

*Copy 1*

B.I.O.S.—FINAL REPORT No. 447

ITEM No. 30

# INTERROGATION OF DR. OTTO ROELEN OF RUHRCHEMIE A.G.

*Hall, E.B., Cranford, S.R., & Gall, D.*

This report is issued with the warning that, if the subject matter should be protected by British Patents or Patent applications, this publication cannot be held to give any protection against action for infringement.

**BRITISH INTELLIGENCE OBJECTIVES  
SUB-COMMITTEE**

REC'D. *JUL 1946*  
TIC L.F. & L. S-C.

LONDON—H.M. STATIONERY OFFICE

**INTERROGATION OF DR. OTTO ROELEN OF RUHRCHEMIE A.G.**

**Reported by**

**Dr. C.C. Hall,  
Dr. S.R. Craxford,  
Dr. D. Gall,**

**on behalf of**

**Ministry of Fuel and Power.**

**B. I. C. S. Target No. 30/5.01.**

**Fuels and Lubricants.**

**BRITISH INTELLIGENCE OBJECTIVES SUB-COMMITTEE**

**32, Bryanston Square, London. W.1.**

(1946)

69 p. diags

## Table of Contents

<u>Introduction</u>	Page (v)
<b>I. Information Concerning the Synthesis as Practised on the</b>	
<u>Full-Scale.</u> . . . . .	1
1. <u>The Synthesis Gas</u> . . . . .	1
Purification . . . . .	1
2. <u>The Catalyst</u> . . . . .	2
Composition . . . . .	2
Kieselguhr . . . . .	3
Manufacture . . . . .	4
Reduction . . . . .	5
Testing . . . . .	8
Possible Improvements . . . . .	8
3. <u>Normal-Pressure Synthesis</u> . . . . .	9
Deterioration of Catalyst during Synthesis . . . . .	9
Starting Synthesis . . . . .	11
Synthesis-Gas Composition and Gas Rate . . . . .	12
4. <u>Medium-Pressure Synthesis</u> . . . . .	13
Straight-through running . . . . .	13
Recirculation . . . . .	13
5. <u>General Considerations</u> . . . . .	14
Plant . . . . .	14
The Licensees . . . . .	16
General . . . . .	17
6. <u>Primary Products</u> . . . . .	18
Diesel Oil . . . . .	18
Wax . . . . .	19
Fatty Acids . . . . .	19
Alcohols . . . . .	20

Table of Contents (contd.)

	Page
7. <u>Secondary Products</u> .....	21
Lubricating Oils ..	21
Fatty Acids .....	21
<b>II. <u>Developments not yet Practised on the Full-Scale</u></b> .....	<b>23</b>
1. <u>Iron Catalyst Synthesis</u> .....	23
Products ..	26
Formation of Oxygen Compounds .....	26
Research work, other than that of Ruhrchemie ...	27
Present Status of Iron Catalysts ...	29
Atmospheric-Pressure Synthesis .....	30
2. <u>Liquid-Phase Synthesis</u> .....	31
3. <u>The Iso-synthesis</u> .....	32
<b>III. <u>Other Developments</u></b> .....	<b>34</b>
1. <u>Ruthenium-Catalyst Synthesis</u> ...	34
2. <u>Incorporation of Acetylene</u> ...	34
3. <u>Reaction Mechanism</u> ...	35
4. <u>Experimental Plant</u> .....	37
Pilot-Plant Scale ..	37
Laboratory Scale ..	38
<b>IV. <u>The OXO-Synthesis</u></b> .....	<b>39</b>
1. <u>Production of Propyl Aldehyde</u> ..	40
2. <u>Catalyst</u> .....	40
3. <u>Starting Materials</u> .....	41
4. <u>Products</u> .....	42
5. <u>Secondary Products</u> .....	43

Table of Contents (contd.)

	<u>Page</u>
<u>Appendix I</u> Professional Career of Dr. Otto Roelen .... ..	45
<u>Appendix II</u> Organisation of Ruhrchemie ..... ..	46
<u>Appendix III</u> An Account of the Development of Cobalt-Thoria-Magnesia Catalysts .... ..	48
<u>Appendix IV</u> Ruhrchemie, 2nd Reichsamtversuch ..... ..	53
<u>Appendix V</u> Synthesis with Iron Catalyst ... ..	54
<u>Appendix VI</u> Direct Alcohol Synthesis ..... ..	56
<u>Appendix VII</u> Catalyst F 2181 ..... ..	58
<u>Appendix VIII</u> Synthesis of Propylaldehyde at Holten ... ..	59

Personnel of Interrogating Team

Dr. C.C. Hall, Ministry of Fuel and Power  
November 6th, 7th, 8th, 9th, 12th, and 20th, 1945

Dr. S.R. Craxford, Ministry of Fuel and Power  
November 6th, 7th, 8th, 9th and 12th, 1945

Dr. D. Gall, Ministry of Fuel and Power  
November 6th, 7th, 8th, 9th, 12th and 20th, 1945

Dr. G.H. Dazeley, Ministry of Fuel and Power  
November 6th, 7th, 8th, 9th, 12th and 20th, 1945

Dr. C.M. Cawley, Ministry of Fuel and Power  
November 20th, 1945

Dr. A.J.V. Underwood, Ministry of Fuel and Power  
November 20th, 1945

Dr. A.R. Morcom, Ministry of Fuel and Power  
November 20th, 1945

Dr. W.S. Faragher, U.S. Technical Industrial Intelligence Committee  
November 12th, 1945

## Introduction

From the investigations of the Field Teams in Germany and from examination of captured documents it seemed probable that Dr. Otto Roelen had a more complete knowledge of the research side of the Fischer-Tropsch process than any other person in Germany. It was known that he had been associated with Franz Fischer in the discovery of the process at the Kaiser-Wilhelm Institut\* at Mülheim, Ruhr, and had been in charge of the research laboratory at Holten from the time when the development of the process passed into the hands of the Ruhrchemie A.G. Among his known achievements were the development of the fine-purification process and the discovery of the 'OXO' reaction.

At the conclusion of the War with Germany he was recuperating from ill-health at a farm belonging to friends near Werben in the zone overrun by the Russian armies. He was later released by the Russians and arrived back at Sterkrade-Holten during October 1945. At the request of the Ministry of Fuel and Power he was brought to London on November 5th for interrogation.

Details of his professional career as supplied by Roelen himself are given in Appendix I., and a chart showing the organisation of Ruhrchemie at various periods, in Appendix II.

It appeared that Prof. Martin favoured the sub-division of the work into separate "water-tight" departments each under a chief who reported directly to him or to Dr. Hagemann. Collaboration between these departments was discouraged and it frequently happened that heads of departments had little or no knowledge of the work of the others. Although basic research on the synthesis process was Roelen's field, if other sectors had ideas in this field they were encouraged to develop them in their own laboratories.

Roelen's knowledge of the work of other departments was limited to information obtained by personal discussions with his colleagues, and was therefore not complete and was possibly inaccurate.

He appeared to be fully co-operative, however, and within the limits of his memory gave full and, it is considered, reliable information on subjects in his own field.

---

\* Hereafter referred to as the "K.W.I."

