions (above C_7). The catalyst to be used was "Granosil", an acid-treated clay.

The plant was about 60% complete when construction was abandoned in the Summer of 1944. The pilot plant tests indicated that the catalyst would have a life of about 6-8 weeks after which it would be discarded. The process involved the removal of carbon deposits by oxidation at intervals of 8 - 10 hours. The olefines were to be used for the production of polymer gasoline.

Ruhrchemie had not carried out alkylation, and, had made no high-octane gasoline or components.

Yield and costs of Fischer-Tropsch Operations.

Martin stated that from an economic standpoint, the principal war-time improvements in Fischer-Tropsch operations were increased yields of primary products, and better utilization of the by-products. Whereas, before the war an average yield of primary products of 140 gms. per cubic meter of synthesis gas was realised, a yield of 150 gms./cubic meter is now obtained from most plants. One plant, Essener Steinkohle, gets yields as high as 160 gms. This particular plant operated at atmospheric pressure, used three stage conversion with 50% of the total conversion taking place in the first stage and 25% (approximately) in each of the remaining two stages. This plant also had a rigid schedule for catalyst changing every six months regardless of activity, and especially good (according to Martin) technique for removing and replacing catalyst; they had constant coke quality and exceptionally good gas purification (including the use of activated carbon). All these factors contributed to making the yields and efficiency of the Essener Steinkohle plant outstanding. The complete utilization of by-products such as of tail gas in cracking and lubricating oil manufacture and the use of CO_2 recovered by Alkazid to blanket the catalyst during the preparation, improves the economics.

The records of the Essener Steinkohle plant should be found at Muessner Allee in Essen (Home Office) and those for the Hoesch Benzin plant at the Hoesch Steel Works in Dortmund. Copies of records of all plants should be at Reelkirchen and there is practically nothing at Ringelheim.

Martin stated that one kilogram of primary product per 5 kilograms of coke was considered the normal yield for his low-pressure plants although in winter it was necessary to bring in process steam not accounted for in the above coke consumption. As a capital investment cost of the plants, the atmospheric or low pressure units were generally figured at 800 marks per tonne annual production capacity (primary products), which is exclusive of land and utilities. The medium-pressure plant cost was somewhat higher. This figure, according to Martin, is difficult to translate to a foreign basis because it is a construction company figure, and the construction firms were steel producers who put their own price on the steel, and may have used unnecessarily large amounts of it.

Martin stated that Ruhrchemie were to deliver olefines to the OXO plant at 45pfg./kg. of feed material, the unreacted portion being returned to them. The estimated cost of production of the alcohols was given as 95pfg./kg. including 10% amortization.
(Note: These costs are higher than those given at Sterkrade, c.f. Report 4, p.40).

Japanese Contacts

Ruhrchemie made a contract several years ago with Mitsui giving them a general license; I.G.Farbenindustrie had made similar agreements with Mitsubischi; Martin professed to know nothing about the details. Koppers built a Fischer-Tropsch plant for Mitsui about five years ago at Müke which is about 30 kilometers from Tokyo. This had an initial capacity of 20,000 tons per year but may have been enlarged since. Then Ruhrchemie periodically gave information on developments to the Japanese in accordance with their agreement, but the Japanese always had 'no information' to exchange. The Japs were quite anxious to have cobalt shipped to them. The last information was passed to the Japs about September or October 1944, and included the latest information on the Ruhrchemie iron catalyst. Records of such information given to the Japs are in Ruhrchemie files at Oberhausen-Holten. Mitsui also was reported to have built a plant in Manchukuo near a steel mill.

The Müke plant had been built with the help of a Dr. Schenk who went to Japan for that purpose and whom the Japs have allegedly never allowed to return nor to send back reports.

Lurgi also had agreements with Mitsui and gave them information on oil processing and on coal gasification. Records of such information should be in Lurgi files in Frankfurt/M. Dr. Hubmann from Lurgi went to Japan in this connection and has since returned.

THE LOCATION OF EVACUATED RUHRCHEMIE PERSONNEL AND DOCUMENTS.

Personnel of Investigating Team

Dr. W.C. Schroeder, U.S., Bureau of Mines, Dept. of the Interior
Dr. A.R. Powell, U.S., Petroleum Administration for War
Dr. G. von Elbe, U.S., Bureau of Mines, Dept. of the Interior
Mr. E.L. Baldeschwieler, U.S., Petroleum Administration for War
Major R. Newman, British, Ministry of Fuel and Power
Capt. C.C. Hall, " " " " " "

Reported by : Capt. C.C. Hall.

General

Documents found at Sterkrade showed that some 726 Ruhrchemie personnel were evacuated to various locations in Germany in the autumn of 1944 and early in 1945. Later, information on the location of certain key personnel and of stores of documents was obtained from Lt. Cmdr. Cameron, R.N.V.R. and from interviews with Prof. Martin and others. This information is summarised below :-

1. Dr. Biederbeck and some documents were reported to be at Haberlah Wiese, between Ringelheim and Gebhartshagen, ca. 20 miles S.W. of Braunschweig.

2. A very large collection of documents and drawings were stored in the outhouses of a small moated castle at Reelkirchen about 4 miles S.W. of Blomberg (Lippe). Dr. Rohe, legal advisor to Ruhrchemie, was stated to be living in the village of Reelkirchen.

3. Dr. Roelen, chemist in charge of Ruhrchemie's research and development laboratories and probably the most valuable member of this Company's technical staff was reported as being:-

   (a) At a farm near Salzwedel (55 miles N.N.W. of Magdeburg).
   (b) At Werben (about 55 miles N.N.E. of Magdeburg).

4. Dr. Roelen's staff and some documents were stated to be at a sugar factory at Grosse Mahner near Salzgitte (S.W. of Braunschweig).

5. Dr. Schaub and the fuel and lubricating oil testing laboratory were reported to be :

(a) At Nutlar) both near Arnsberg (ca. 30
(b) At Willingen) miles S.E. of Hamm.)

6. Herr von Asboth, Chief Engineer of Ruhrchemie, reported to be at Laube near Schandau, S.E. of Dresden on the Czecho-Slovak border.

7. Dr. Heckel, in charge of iron-catalyst development under Roelen, said to be ill and with his family in the village of Hof, Bavaria.

The reported locations of Dr. Roelen and von Asboth were in areas which were not open to C.I.O.S. teams and a start was, therefore, made in the Braunschweig area.

Investigations in Braunschweig Area, April 25th to 27th, 1945.

The sugar factory at Grosse Mahner was visited at midday on April 26th. It appeared that Ruhrchemie personnel were no longer at the factory although some documents had been left there. These were examined and a number removed. In the village of Grosse Mahner Dr. Büchner, who claimed to be in charge of the analytical laboratory, under Roelen, was located and interrogated.

He stated that it had been intended to carry-on with the development of iron catalysts on a small-scale in the laboratory attached to the sugar factory. No material (stores and apparatus) had, however, arrived, and so this work was never started. Büchner had left Sterkrade on February 22nd to obtain billets, Dr. Noeske being left behind to supervise the packing of the material for evacuation. He believed that Dr. Gehrke had been "called-up" for the armed forces. The only other Ruhrchemie personnel in the Grosse Mahner area were juniors.

Büchner claimed that although he was responsible for analyses of iron catalysts and their synthesis products, the samples were sent in to him with a code number and he could not tell which catalysts were the best or which products were derived from a given catalyst or under what conditions they were prepared.

He was, however, able to give the following general information: The iron catalyst was in a state of development and frequently gave undesirable oxygen-containing products. The chemical composition was of less importance than the conditions of preparation (i.e. precipitation) and reduction. He understood that the catalyst was precipitated with alkali from a solution of the nitrates of iron, calcium and copper. Catalysts precipitated with sodium carbonate gave lower-boiling products than those precipitated with caustic soda or potash. He believed that for 100 pts. Fe there were 10 pts. CaO and not more than 5 pts. copper. The catalyst contained about 50% by weight of iron and only a small proportion of kieselguhr, as this material had an adverse effect on the catalyst life. The presence of copper facilitated reduction; the proportion was not critical.

The reaction temperature was about 240°C. and the product yield, about 100 gm./Nm^3 water gas, in one stage operation. The products in some cases contained as much as 60% of alcohols.

The experiments were on a scale of 1-5 litres catalyst capacity. There were 10 plants of this scale available for use.

Later in the afternoon of the 26th, <u>Dr. Biederbeck</u> was located in the hamlet of Haberlah Wiese and he led the way to a wooden 'barrack' built among trees on a hillside adjacent to iron-ore workings. A number of Ruhrchemie workmen were apparently living in this wooden hut and had accumulated considerable stocks of food there. In several rooms packing cases containing documents and letter files were found; there was only time on that occasion to examine the contents of one of these cases.