# I. Information Concerning the Synthesis as Practised on the Full-Scale

## 1. The Synthesis Gas

Purification. Roelen was asked whether the present method of removing organic sulphur (fine-purification) had any disadvantages, or whether any other methods were being considered. He replied that the only disadvantages of the present fine-purification material were the softness of the granules (which tended to form dust) and the fact that the spent contact could neither be regenerated nor used in other ways - except possibly for the removal of hydrogen sulphide in the initial purification of the synthesis gas.

For the extreme degree of purification required for the synthesis no other process known to Roelen was possible. Methods in which the organic sulphur was decomposed to  $H_2S$  suffered from the disadvantage that, when used on the large scale, some organic sulphur compounds were formed from CO and  $H_2S$  in the presence of iron surfaces and iron sulphide dust.

For the methanisation of coke-oven gas, however, where the degree of purification was less critical, Ruhrchemie had used a process in which the organic sulphur compounds were reduced to  $1g./100 m^3$  by decomposition at  $425^\circ C$ . on spent Ni or Co catalyst at a rate of  $1 m^3$  gas/  $1.5 l. cat./h.$  and the  $H_2S$  formed removed in the usual manner. This process might be applied to the purification of gas for the Fischer-Tropsch synthesis if it were followed by quite a small fine-purification stage to remove traces of organic sulphur. Its success would depend on the nature of the sulphur compounds in the gas to be treated, and there might be trouble in regenerating large quantities of sintered catalyst containing a high proportion of sulphur. Ruhrchemie were in the process of developing a method, which Roelen considered very promising, by which organic sulphur compounds were decomposed in the presence of hydrogen on the surface of empty alloy-steel tubes at  $600^\circ C.$ .

The normal fine-purification process is completely successful for purifying 'clean' water-gas, but it is not so successful in the case of other gases such as coke-oven gas where the nature of the sulphur compounds, or the proportions present, are different. Furthermore, the purification of gases derived from coal gasification requires the insertion of an active carbon unit, before the fine-purification plant, to remove resin-forming constituents.



The Lux - or Lautmasse used in preparing the fine-purification material was found to be reasonably constant in properties and no serious variations in the performance of the material were observed. Bog-iron-ore can be used in the preparation provided the organic matter present is first removed by heating.

Normally, no trouble due to synthesis of hydrocarbons in the purification plant is experienced provided sufficient oxygen is present in the synthesis gas to maintain the iron in the oxidised state and care is taken to operate at a low temperature when the contact mass is new.

Brabag have apparently developed a special method of preparing fine-purification material which, they claim, produces a more porous granule.

## 2. The Catalyst

Composition. Roelen was asked the reasons for the change, firstly from the Co 100: ThO<sub>2</sub> 18: kieselguhr 100 catalyst used by Fischer at Mülheim to the Co 100: ThO<sub>2</sub> 15: kieselguhr 200 catalyst used originally at Holten, and secondly from the latter to the modern magnesia-containing catalyst used in all German plants.

In reply, Roelen said that the original K.W.I. catalyst - Co 100: ThO<sub>2</sub> 18: kieselguhr 100 - was found to be slightly less active than catalyst of composition Co 100: ThO<sub>2</sub> 15: kieselguhr 100. This catalyst however had a short life (probably due to its high catalyst-wax production) and a high methane production due to its high cobalt density. Roelen's first step was to reduce the cobalt density by making a catalyst of composition - Co 100: ThO<sub>2</sub> 15: kieselguhr 200, which could be used on the technical scale.

It had been found that magnesium oxide was a promoter and that cobalt-magnesia - kieselguhr catalysts gave very low yields of wax whereas thoria increased wax production. Cobalt-magnesia catalysts were very sensitive to temperature and difficult to control but Roelen found that addition of thoria to give a Co: ThO<sub>2</sub>: MgO: kieselguhr catalyst resulted in easier running, higher activity and a well balanced product. The mixed catalyst was also cheap and easy to regenerate, and was not sensitive to the influence of impurities and mechanical treatment while in the form of wet filter-cake (see later). A considerable variation in the proportions of

the constituents has little effect on the activity and the catalyst is therefore suitable for large-scale manufacture.

A more detailed account of catalyst development was prepared by Roelen in writing, and a translation appears as Appendix III.

Kieselguhr. The best kieselguhr so far discovered for the preparation of the catalyst was a sample, S 11, used many years ago for the small-scale work at the K.W.I., but there was not sufficient available for full-scale preparations. A constant mixture of poorer, but readily obtainable, kieselguhrs was therefore taken and made reasonably suitable for catalyst manufacture by heating to 1000°C., to volatilize some of the impurities (S, Cl etc.) and convert others into insoluble silicates. Unfortunately considerable sintering occurred at the same time, so that catalysts prepared with it did not have the highest activity. This 'Gluhgur' had, however, the great advantage that the bulk density was very constant, from batch to batch, at 120 g./l., and it is known therefore as 'kieselguhr 120'.

Later, a better kieselguhr was prepared by subjecting selected, but readily obtainable, kieselguhrs to a milder treatment at 400 - 700°C. in a moving layer. The product, 'Röstgur' varied in its properties, the bulk density varying from 60 to 100 g./l. so that varying proportions of kieselguhr had to be used in the catalyst to maintain a constant cobalt density. But it gave more active catalysts than 'Gluhgur' on account of its greater porosity.

Various tests were used to indicate whether a raw kieselguhr was suitable for the preparation of 'Röstgur', and a Ruhrchemie chemist was employed at the kieselguhr mines to supervise these tests. The type of diatom in the kieselguhr was not important and no correlation was found between suitability and surface area, but this was only measured by adsorption of dyes. The content of sand, as measured by sedimentation analysis, must be low, as sandy kieselguhr gives a soft catalyst. The amounts of soluble iron and calcium should also be low.

The temperature necessary in the heat treatment was correlated with the loss on ignition at 1000°C. (equivalent to the content of organic material, S, etc.) and was varied in accordance with this loss. The average temperature of treatment was 600°C.

Kieselguhr fulfilling the conditions for the preparation of active catalysts gave rise to no difficulties in the wet regeneration of the catalysts. The kieselguhr itself was not recovered for further use; passage through pumps etc. during regeneration broke down the diatomaceous structure, as could be seen under the microscope, and rendered the kieselguhr unsuitable. There were ample supplies of kieselguhr available in Germany suitable for conversion to 'Röstgur' and little work had been done on kieselguhrs from other sources.

Asked about the effect of washing kieselguhr with acids, Roelen replied that washing with dilute acid, e.g. 5% nitric acid at 60°C. for 1 hour, normally improves the kieselguhr, but that 'Röstgur' was considered to be satisfactory without acid washing.

Although other materials had been tried as catalyst supports, none even approached kieselguhr in suitability.

Catalyst Manufacture. The catalyst should be prepared by precipitation from a solution of the nitrates of cobalt, magnesium, and thorium with sodium carbonate solution, at a temperature of not less than 80°C. and preferably at the boiling point. The concentrations of the solutions used are not critical but simultaneous precipitation of the Co, Mg, and Th is very important. The kieselguhr may be added during or immediately after the precipitation. The conditions used are designed to give the maximum of disorder in the structure of the catalyst mass because this has been shown experimentally to be beneficial. Roelen did not know the excess of alkali used in the precipitation nor the pH value immediately after the precipitation, and promised to find these figures if possible. Since calcium poisons cobalt catalysts, the water used for washing the precipitated catalyst must be free from calcium. At Molten condensed steam free from dissolved carbon dioxide was used.