On the following day (April 27th) the contents of all the boxes were examined and a number of files and documents removed. On this occasion, <u>Herr Waibel</u>, the financial expert on the Ruhrchemie 'Vorstand' who lived in the nearby village of Gebhartshagen put in an appearance and was interrogated. He claimed persistently to have no knowledge concerning the technical side, his field being entirely business and finance. He referred to a Dr. Spieske as being equal in importance to Roelen in the field of hydrocarbon research and production. He did not know this man's present location. He confirmed that technical documents had been evacuated to the castle at Reelkirchen but claimed that before they left Sterkrade, all laboratory, research, and secret reports had been burnt in the boiler house on the orders of the Vorstand.

On the Haberlah Wiese site an underground nitrogen plant was under construction. This was known as 'Lack 2'. The entrance tunnel in the hillside where the 'barrack' was situated was found and explored, but the excavations had apparently not proceeded beyond the construction of this tunnel.

Dr. Biederbeck, who was apparently in charge of the nitrogen plant at Sterkrade, was not interrogated.

This completed the investigations in the Braunschweig area.

Investigations in the Blomberg (Lippe) Area, April 28th to May 1st, 1945.

The village of Reelkirchen was located at noon on April 28th, and the small "Wasserschloss" found in accordance with the advance information. The "castle" was more accurately a moderate-sized country house surrounded by a massive wall and a picturesque moat. The main gateway through the encircling wall was flanked by buildings divided into a number of small rooms, which were stacked from floor to ceiling with packing cases and paper sacks containing letter files, drawings, miscellaneous papers, office equipment, etc.

It appeared that Ruhrchemie had equipped these rooms as offices, with a telephone, typewriters, office tables, etc. and when the military authorities in Blomberg first examined the place, only a relatively small number of unopened packing cases and sacks were found there. Later, however, a member of the unit stationed in the district noticed a small boy playing with some blueprints. The boy was questioned concerning the origin of these drawings and as a result a further large number of cases and sacks of documents were found in barns, farm buildings, hay ricks, etc., scattered round the Reelkirchen area. These were collected and stored in the gate-house buildings at the "Wasserschloss", the rooms locked and a guard posted until an investigating party could arrive to examine them.

The afternoon of the 28th and the whole of 29th, 30th and the 1st of May, was spent in opening the cases and bags and examining the contents. A careful examination of the many hundreds of files and drawings thus revealed would have taken several weeks, and it was only possible to segregate those documents which appeared, from a cursory examination, to contain matter of interest to the CIOS investigation. In this way, 6 packing cases of documents were collected for more careful examination in London.

Dr. Rohe was located in the village and told that the rooms were being sealed up and that he would be held personally responsible for any interference with them on the part of Ruhrchemie personnel.

The rooms were duly sealed and the U.S. Army Unit in Blomberg given permission to remove the guard.

This completed the investigations in the Blomberg area.

It was felt that the party would not be justified in spending further time following up the other, less well authenticated clues to the whereabouts of personnel and documents, at this stage. It seemed likely that the main mass of evacuated papers had been found at Reelkirchen and if the detailed examination of the material extracted from this location indicated that important information was still lacking, efforts could be made to follow up the remaining clues.

A German-compiled list of Ruhrchemie works and departmental managers, obtained from Lt. Cmdr. Cameror is appended to this Report.

Appendix to Report 7

Ruhrchemie A.G.

Betriebs- und Abteilungsleiter

Prof. Dr. Martin
Dir. Dr. Hagemann
Dir. Waibel
Dir. v. Asboth
Bärtges
Bibus
Dr. Biederbeck
Dr. Biermann
Dr. Blank
Briele
Clar
Döring
Ernsting
Dr. Feisst
Dr. Förster
Dr. Gehrke
Dr. Goethel
Gottlob
Götz
Gubin
Hartwig
Heger
Henke-Stark
Hesseln
Holliger
Kagermeier
Kalk
Kleinhans
Knöllinger
Kolling
Köppern
Dr. Krüger
Krusekopf
Kuhlmann
Lassmann
Lindemann
v.d. List
Lüben
Meier
Dr. Meyer
Metz
Neweling
Pabst
Redemund
Redicker
Rieping
Dr. Roelen
Dr. Rohe
Dr. Rottig
Dr. Schaak
Dr. Schaller
Dr. Schaub
Scheepers
Scheidt
Dr. Schmatloch
Schmidt
Dr. Schuff
Schulte
Seeger
Sommer
Dr. Spanier
Spiske
Sprunken
Steffe
Dr. Stodt
Strauss
Strötgen
Stubner
Stuhlpfarrer
Tenter
Traut
Dr. Velde
Velder
Volk
Wächter I
Wächter II
Dr. Zilly