The moist catalyst filter-cake has such a colloid structure that when dried naturally it produces a hard and porous solid. If however the moist cake is stirred or shaken vigorously or subjected to similar mechanical treatment it exhibits thixotropy and liquifies, the gel structure being destroyed. On drying, the final catalyst is then both soft and non-porous. It is essential therefore to preserve the original colloid structure before drying, during any process the moist material may be subjected to in order to produce suitable granules, and during drying.

The granulation process used on the large scale produced 30% dust, but as this dust still maintained its original structure, it

could be mixed with a subsequent batch of moist filter-cake and re-granulated.

A different method had been tried on the semi-technical scale, by which little balls of catalyst, 'Eirichkorn', were formed by simultaneous drying and slow stirring. Very little dust was produced and although the granules were hard, they were not sufficiently porous and gave higher yields of methane.

An improved type of granule was the 'Fadenkorn' which was tried out extensively on the pilot plant scale, and also on the technical scale at Litzkendorf (Wintershall A.G.). This was prepared by extrusion of the moist filter-cake through an orifice. Normally, the orifice would soon become blocked on account of sedimentation of the kieselguhr, but this was prevented by an oscillating shutter, the rate of movement being sufficiently low to avoid breaking up the original gel structure. The catalyst paste was fed to the orifice by a series of paddle wheels. The extruded thread was dried on a conveyor belt by hot air and was then broken up to particles of suitable size by passage down a vertical cylinder fitted with baffle plates and with a special stirrer which threw the catalyst against the walls of the cylinder. This process gives a lower proportion (4-5%) of dust and a better shape of granule, with rounded ends, than cutting the extruded thread. The 'Fadenkorn' give a better gas distribution than the normal catalyst granules and allow easier emptying of the reaction chamber, but Roelen thought that further investigation into their large scale preparation was required.

Asked for comment on a suggestion that the catalyst fines could not be reincorporated due to deactivation by oxidation, Roelen replied that if the fines were returned immediately into the process no deterioration was observed, but that otherwise it did occur. The oxidation effect might be due to the conversion of  $\text{Co}^{++}$  to  $\text{Co}^{+++}$  or to the adsorption of carbon dioxide or water, the cobalt catalyst being sensitive to moisture. Roelen admitted the possibility of the deterioration of unreduced granular catalyst during storage.

Catalyst Reduction. Roelen stated that this was the most crucial step in the whole process and that the success of a catalyst depended on correct reduction. The general principle was that sintering of the reduced catalyst must be avoided at all costs. Hence reduction must be done (i) with the catalyst arranged in a short bed and using a high rate of  $\text{H}_2$  which contains no oxygen or

oxygen containing gases or vapours, (ii) at the lowest temperature and (iii) for the shortest time compatible with sufficient reduction. When the reduction is finished the catalyst must be cooled from the reduction temperature as quickly as possible.

The conditions grouped under (i) all aim at preventing the back reaction as far as possible. It had been found, for example, that for a given catalyst, temperature and gas rate, the extent of reduction approaches a limiting value as the time of reduction increases and that the limiting value decreased as the amount of free and combined oxygen in the hydrogen increased. By going to the extreme of reducing the catalyst bed to 1 cm. thickness, reduction could be completed at 400°C. in 1 min. or even at 250°C. in 1 hour.

The conditions (ii) and (iii) are mutually exclusive and it has been found that moderate values of both factors give better results than extreme values of either. Thus catalysts reduced for a very long time at a very low temperature are less active than those reduced for a moderate time at a moderately high temperature.

Although it was recognized that if reduction could be carried to completion without sintering taking place the catalyst would be more active than an incompletely reduced sample, it was found in practice that the most active catalysts were obtained by stopping the reduction before all the cobalt was reduced to metal. The percentage reduced was called the Reduction Value. The most active catalysts had reduction values of 65 - 70, and the usual technical scale catalysts 55 - 65. But active catalysts had been obtained with reduction values varying from 40 to 90. Reelen considered that the unreduced cobalt oxide may have a very important role in preventing sintering so that when it is removed by completing the reduction, sintering occurs much more readily. Alternatively the cobalt oxide may be a promoter for the synthesis itself.

The ease of reduction of a catalyst, as given by the temperature and time required to reach a given reduction value, varied with the composition and method of preparation. In particular it was found to depend directly on the cobalt-density. Hence in order to be able to keep the reduction conditions constant on the technical scale, the cobalt-density of the catalysts must be kept constant. Since the kieselguhr used in the catalyst preparation varied in density, the proportion of kieselguhr in the catalyst had therefore to be varied to keep the cobalt-density constant.

In general, Ruhrchemie had found that those catalysts which were the most difficult to reduce were the most active, and in particular, had a high activity at a low temperature. This observation was turned to advantage in predicting the activity of catalysts, three samples of the catalyst being reduced for 1 hour at a standard hydrogen rate but at three different temperatures. The ease of reduction, as given by the resulting reduction value - temperature curve showed a good correlation with the catalyst activity.

In the case of the catalysts which contained magnesia and which are very active, Roelen suggested the following explanation. The unreduced catalyst is supposed to consist of mixed crystals of magnesia and cobalt oxides. Such mixed crystals should be difficult to reduce on account of the insulating action of the magnesia which prevents the conduction of the heat of reduction from one cobalt atom to the next, and they should also give very active catalysts because the dispersal of the cobalt throughout the mass of magnesia will give the finest sub-division of the cobalt and will make sintering difficult. (A similar effect of mixed crystal structure in giving high catalytic activity is well known for ammonia synthesis catalysts).

Since the final loss of catalytic activity after a long period of synthesis, the loss that cannot be restored by solvent or hydrogen treatment, or by dry regeneration, is due to sintering of the cobalt during synthesis, these catalysts which sinter easily will have a short life and conversely. Ruhrchemie determined the ease of sintering by determining the activity after reduction under extreme conditions, i.e., at higher temperatures and for longer times than the normal. Catalysts which were active after such a reduction were clearly resistant to sintering and hence should give a long life for synthesis.

Impurities such as calcium, lead or copper are harmful as they promote sintering, and for this reason Roelen said he could see no future for catalysts in which copper or silver had been introduced in order to lower the temperature necessary for reduction.

After reduction, admission of carbon dioxide to the catalyst must be done at a low temperature. At temperatures above  $100^{\circ}\text{C}$ . carbon dioxide could destroy the activity, and even at lower temperatures heat was sometimes generated. Roelen had carried out no comparative experiments to discover any loss in activity due to the normal use of carbon dioxide when storing and transporting the reduced catalyst. (Generation of heat was also found on admitting carbon dioxide to reduced iron catalysts).

Testing of Catalysts. Samples of reduced catalyst from the factory, usually one from each K&bel, were normally tested for a period of 200 hours, the oil and water yields being measured. The test was carried out in a 12 mm.-bore tube and synthesis was started at 185°C. with a gas rate of 1 litre per g. cobalt per hour. An active catalyst at first produced mainly methane with a gas contraction of 55 - 60%; after about 24 hours, production of liquid hydrocarbons began and the contraction rose to 70 - 75%. A catalyst which made mainly liquid hydrocarbons from the beginning was considered less active. This held good only if synthesis was started at ca. 185°C. If the reaction was started at ca. 170°C. oil was produced from the beginning.

No short test was available which could be applied to a reduced catalyst to predict its life, although the life of the catalyst before dewaxing was necessary could be taken as a very rough guide. At a later period fewer tests were carried out, but they usually extended over three months instead of 200 hours.

Suggestions for Improvements in Catalysts. Roelen was of the opinion that increases in yield /m<sup>3</sup> from cobalt catalysts were unlikely, and that further developments would probably be in the direction of catalysts favouring the production of special types of product. To increase the space-time-yield, either more active catalysts must be developed or the existing type adapted to work at higher temperatures, which is very difficult if excessive methane production is to be avoided. Roelen thought that it was unlikely that such cobalt catalysts could be obtained. He considered that further investigations of Co: Mn: kieselguhr catalysts, which had a high activity at low temperatures (165°C.), might be profitable, with or without the addition of thorium. Manganese favoured the production of high-molecular-weight hydrocarbons and such catalysts would therefore be more valuable for medium-pressure than for normal-pressure synthesis. Wet regeneration of these catalysts might prove difficult owing to the presence of the manganese. Roelen could not remember the composition of any manganese catalyst tested.

Alloy-skeleton catalysts had not been investigated by Ruhrchemie on account of the large amounts of metal required. Roelen had tried the incorporation of water-glass in cobalt catalysts as recommended by Schaffgotsch in 1943 but could not reproduce the good results claimed.

Mixed cobalt-nickel catalysts had been tried but without improvement over cobalt alone. Up to 10% of nickel had little effect on the performance of cobalt catalysts; the amount of nickel normally occurring in technical cobalt salts was therefore

no disadvantage. Higher proportions of nickel in the mixture, especially with nickel above 20%, gave catalyst granules which were too soft for use. The possibility of producing self-hydrogen-dewaxing catalysts by the incorporation of nickel seemed unlikely.

### 3. Normal-Pressure Synthesis

Deterioration of Catalyst. Roelen said that this is due to the following causes:-

- (i) Blocking of the pores of the catalyst by the wax formed in the synthesis. Some of this, the more soluble and probably lower molecular weight fraction, can be removed by extraction with solvents or by treatment with hydrogen at synthesis temperature or thereabouts, and as a result the catalyst activity is largely restored. Some of the wax however, or possibly decomposition products of it, cannot be removed in this way and requires hydrogen treatment at a much higher temperature.
- (ii) Poisoning by elementary carbon (produced in a side-reaction), by oxygen or by sulphur. All these substances can be removed, either in whole or in part, by treatment with hydrogen at the higher temperatures.
- (iii) Sintering, which can never be reversed.

He made the following comments about these individual effects.

(a) Wax. The formation of wax is most pronounced for Co: ThO<sub>2</sub>: kieselguhr catalysts and least for Co: MgO: kieselguhr, mixed catalysts of Co: ThO<sub>2</sub>: MgO: kieselguhr being intermediate between these two extremes. For a catalyst of a given composition the deterioration due to a given amount of wax varies with the quality of the kieselguhr, being less with less dense kieselguhrs. This, he said, is easily understandable because the pore volume that has to be filled with wax before the pores become blocked, will vary from kieselguhr to kieselguhr and will be greater the less its density.

In the laboratory, extraction with solvents is a more effective way of removing wax than treatment with hydrogen at synthesis temperature, but on the large scale both methods are about equally effective, and the different plants used either the one or the other treatment, or both. No decision has yet been reached.



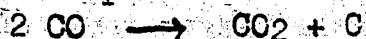
whether, when extracting with solvent on a large scale, the oil should merely be allowed to trickle over the catalyst, or whether the catalyst vessel should be filled up completely with oil. Although the total amount of wax on a catalyst is less the higher the synthesis temperature, the amount that is resistant to the normal hydrogen and solvent treatment is substantially unaffected. This can be removed by treatment with pure dry hydrogen at about 400°C., using a high gas rate, as in the original reduction. The temperature must however, be raised slowly, at, for example, 50°C./h., from synthesis temperature to 400°C. If more rapid heating is used, the wax decomposes to give carbon which is not in a sufficiently reactive state to react with hydrogen. This process is known as 'Dry Regeneration' and had been worked out thoroughly in the laboratory but had not yet been tried on the full-scale plant.

(b) Sulphur. This is undoubtedly a major cause of catalyst deterioration but Roelen had not tried to find the exact amount which could be dealt with by the catalyst before activity declined to a level too low for further use. It was known that a catalyst of low activity was put out of action by a smaller amount of sulphur than a more active catalyst. Roelen thought that figures were available at Holten for the sulphur content of spent catalysts and that an examination of these figures might be of interest. The presence of thoria in the catalyst confers a certain amount of resistance to sulphur poisoning but this effect varies with the sulphur compound in question. In view of the other causes of deterioration, Roelen could give no opinion as to whether the reduction of the thoria content made the Co: ThO<sub>2</sub>: MgO: Kgr. catalyst less resistant than the Co: ThO<sub>2</sub>: Kgr. catalyst.

Asked about the possibility of increasing the resistance of the catalyst to poisoning by sulphur by introducing alkali, Roelen said that although he had prepared such catalysts for another purpose he had not examined them for resistance to sulphur poisoning.

The dry-regeneration process removes about 70% of the sulphur that the catalyst has taken up and therefore, on this account alone, it restores a large part of the original activity.

(c) Carbon. Roelen considered that the formation of elementary carbon on the catalyst played a very important part in deterioration. A normal synthesis catalyst was rendered inactive for further synthesis if 5% C were deposited on it by the reaction



and if this reaction takes place under synthesis conditions to the

extent of 0.01% of the carbon monoxide present, 5% of carbon (calculated on the weight of catalyst) will be formed in six months. The formation of carbon during synthesis had been observed with Co: Mg and Co: Th: Mg: kieselguhr catalysts. In the first case, due to the absence of kieselguhr and the low amount of wax formed, it was possible to dissolve the catalyst (after synthesis) in acid and weigh the carbon present. For the Co: Th: Mg: kieselguhr catalyst, synthesis experiments were carried out with hydrogen-rich gas, normal synthesis gas and water-gas, and the catalysts were treated with acid to leave a residue of kieselguhr. The colour of this residue indicated that carbon deposition was higher with increasing proportions of carbon monoxide. Although he could give no experimental evidence, Roelen thought that this carbon would be removed by dry regeneration because finely-divided carbon in a reasonably active state should react under these conditions.

(d) Oxygen. Roelen stated that there were no indications of oxidation of the cobalt during synthesis, the reduction value being unchanged after 6 months synthesis.

(e) Sintering. The contribution of sintering, that takes place during actual synthesis, to the catalyst deterioration was considered to be small. Thus Roelen had maintained fresh catalyst in hydrogen or nitrogen for 1000 hours at synthesis temperature without loss of activity. (This does not prove that sintering would not have occurred if synthesis had been going on during that period). At higher temperatures (400 - 450°C.) a diminution in activity was found, proportional to the temperature and the time, but Roelen could not give figures. The efficacy of dry regeneration however shows that for short periods at 400°C. the loss of activity due to sintering is not very great. If however dry regeneration has to be repeated several times in the life of a catalyst, it becomes less effective each time and this is thought to be due to the sintering.