Report 8. Interrogation of Dr. Velde

Subject: Oxidation and Chlorination of Fischer-Tropsch Waxes.

Location and Date: Nienburg, May 11 and 12, 1945

Interrogation conducted by: Major D. Morten, British, Ministry of Fuel and Power.

Reported by: Major D. Morten.

General

Dr. Velde, aged 40, educated at Frankfurt-on-Main, was in charge of one of the Ruhrchemie research laboratories at Oberhausen Holten. He was evacuated, and was going to continue his research work at the W.I.F.O. depot at Schaefferhof, five kilometres from Nienburg. He had practically no documents with him, as all his effects and papers had been lost on the railway, but he was quite willing to talk and has made a personal report of his recent work and proposals for future work, which is attached as an appendix to this Report.

The bulk of the work on further processing of Fischer-Tropsch waxes was designed to produce materials which are in short supply, but does not seem to have been pushed with particularly great activity, and, in accordance with general Ruhrchemie practice, seems to have been very departmentalised.

Oxidation of Waxes

The general purpose was to produce a Montan wax substitute, as Montan wax was in short supply. Such material would be used as an emulsifier, but only gives emulsions of the solid type such as boot-polish, hand-cream, etc. and waterproofing agents for the textile industry. It could also be used to help out the supply of low water-soluble industrial fats. Work would have continued on the separation of the acids with solvents, to find more applications. The process of manufacture was as follows:- The feed material was a residual hard wax of 90°C. melting point. Lighter distilled grades, melting point 30°/35° and 50°C. were used to meet normal wax requirements. This residual wax had a molecular weight of 600, which means a carbon chain length of about 40, almost all of which was in straight chain form.

The wax is melted and heated to 125°C. and stirred with concentrated nitrosyl sulphuric acid, the proportions being 75 kilos of wax, 15 litres of acid, for a period of 8 to 12 hours. The best material for conducting this reaction is enamelled cast iron. During the process of the reaction, nitrous gases, produced from ammonia oxidation and containing about 8% of NO_2, are bubbled through the mixture. This gives a material of mixed molecular weight, but approximately C_{20}, of an acid value of 60/70 or even higher. The mixture is neutralised with KOH, using a solution of about 30/40% concentration, and the unreacted paraffins are extracted with S.B.P., boiling point about 90°C. It was stated that 100 kilograms of wax would give a yield of 80 kilograms of pure acid, of acid value 140/150. This was obtained by recycling the unchanged wax.

The research started in 1940/41, but although the process appeared to have been successful it was never put into large-scale production. The experimental plant produced about 3 tons of raw acid per month, known as OP.3; the purified form was known as OP.32. The acids were yellow in colour and could be purified with sodium dichromate, though both the pure and impure form had a nitrogen content of about 0.5% N_2. No work had been done by Velde on the production of edible fats or soaps from these acids.

Chlorination of Wax

The feed material here was a range of Fischer-Tropsch waxes from 30° to 90°C. melting point. Apparently there was no interest in the chlorinated material as such, and this step in the process was merely used to produce olefins which could either be oxidised with dichromate, or sulphated, or alternatively used for the production of synthetic lubricating oils. Velde had done some work on this latter process, but this was apparently unknown to Clar, who was interviewed later and was working on synthetic lubricating oils. Velde had started with a wax of about 30° melting point, and produced therefrom by chlorination and dechlorination olefines of the same boiling range, i.e. 300°/400°C. These had been polymerised with aluminium chloride to give an oil of an average viscosity of 50°Engler at 50°C., with a viscosity index, given by a Pole height of 1.6, equivalent to 110+.