Finally, Roelen said that there was no evidence that the formation of cobalt silicate occurred to any appreciable extent during synthesis and that it therefore played no part in the deterioration of the catalyst.

Starting the Synthesis. If a freshly reduced catalyst is put into contact with synthesis gas at the normal gas rate and normal synthesis temperature it will usually react so vigorously that the temperature will rise uncontrollably in the top layers of catalyst and as a result methane will be formed instead of oil, and carbon formed on the catalyst. This effect had been studied by K.W.I. by temperature measurements taken at many points in a multi-plate-type reactor, and.

according to Roelen, synthesis started at a number of points and not generally throughout the catalyst. The gas contraction resulted in an increased flow of gas to these points and hence a rapid increase in temperature. This effect is not obtained in a narrow tube reaction vessel such as was used for laboratory work, but may occur in a multi-tube converter by concentration of synthesis in a small number of the tubes.

Since both the rise in temperature and the carbon deposition cause deterioration of the catalyst the control of the reaction during the first few days of synthesis is a matter of the utmost importance. The following methods have been tried:-

- (a) Impregnation of the catalyst with oil (synthesis product below the wax range) immediately after reduction. This was a good method but was expensive and laborious. On the laboratory scale impregnation with wax had been tried and found successful. It had the further advantage of rendering the reduced catalyst stable and easily transportable.
- (b) Deposition of carbon on the catalyst up to a content of about 1% by the decomposition of carbon monoxide. This suppressed methane synthesis almost entirely but shortened the life of the catalyst.
- (c) Dilution of the synthesis gas with inerts at the beginning of a run was successful but expensive.
- (d) Starting a fresh catalyst in the 2nd stage of a plant (i.e. practically equivalent to (c) ) was used in the majority of cases and very little trouble was given on the technical scale.

If 'bolting' did occur, Roelen said that it could be stopped by shutting down the gas flow or by injecting steam; the latter procedure gave an immediate result but might cause oxidation of the cobalt.

Running-in was controlled by gas rate rather than by a temperature schedule.

Synthesis Gas and Gas Rate. Asked whether the inert content should be kept as low as possible, Roelen said that this was not the case. Even under laboratory conditions a rich gas tended to increase carbon deposition. It also made temperature control more difficult. Of two catalysts, the more active with a rich gas would generally be more active with a diluted gas. Ruhrchemie had made no deliberate attempts to find a catalyst specially suited to a dilute gas i.e. with ca. 15% inerts. Concentrated gas generally gave a higher production of wax.

Asked about gas rate, Roelen said he did not think that 1000 m<sup>3</sup> gas per full-scale reactor (holding 10-12 m<sup>3</sup> catalyst) per hour was the maximum permissible throughput and said that the first stage in a multistage plant could be run at a higher rate. The average gas throughput for a three stage plant was 600 m<sup>3</sup>/ reactor /hr. The use of higher throughputs increases the plant output but decreases the yield/ m<sup>3</sup> of synthesis gas. Whether or not this is justified, therefore, depends mainly on the price of synthesis gas.

#### 4. Medium-Pressure Synthesis

Straight-through Running. It was found that medium-pressure synthesis works best, from the point of view of smooth running and olefine production, with synthesis gas with H<sub>2</sub>/CO = 1.5. Since, for a complete plant, it is desirable on economic grounds that the overall synthesis gas should have H<sub>2</sub>/CO = 2, medium-pressure synthesis must therefore be operated in several stages with adjustment of the gas composition between the stages.

On being asked, Roelen said that hydrogen treatment at synthesis temperature and solvent dewaxing had been tried for medium-pressure catalysts but that dry regeneration had not. The hydrogen treatment had no reactivating effect. This fits in with Roelen's picture of catalyst deterioration already given for atmospheric-pressure synthesis, because hydrogen at synthesis temperature only causes reactivation in that case by removing wax from the pores of the catalyst, whereas for medium-pressure synthesis, on account of the very different conditions, the catalyst is always saturated with wax and wax formation is not therefore a cause of deterioration.

Reactivation was found possible, however, by oxidation with steam followed by reduction, but this technique was very difficult to carry out successfully. Roelen considered that carbon was removed but that, in addition, deleterious changes might also occur, such as changes in the kieselguhr. Also, cobalt oxide formed by the oxidation of cobalt metal may be in a different form from that obtained on heating carbonate, and its reduction may lead to a less active catalyst. Production of trivalent cobalt may also occur. Some success had, however, been achieved by this method.

Recirculation of Residual Gas. The advantages of recirculation of gas were first demonstrated by Lurgi at the Hoesch-Benzin works. They showed that good results were obtained by recycling synthesis gas (H<sub>2</sub>/CO = 2) at medium pressure but their trials had not been followed up, probably due to external circumstances.

Recirculation with water gas was designed to increase the olefine content of the products, with a view to the preparation of lubricating oils, OXO-products etc. If a high olefine content was not desired, Roelen doubted if there was any advantage to be gained by recirculation as against the straightforward multistage process. The catalyst life could be as high with recycling, but the operational risks were greater. Using synthesis gas, recycling should give easier reaction control but this alone would not be enough to outweigh the extra cost and other disadvantages. Certainly recycling had no worthwhile advantages if very cheap water gas was available.

Roelen admitted that recycling decreased carbon deposition on the catalyst, due to the reduction in the partial pressure of the carbon monoxide, and also that methane production was lower but thought that, even allowing for this, wider reaction tubes could not be employed. In straight-through running at medium pressure, water gas gives less methane than synthesis gas but wider tubes cannot be used as the increased proportion of carbon monoxide requires very accurate temperature control to avoid the possibility of carbon deposition.

Roelen thought that accurate results could be obtained when running small-scale recycle experiments, but Ruhrchemie had had difficulty (due to war-time conditions) in obtaining pumps free from leaks.

Asked whether he could confirm the statement\* that a catalyst of composition Co 100: MgO 45: kieselguhr 200 was contemplated for recycle running, Roelen said that he had no information about this but thought it might be possible. He thought a content of 20% C<sub>6</sub> - C<sub>10</sub> alcohols in the product an overestimate: his own maximum estimate would have been 5 - 10%.

## 5. General Considerations.

Plant. Roelen was not questioned about the details of the design of the full-scale plant, because he knew very little about it, but he gave the following more general information.

The double-tube reactor was entirely satisfactory as far as ease of filling and emptying was concerned and it was easier to

\* Sample sentry Report on Ruhrchemie A.G., Sterkrade-Holtien  
by W.F. Forcher et al. File No. XXXII - 96.

remove spent catalyst from the 10 mm. annulus of the double tube than from 14 mm. tubes used in some of the pilot plants. No trouble was experienced due to warping of the central tube. One disadvantage of the double-tube reactor was that when the tubes were filled with catalyst up to the level of the tube-plate, the top of the catalyst bed tended to overheat as there was some difficulty in ensuring an adequately high water level on account of local pressure differences set up at the steam exit. The 'Wulstofen' was designed to overcome this difficulty, which was done by fitting each reactor with its own steam drum, made in the form of an external annular protuberance situated at the level of the upper tube plate (see C.I.O.S. Report XXVII-69, The Fischer-Tropsch plant of Ruhrchemie A.G., Sterkrade-Holten, p.17). This arrangement made it possible to provide a number of apertures through which steam could pass from the water-space in the reaction vessel to the steam drum.

Up to now, double-tube reactors had only been used for medium-pressure plant, and multi-plate ones for atmospheric pressure, but Roelen could see no reason why the double-tube reactor could not be used at atmospheric pressure. Theoretically, it was superior to a multi-plate reactor because a direct cooling surface was better than an indirect one. In addition, it gives a better catalyst distribution and ought therefore to give more even synthesis. If erecting a new plant he would design one suitable for both atmospheric and medium-pressure synthesis and would therefore use the double-tube reactor. If it were desired to increase the size of the individual reactors, then Roelen considered that this should be done by multiplying the number of tubes and not by increasing their length. Although he could give no experimental evidence to show how results were changed by changing over from a short to a long catalyst bed, he recommended always using the same length of tube in the pilot plant as in the full-scale reactor. A factor leading to differences was the entirely different sulphur distribution over a short and a long catalyst bed.

One problem that Ruhrchemie had constantly in mind was the possibility of designing a reactor to work at a higher temperature so that it could be used with existing iron catalysts. If water-steam cooling were used, this would involve making plant to stand much higher pressures. Roelen, however, favoured oil cooling instead. He had tried out a Diesel oil fraction, with initial boiling point above the highest temperature required for synthesis, as cooling liquid on a pilot plant scale. This worked perfectly satisfactorily for six months without any substantial change occurring in the viscosity of the oil. Thermal circulation was

sufficient on this scale but forced circulation might be required on the full scale. A chlorinated oil could be used to reduce the risk of fire, but Roelen thought that corrosion due to decomposition of the oil to give HCl would have to be watched for.

In the existing plant, corrosion has to be guarded against in the condensation system.

The wax from medium-pressure synthesis passes through the main from the reaction vessel and collects in a tank situated below the cooler. It is withdrawn mixed with some of the Diesel oil, the mixture having the consistency of cream. Corrosion (due to fatty acids) does not take place unless liquid water is present, so the main and collecting tank are kept hot enough to prevent condensation of water; this has the added effect of helping to prevent formation of wax-fog. In general it was important so to design the bottom of the reactors and the tubes leading from them that the issuing gases are not cooled too rapidly. Otherwise wax-fog is formed which is very troublesome in the condensing plant.

The Licensees. Although it was realized that the subject was outside Roelen's particular field, he was questioned about the main features of the Fischer-Tropsch plants in the Russian-zone of Germany, because little was known about them. He had not much new information however. He said that the plant at Ruhland - Schwarzhelde (Brabag) comprised only atmospheric-pressure units, and started production in 1939. Synthesis-gas was derived from brown coal, partly by the Koppers and partly by the Didier process. Roelen believed that both processes worked well after some initial difficulties. Each charge of catalyst was used for a fixed period (4 - 5 months) regardless of activity. This increased the catalyst costs but gave a more uniform output of products. The plant had its own catalyst factory, which, being erected later than that at Holten, incorporated some improvements, but Roelen could not remember what these were.

He was not certain what system of gasification was employed at the plant at Odertal (Schaffgotsch - Benzin), but stated that the synthesis plant there was entirely medium pressure and used the wide-tube reactors previously referred to by Prof. Martin. Heat transfer in these wide tubes was poor and temperature control was therefore difficult.

Asked about the high yield obtained at the plant at

Kamen - Dortmund (Essener, Steinkohle A.G.), as compared with the other German Plants, he attributed it to a variety of causes, the 'personality' of Dr. Schwenke and Dr. Löpmann, good plant control, possibly the use of active carbon purification of the gas before the fine-purification stage, possibly the use of a rigid time schedule for recharging the reactors, use of coke and coke-oven-gas from coke-ovens on the same site.

Roelen agreed that the performance of Ruhrchemie's plant at Holten was the poorest of all (except Wintershall) and said that this was due to the constant interference with the normal running of the plant by experimental work.

General. Roelen was of the opinion that a choice or comparison between atmospheric pressure and medium pressure could only be made on economic grounds. From the chemical standpoint the processes were very similar. Medium pressure gave a lower methane production but on the other hand the plant cost was higher.

Recent developments had not been fully examined economically. The costs of catalyst production at Lützkendorf, where special precautions were taken to cut down cobalt losses and dust formation to a minimum, would repay study. It was possible to use sulphuric acid in place of nitric acid in the preparation of catalyst (with considerable reduction in cost) if a special washing technique was employed involving washing with a dilute solution of alkali and then washing with water.

The cost of reduction of the catalyst might also be lowered. Trials had shown that a gas containing 70% H<sub>2</sub>, 30% CH<sub>4</sub> could be used successfully, the reduction temperature being just below the decomposition point of the methane. The use of converted coke-oven or town's gas thus appeared feasible with considerable saving in cost compared to pure hydrogen.

When asked, Roelen stated that recycling at atmospheric pressure improves the process but the gain is not sufficiently high for it to be economic.

Roelen was asked several questions as to the economic position of the Fischer-Tropsch synthesis. He said that the synthesis plants did in fact show a profit, with the help of indirect subsidies, including freedom from the tax imposed on imported fuel oils. The erection of new plants was also subsidised



indirectly. Changing over from fuel production to other products e.g. production of the maximum amount of wax to be sold as such, coupled with the maximum production of OXO - products might be more profitable but would depend entirely on the demand. The demand in Germany for hard wax had been almost completely satisfied (ca. 1943 - 4), and the sale of this product had become difficult.

## 6. Primary Products

Roelen described investigations which he had carried out on the determination of the content of  $\alpha$  - olefines in synthesis product by ozonization and estimation of the amount of formic acid formed. The method was simple and gave good results. The content of  $\alpha$  - olefines could be correlated with the origin of the spirit, being greatest for product from synthesis with recirculation and least for spirit obtained by catalytic cracking.

Production of an increased content of iso-compounds could be achieved with certain iron catalysts. Roelen quoted an octane number of 72 for the spirit boiling below 200°C. from a "Catalyst D" (composition unknown, but may have contained Tonsil as support). A high content of iso-compounds was proved by physical data of fractions from fine distillation. Catalysts giving this kind of product, however, gave a low conversion.

Diesel Oil. As far as Roelen knew, Fischer-Tropsch Diesel oil was used only in admixture with lower grade oils. Used alone it had too low a viscosity, which, however, could be overcome by adding a small amount of lubricating oil, and also too high a rate of ignition for the normal Diesel engine, leading to overheating. It was found to be excellent when used in specially designed engines.

Mixtures of aromatic oils with Fischer-Tropsch Diesel oils gave trouble due to continuous slow precipitation of sludge. Roelen had tried to improve this by adding an excess of the Fischer-Tropsch oil and filtering: Kälbel (of Rheinpreussen) had found a successful method in shaking the mixed Diesel oil with aqueous acid and salt solutions of a definite pH; this destroyed the colloid form of the sludge, which could then be filtered out.