For the chlorination process, using a distilled wax of boiling point 300°/400°C., the wax was melted and heated to 50°/80°C. and chlorine passed-in in the dark. Only glass apparatus was used on a scale of 5 litres. The olefin was prepared from this, using a vapour-phase process at a temperature of about 350°C. Two types of catalyst were available: (a) natural, Stuttgarten Masse; (b) artificial, highly heated aluminium silicate. It was stated that this catalyst was prepared at a temperature of 1,000°C. and must be sintered. It was finally prepared in small lumps of 2 to 3 mm. size.

The olefins produced would be of the C_{16}/C_{27} range, and were sulphated with 96% sulphuric acid. Dr. Velde does not know the exact proportions of the yields owing to the absence of his notes. The work was not finished, and sulphation experiments were in hand at various temperatures from below 0°C. to 35°C., to determine the best reaction conditions. The sulphated mixture was neutralised with caustic potash or soda and the unsulphonated material extracted with petroleum ether. The finished materials were both oil and water soluble, and gave good emulsions for cutting and soluble oils without the addition of any other emulsifiers such as alcohols or fatty acid.

Nothing had been started in the way of research on the production of higher alcohols, but this was one of the projects planned for the work at Nienburg.

Work had been carried out on the oxidation of olefines by a mixture of sodium chromate and sulphuric acid, but it appeared that the lack of electrolytic apparatus for the recovery of the chrome sulphate had proved too much of a difficulty for much progress to be made.

The other problems on which work was to be carried out at Nienburg were :-

(1) Separation of raw wax by selective solvent treatment instead of by distillation.

(2) Further study of the oxidation of wax to cover the full range of waxes and to be extended to the Fischer-Tropsch diesel oil fraction.

(3) Production of lubricating oils and cutting oils from soft paraffin by chlorination/dechlorination and either polymerisation or sulphonation.

(4) Further work on the Fischer-Tropsch synthesis, using pressures up to 6 atmospheres, particularly the effect of methane in the synthesis gas. This seemed to be of the nature of the further understanding of the general mechanism of the reaction with a view to improving the yield, reduction of methane, etc., but carried out independently of the catalyst. It was proposed to use the normal cobalt/magnesium/thorium catalyst.

(5) Work on the waste water from the Fischer-Tropsch plants, which causes considerable corrosion difficulties.

(6) Development of apparatus for measuring vapour-lock tendency.

(Translation of a Report Prepared by Dr. Velde)

Ruhrchemie A.G.
Oberhausen-Holten
BL KW V/Wk.

13th May, 1945.

A Report on the Work carried out in the Research Section of the Plant Laboratory K.W.

Oxidation of Paraffin Wax

The oxidation of paraffin wax was carried out by us to provide both emulsifiers and a softening material for I.G. waxes and Montan wax which could no longer completely satisfy the increasing demand for wax acids owing to the shortage of natural waxes.

The starting material for the experiments was R.B. hard wax with a melting point of about 90°, slab paraffin with a melting point of 50/52° and to a small extent also, soft paraffin, but since the particularly required high molecular weight acids could only be derived from R.B. hard wax the tests on these two materials were carried out only to a small extent and the R.B. hard wax was preferred as the starting material. The following results apply mainly to this product.

As an oxidising agent we used not air, in spite of its wide availability but chemical means so that the first tests were carried out with a mixture of sodium bi-chromate and sulphuric acid. We succeeded in converting hard paraffin wax into fatty acids by repeated treatment at a temperature between 100/105° with mixtures of bi-chromate and sulphuric acid in fixed amounts. The results of these tests were nevertheless unsatisfactory. The acid value obtained after 5-fold oxidation amounted only to 35.

Improved results were obtained when the paraffin wax was first chlorinated to a chlorine content of about 5/6%; then the chlorine was split off by thermal treatment at 350° and the resulting mixture of olefines underwent oxidation with chrom-sulphuric acid in the same way as was applied to the paraffin wax. By this we obtained with only a 2-fold oxidation an acid value of the order of magnitude of 80/90. The paraffin wax was in this test converted to the extent of about 50% into acids.

In the oxidation with chrom-sulphuric acid the bi-chromate added produces chromium sulphate which can be further converted to bi-chromate by anodic oxidation. This oxidation can be smoothly carried out.

However, since it was extremely difficult to obtain the necessary equipment for the anodic oxidation of chromium sulphate, other methods of oxidising the paraffin wax were investigated. Satisfactory results were thus obtained by oxidation with nitrous vitriol. The nitrogen dioxide can be obtained either pure or in the concentration resulting from the oxidation of ammonia, viz: about 8/9%.