The material known as "Ruhrchemie Cetane" was a narrow fraction of synthesis product distilled to give a cetane number of 100 for use as a standard of comparison and was not pure cetane. The original material sold as Diesel oil had boiling range 180 - 320°C., but about 1940 this was cut into two fractions the higher boiling one being used as starting material for the detergent 'Mersol'.

**Wax.** Apart from Ruhrchemie, the plants sent practically all their wax to Märkische Seifenindustrie at Witten, to be subjected to the air oxidation process. Ruhrchemie had their own wax factory, where the wax was separated into different fractions by distillation and sweating. (Roelen could not remember the exact details of the separation). Three main products were marketed:- hard wax, block wax (Tafelparaffin) and plastic wax. The hard wax was used for candles, polishes, the impregnation of paper and cardboard, e.g. for cartridges etc. and as a substitute for carnauba wax. The 'Tafelparaffin' was used as a constituent of polishes and lubricating emulsions. A certain proportion of the lowest fraction was combined with hard wax to give plastic wax; this mixture was used for the impregnation of paper, for electrical purposes, and as a general substitute for ceresin.

Waxes of high melting point (ca. 120°C.) could be obtained by extraction with solvents, in particular chlorinated solvents, on the laboratory scale, but no special use for these was known which would repay the cost of preparation. True plastic waxes which were probably iso-paraffins had also been obtained in the laboratory, but not on the technical scale. When asked as to the amount of iso-compounds in the wax fractions, Roelen replied that the position was not clear. I.G. assigned branched chain content to their waxes based on an estimation using antimony pentachloride but this was probably not very accurate.

In Roelen's opinion there was no real structural difference between cobalt normal- and medium-pressure waxes. Iron catalyst wax contained more branched-chain hydrocarbons than cobalt waxes.

**Fatty Acids.** Fatty acids in the primary products were recovered as fully as possible, the technique varying from plant to plant. Some of the licensees washed the total condensate with alkali giving the whole range of acids in a single solution. Ruhrchemie washed the various fractions after distillation and thus obtained several acid fractions. The most valuable was obtained by alkali extraction of the heavy oil as this contained the acids in the soap range C<sub>10</sub>-C<sub>17</sub>, mainly C<sub>11</sub>, C<sub>12</sub> and C<sub>13</sub>, and these were converted to soap, which was issued to the Ruhrchemie workers, production being at the rate of several thousand soap tablets per month. The process was never costed, but recovery of total fatty acids was  $\frac{1}{2}$  to 1 per cent. of the total primary product, about 40% of the total acids being suitable for soap.

The soap acids were not all straight-chain acids, as

shown by their having lower melting points than the n-acids of the same mean molecular weight. The smell of the soap was bad, but quite different from that of soap prepared at Witten, and it could be reduced to a large extent by evaporating the aqueous soap solution to dryness in a kneading machine and blowing the small particles of soap so obtained with hot air (at 140°C.). The purified soap had a brown colour due to the presence of iron, but in Roelen's opinion was better than most soaps then available in Germany.

Conditions had been found which led to an increase in fatty acid production (up to 2%) but only at the expense of the catalyst activity. Roelen thought, however, that a direct process to give fatty acids might be possible. Production of fatty acids depends on the amount of alkali in the catalyst, but addition of acetic acid to the synthesis gas, previously reported by Martin as a promising method of increasing fatty acid production, was not successful. Roelen's view was that the reaction giving fatty acids might be isolated from the hydrocarbon-synthesis reaction, as he had already done with the OXO-reaction which was originally considered to take place only as a side reaction during synthesis.

I.G. had claimed the direct synthesis of fatty acids from a gas mixture (identity not disclosed to Roelen) at Ludwigshafen: Roelen thought the process might be a reaction between carbon monoxide and steam.

Alcohols. A considerable proportion of the alcohols produced in the reaction is found in the reaction water and these alcohols can be obtained in a concentrated aqueous solution by distilling them off with about 10% of the water. The main constituent is ethanol but the amount produced from the cobalt catalyst process is not of peacetime technical interest.

The higher alcohols formed are present mainly in the spirit fraction; there are practically no alcohols present in the Diesel oil or higher fractions. Extraction of the alcohols with liquid SO<sub>2</sub> was not very successful. Extraction with calcium chloride solution had been tried in the laboratory, as had treatment with sulphuric acid to give the sulphuric acid esters. I.G. had tried an extraction with methanol but this did not give a sharp separation.

Roelen could give no information on the factors giving increased yields of alcohols or on possibilities of a direct synthesis of alcohols using a cobalt catalyst.

## 7. Secondary Products.

Lubricating Oils. Roelen could give little information on lubricating oil research or production. He was asked if there were any difficulties in using iron catalyst products as starting material. He could not remember details, but said that oxygen compounds had to be removed. He also thought that some iron products were difficult to polymerise and suggested that different iron catalysts might give different types of olefine. He said that zinc chloride had been used to remove oxygen compounds but thought that it had been superseded. Only aluminium chloride was used as polymerising agent as far as he knew.

He had no knowledge of investigations on Voltelisation at Holten.

Fatty Acids. The processes tried out for the production of fatty acids were:-

- (1) Oxidation of wax with air
- (2) Oxidation of wax with chromic acid
- (3) Oxidation of wax with oxides of nitrogen
- (4) Oxidation of OXO-aldehydes
- (5) Fusion of alcohols with alkali hydroxides
- (6) Electrochemical oxidation.

Ruhrchemie had discussed the various methods with I.G. and Henkel et Cie, and there was general agreement that none of the methods was satisfactory; all were laborious and gave a low yield of the acids most in demand. The development of the processes was largely determined by the war situation and it must be remembered that development in the future will be conditioned by other considerations. Roelen thought that synthetic fats would never replace natural fats as food as the former have a considerable content of branched-chain acids, and contain the odd numbered carbon chains as well as the natural even numbered ones; despite the assertions of Merkische Seifenindustrie he did not believe that sufficiently thorough biological tests had been carried out.

Many industrial applications had been found for the acids, including those acids which were originally considered to be by-products e.g. those of low molecular weight produced at Witten.

On the separate processes Roelen made the following comments.

The Witten air oxidation process does not run smoothly with paraffins of high molecular weight, and their normal starting

material was arranged therefore to have a final boiling point of 450°C. The reason for the bad smell of the soap made was not known, but Märkische Seifenindustrie claimed they could remove the smell (by a method unknown to Roelen).

The chromic acid oxidation process, which was investigated by Dr. Velde of Ruhrchemie, was inferior, both chemically and technically, to oxidation using oxides of nitrogen and nitrosyl-sulphuric acid. This latter process gave commercially valuable products from hard wax (these were the Ruhrchemie O.P. products), but Roelen believed that Velde was mistaken in thinking that very long-chain acids ( $C > 20$ ) were produced. He himself had examined acids which Velde believed to be practically pure, and was of the opinion that they contained considerable amounts of unsaponifiable material, so that no deduction as to their molecular weight could be made from their acid numbers. He had made up a synthetic mixture of hard wax and  $C_{12}$  fatty acid (prepared from OXO-products) which Velde regarded as a typical O.P. product.

Alkali salts of the fatty acids can be obtained by fusion of alcohols, which may be derived from the OXO-process, with caustic alkalis. The process gives a good clean product, but is expensive. A large-scale plant at Dessau operated this process before the war using naturally-occurring alcohols derived from whale oil etc.