The oxidation was carried out in the following way:- In a large agitator capable of being heated, 75 kilograms of paraffin wax were melted and the factory nitrous vitriol introduced. Then with continuous stirring and introduction of nitrous vitriol, 15 litres of nitrosyl sulphuric acid were added. After circulation for about ten hours the process is stopped and the reaction products drawn off. After separation of the nitrosyl sulphuric acid, washing of the acid residues remaining in the reaction products and drying, 70/71 kilograms of crude acids with an acid value of 70/75 remain. These crude acids, reference OP.3, still contain about 50% of paraffin wax. For the preparation of the pure acids the crude acids are saponified with high concentration alkali, the resulting soaps dried, purified and the unaltered paraffin wax removed by extraction with a benzine fraction with a boiling point of about 90°. Since the paraffin wax obtained by extraction practically corresponds to the starting material it can be further submitted to oxidation. By this means from 100 Kilograms of paraffin wax about 80 Kilograms of pure acids were prepared with an acid value of about 140/150. The pure acids contain about 0.5% of nitrogen. Just as the starting material is not a simple product but has an average carbon number of 40/45 corresponding to a molecular weight of 600, so the acids consist of a whole number of fatty acids of which the acids with carbon numbers over 20 predominate. The pure acids have a melting point of 80/85°.

Fields of application for the acids are inter alia consistent fats with very special properties, for example these fats are particularly water insoluble impregnants for the textile industry for the preparation of water resistant fabrics, printing colours, etc.

By partial saponification we succeeded in preparing very effective emulsifiers which enabled the preparation of solid and semi-solid emulsions. Besides oil, benzine, diesel oil and paraffin can be emulsfied with water. Fields of application for the emulsions are, for example, emulsified shoe creams or emulsified floor creams, emulsion lubricants, drilling lubricants. Some of the products mentioned can also be produced with the crude fatty acids previously referred to as OP.3.

After bleaching OP.32 which can be effected by a mild oxidation with bichromate-sulphuric acid, a stable white product is obtained with the help of which skin cream types of emulsions can be produced.

Chlorination of Paraffin Wax.

As briefly mentioned in the oxidation of paraffin wax, chlorinated hard paraffin wax is an intermediate stage in the oxidation with bichromate-sulphuric acid, which is easily prepared by thermal chlorination at slightly over the melting point. In a further continuation of these tests it was ascertained that the lower molecular weight paraffins, e.g. soft paraffin, can be just as easily transformed to chlor-paraffins by thermal chlorination. The starting material is also necessary in order to obtain the products selected by us as the object of our investigations, i.e. lubricating oil with outstanding properties and cutting oils.

For these tests the starting material was a synthesis paraffin with a boiling range between 300 and 400° corresponding to C17 to about C24 or of 300/450° corresponding to C17 to about C27, the melting point of the mixture being about 30/35°. This soft paraffin was treated with gaseous chlorine at about 100° with stirring, until the chlorine absorption amounted to about 26%, then the process was stopped and the chlorine split off later. The splitting off of chlorine can be carried out either in a purely thermal batch process at about 350° or in a continuous process by introduction of chlorine containing materials with the addition of certain catalysts. We have found of particular value in this connection SiO_2 and Al_2O_3 containing materials, e.g. the product of Stuttgarter Masse (Schuhmachersche Fabrik, Bietigheim). A particular characteristic of all the catalysts used is a definite sintering which is obtained by preheating to about 1000°.

From materials of this type we obtained on the introduction of chlorine containing products at about 350°, a mixture of olefines with extraordinarily high iodine values. The olefin mixture obtained by chlorination and dechlorination corresponds very largely in its molecular construction to the original paraffin used. Cracking and polymerisation occur only to a small extent if the dechlorination is carried out correctly.

This olefin mixture can be further converted by polymerisation with aluminium chloride into lubricating oils which have viscosities over 50°E at 50°C. and a "viscosity pole height" of about 1.6 (viscosity index not determined but over 100) or one can produce sulphonates by sulphonating with concentrated sulphuric acid and neutralisation, these permitting the manufacture of outstanding cutting oils. Tests on the cutting oils have only just been begun. The reactions involved are sulphonation, neutralisation, extraction of the unsaponifiables and drying. The fluid sulphonates obtained are oil and water soluble and produced stable emulsions capable of extreme dilution.

Work on Benzine

(a) Refining of Benzine

In the journal 'Öl und Kohle' Vol. 37, 1941, page 143, an article of mine appeared under the title "Methods of Refining the Primary Products of the Synthesis Process and their application to the working up of Crude Oil", in which is described a process which I developed some years ago for increasing the octane number of benzine containing olefines by catalytic treatment which is carried out without appreciable loss of product. In this the benzine is led at a high temperature but below the cracking temperature over a bleaching earth catalyst which has the properties of causing isomerisation. Apart from a small amount of true isomerisation which leads to branching, in this process the double bonds in the olefines are displaced from the ends of the molecule to the middle whereby the octane number can be appreciably raised, thus, for example, octane number increases of 10-12 points were obtained according to the olefin content of the starting material. Also in the case of petroleum cracked benzines octane number increases of 5/6 points were obtained. Further details can be obtained from the article mentioned.

(b) Behaviour of Primary Benzine on Storage

Further investigations concern the storage stability of primary benzine and cracked benzine from primary products, in which the most important point is that an increase in peroxide content was observed without the commencement of gum formation. By the addition of inhibitors the alteration on storage can be easily prevented. A publication of mine on this subject appeared in "Öl und Kohle" 1943 under the title "On the dependence of octane number on peroxide content of synthesis benzine"

(c) Gassing of Benzine

Jointly with the Director of our Testing Station Dr. Schaub, work was carried out on the gassing tendency of fuels and an apparatus developed in order to investigate gassing in motor spirits. A publication on this work followed in "Automobiltechnischen Zeitschrift 1941". A further publication was in preparation but could not be completed.

(d) The working up of Paraffin Wax by Distillation and Selective Extraction

At the Ruhrchemie the paraffin was divided by fractional distillation, pressing and sweating, into soft paraffin, slab paraffin and hard paraffin.

The crude paraffin produced in the synthesis process termed "oven" paraffin was first topped at 320° in a continuous distillation and by this means practically all the diesel oil components removed. The residue was subjected to a vacuum distillation and cut at 450°. The residue was a hard paraffin with melting point 90° and from the distillates the slab paraffin components with a melting point of 50/52° were obtained by pressing and sweating. The remainder consisted of soft paraffin with melting point of 30/35°.

In my research laboratory the question was investigated as to whether it was possible to prepare hard paraffin and slab paraffin from oven paraffin without distillation, by selective extraction/with solvents. As solvents the most important were acetone and benzin of different boiling ranges. The work has only just started so that no final process has yet been fixed.

(Signed) VELDE

Report 9. Interrogation of Herr Clar

Subject: Synthetic Lubricating Oils.

Location and Date: Nienburg, May 13, 1945.

Interrogation conducted by: Major D. Morten, British,
Ministry of Fuel and Power.

Reported by: Major D. Morten.

Introduction

K. Clar is aged 58. Although seven names had been given in the Assessor's report as having arrived at Nienburg, five of these were only "Laborants", so apart from Velde, Clar was the only other one examined.

He was also Manager of one of the Ruhrchemie research laboratories dealing with the synthesis of lubricating oils including pilot plant and production. This work was carried out in connection with the German Air Ministry.

GENERAL:

The synthesis was made from quite a wide range of olefines, of a boiling range 60°/200°C. equivalent to fractions from C_6 to C_{13}. These could be obtained from cracked Fischer-Tropsch spirit, or from the primary products from either the cobalt or iron catalyst, the whole thing depending entirely on the olefin content, which could be up to 70%. The primary olefines were the best, but others could also be used. It was essential to purify them considerably before the polymerisation process, and this purification consisted of washing with caustic potash to remove any alcohols and a vapour-phase treatment over alumina to remove all oxy compounds.

Polymerisation took place by simple agitation in contact with $AlCl_3$, using as low a temperature as possible to get reasonable reaction time. The best yield of high viscosity oil was then obtained at about 15°C., and a 24-hour reaction time using 100 parts of olefines and 6 parts of $AlCl_3$. Using this type of olefine feed the aluminium chloride goes fluid and forms a bottom layer known as contact oil. Clar had found that certain selected olefines, such as heptene,

C_7H_{14}, gave no contact oil and produced an excellent lubricating oil of viscosity 8 to 10°E. at 50°C., with a V.I. of 125/130, but the conditions had been modified, at least in the laboratory, to give a bright stock of viscosity 50°E. at 50°C. Work on the selection of the best feed would have continued at Nienburg. Aluminium chloride can be added to the contact oil as necessary, and the temperature increased as the material loses its activity. The top layer contains the unchanged paraffins of gasoline boiling range, as well as the lubricating oil; and before distillation this was given a treatment of 3 hours at 170°/200°C. in an autoclave to reduce the chlorine content, using refining earth, MgO, ZnO, or zinc metal. The finished lubricating oils were separated by the usual distillation process. Although the oils were of excellent viscosity index, they were unstable to the action of heat and oxygen, and one of the main difficulties was to improve these properties against the B.A.M. oxidation test, or a modification developed by Clar. The details of this modification were to pass 15 litres of pure oxygen per hour through 175 grams of oil at 140°C. for 24 hours. No catalyst was used and the test does not appear sufficiently drastic. Various methods of treating the oils were tried :-

(1) Earth contacting at 200°C. This gave no success.

(2) Further heating with aluminium chloride using about 2% for 3 hours at 170°/200°C. This was found to improve the stability considerably, and gave fairly satisfactory results on the large scale.

(3) Various ways were being developed of adding sulphur to the oil as a stabiliser, a remarkable point being that this was added <u>before</u> the synthesis stage, and not in any way as a normal inhibitor to the finished oil.

The latest approved oil was made using 0.2/0.5% of phenthiazin. This material was made by heating diphenylamine and sulphur in the molecular proportion of one of the former to two of the latter; these were melted together and the temperature raised to 150°C. to react. The formula is :-

$$C_6H_4 \genfrac{<}{>}{0pt}{}{NH}{S} C_6H_4$$

Two other "inhibitors", β-thionaphthol and its anthracene analogue, have also been used in this way, but laboratory results had indicated that ordinary flowers of sulphur was superior to sulphur in the combined form. This sulphur was added to the extent of 0.1/0.2% before the polymerising process, a second treatment with aluminium chloride being necessary to remove the smell from the first stage products. This oil was said to be oxygen-proof by Clar's method of test, and gave a viscosity change of only 10/20%, but the process had not been tried out on a large scale.

It was stated that the sulphur content of the finished oil was only a trace by analysis, and that the oil was non-corrosive to copper test. This oil had not yet been approved by the German Air Ministry, and Clar said that it was quite a new development.

The total aluminium chloride consumption is about 4% and one of the still outstanding problems was to dispose of the contact oil/spent catalyst mixture. This did not seem very difficult, as the oil could be separated merely by adding water.

As mentioned in the report on Velde's work, Clar's work was only on fractions boiling to 200°C., and he knew nothing of the work on the 300°/400°C. boiling range olefines.

The aluminium chloride catalyst does not need to be particularly pure, and can contain iron. In fact, for motor oils of 5°/8°E. viscosity it is possible to use mixed catalysts consisting of the chlorides of bismuth, iron and lead, but experiments on this were not completed. Molecular distillation of the lubricating oils in the laboratory gave fractions of about 2°E. viscosity with pour points down to -70°C., but normal fractionation on the large scale would give pour points down to -40°C.

Report 10. Interrogation of Dr. Zorn (of I.G.)

Subject: Ruhrchemie Synthetic Lubricating Oils.

Location and Date: Leuna, May 15, 1945.

Interrogation conducted by:

Major D.A. Howes, British, Ministry of Fuel and Power
Mr. J.G. Allen, U.S., Petroleum Adminstration for War
Mr. H. Schindler, ...

Reported by: the above.

Utilisation of Ruhrchemie Synthetic Lubes.

The olefine-polymer oil of viscosity 2.5°E. at 100°C. was known as SS1202 and was used in military vehicles in the following blends :-

Winter Grade	40%	SS 1202
	60%	Refined petroleum oil 6.0-6.5° Engler vis. at 50°C.
Summer Grade	25%	SS 1202
	75%.	Refined petroleum oil, 8° Engler vis. at 50°C

Special Grade for African Campaign

25%	SS 1202
75%	Refined petroleum oil, 12° Engler vis. at 50°C.

The petroleum oils for this blending were produced in four plants :

Lützkendorf
Oslebhausen (near Bremen)
Kolin (Vacuum Oil Co., near Prague)
Nerag - Hannover