The production of acids from the OXO-process aldehydes was easily effected by treatment with air at room temperature in the presence of alkali ( $CaO$  or  $Na_2CO_3$ ). Any smell present in soaps obtained by this method can be removed by treating the solid soap with hot air. One advantage of deriving washing materials from the OXO-process is the choice available between soaps, prepared by oxidation of the aldehydes to the fatty acids, and sulphonated alcohols, prepared by reduction to the alcohols and treatment with sulphuric acid. The sulphonated alcohols give a greater washing power per hydrocarbon unit.

Roelen had no information on the production of fatty acids by electrochemical methods.

## II. Developments not yet Practised on the Full - Scale.

### 1. Iron Catalyst Synthesis.

The more recent research work on iron catalysts was directed towards the production of a catalyst which could be used in the existing (cobalt) medium-pressure reactors, i.e., a catalyst suitable for a maximum working temperature of 230°C. The main criteria used for evaluating catalysts were:-

- (i) The percentage conversion of carbon monoxide and hydrogen to hydrocarbons, including methane, U.
- (ii) The amount of methane formed,  $M_v$ , expressed as a percentage of the total carbon monoxide and hydrogen converted.
- (iii) The utilisation ratio, X, the ratio in which the hydrogen and carbon monoxide have reacted, expressed as  $H_2/CO$ .

It is much more important for  $M_v$  to be small and X to have a suitable value, 1 or greater, than for U to be high, although naturally U should be as high as possible. The reason for this is that, if  $M_v$  and X are right, U can be increased to any desired amount by adding further stages, whereas if X is unsuitable such stages cannot be added, and if  $M_v$  is large synthesis gas is wasted.

Developments on the lines indicated above i.e., low-temperature medium-pressure synthesis, were tested by an official comparative test (the Reichsamtversuch) in 1943 at Ruhland-Schwarzheide, for which a number of firms submitted their best iron catalysts. Roelen gave the following account of Ruhrchemie's part in this test. The first catalyst submitted had the composition Fe 100: Cu 5: CeO<sub>2</sub> 10: kieselguhr 50. It gave U = 54.2,  $M_v$  = 3.9 and X = 0.722. The yield of products /m<sup>3</sup> was comparatively low, but the yield referred to the iron content was high since the catalyst only contained 240 g. Fe/l. as compared with figures of 500-1000 g. Fe/l. for other catalysts. Further, the Ruhrchemie catalyst was easy to run, during both the main course of the experiment and the starting up period. The result of the comparative trial was inconclusive and a repeat was proposed.

For this Ruhrchemie developed another catalyst, containing no cerium, of composition Fe 100: Cu 5: CaO 10: kieselguhr 50, containing 270 gm. iron per litre of catalyst, which gave  $M_v$  = 5.9%, U = 51% and X = 1.15, U being comparatively low but X good. Results for a test run of this catalyst are given in Appendix IV. The second Reichsamtversuch, in which only Ruhrchemie and one other firm (which Roelen thought was I.G. Farbenindustrie A.G.) took part, was

cut short by external circumstances after 170 hours.

Details of a further improved catalyst, according to Roelen the most active made by Ruhrchemie, are given in Appendix V (Experiment 595). This had the composition Fe 100: Cu 5: CaO 10: kieselguhr 30 and gave  $M_v = 7\%$ ,  $U = 63\%$ ,  $X = 1.1$ . It was run with recirculation, ratio 1: 2.2, and was still of high activity after 5 months, when the reaction temperature was  $220^\circ\text{C}$ .

Roelen stated that the method of preparation, amount of alkali added and the method of adding it, washing and reduction were of greater importance in determining the properties of iron catalysts than for cobalt, and could effect wide variations in catalysts of the same composition. He had not tried amounts of kieselguhr lower than 30 parts per 100 parts iron for normal purposes, as he considered that large-scale filtration would be very difficult with lower kieselguhr contents.

The kieselguhr used for iron catalysts was the same as for cobalt, and no attempt had been made to select kieselguhrs specially suitable for iron catalysts.

Roelen had tried many iron catalysts and although it was known that variations in the CaO and Cu content of the catalyst affected the results, and in particular X, research had latterly been restricted to catalysts with the basic ratio Fe 100: Cu 5: CaO 10, so that the influence of the other variables could be investigated first. The effect of some of these variables was then discussed. Increasing the amount of alkali increases the catalyst activity and the average molecular weight of the product, but decreases X, i.e., leads to increased production of  $\text{CO}_2$ . A change from straight-through running to recirculation always causes a marked increase in the value of X. Increasing the amount of kieselguhr decreases the average molecular weight of the products. Reduction with hydrogen gives a catalyst favouring the production of methane and lighter hydrocarbons. Ruhrchemie had found that pre-treatment with water-gas in place of hydrogen, as suggested by the K.W.I., decreased methane production, an effect which had not been found by Pichler at the K.W.I. The advantages of carrying out the pre-treatment with water-gas at  $1/10$  atm. pressure, as originally described by the K.W.I. could be reproduced by diluting the water-gas with nitrogen and using a partial pressure of  $(\text{CO} + \text{H}_2)$  of  $1/10$  atm. at a total pressure of 1 atm.

Asked whether the results obtained for single-stage working could be used to estimate performance with 2 stages, Roelen said calculation would give a general idea but as X was rarely ideal,

the second stage would be using a gas of different composition from the first and the effect of this could not be estimated exactly.

The calculation of X for recycle operation from the value obtained with the same catalyst in straight-through running had not been attempted but Roelen thought it might be possible to correlate the values from figures already determined, and promised to look into this point. For direct running a change in the ratio of  $H_2/CO$  in the synthesis gas would affect X but only to a slight degree. Roelen estimated that a catalyst giving  $X = 1.10$  for gas of  $H_2/CO$  ratio of 1.25 would give  $X = ca. 1.08$  for a gas of ratio 1.10.

When asked specifically whether a Reduction Value was determined for iron catalysts as in the case of cobalt, Roelen said that the accuracy of the determination was low and a thorough investigation had not been carried out. It had been found that too much reduction increased methane production and decreased activity in general. A special trial was really needed for each iron catalyst made.

When asked, Roelen said that iron catalysts were much more difficult to reproduce. Good reproducibility was obtained for different batches if all the steps were decided in advance and adhered to strictly, but there were more factors requiring great care than for cobalt. In addition, the differences that might arise from uncontrolled and unnoticed variations in the experimental technique for the preparation were sometimes as great as were to be expected from a deliberate variation in the chemical composition of the catalyst. This is a result of the extreme flexibility of iron catalysts.

Mixtures of the catalytic metals had been considered by Ruhrchemie. Cobalt-iron mixtures were impossible (iron being a poison for cobalt) but nickel-iron mixed catalysts were tried and found to give saturated products with high methane production.

When asked for his views on the use of synthesis gas enriched with carbon monoxide, Roelen said that he regarded this as a retrograde step. Originally gas with a  $H_2/CO$  ratio of 0.67 had been used with iron catalysts because this represented the proportions in which the gases reacted with early types of catalyst. In developing catalysts which would utilise carbon monoxide and hydrogen in the ratio approximating to that found in water gas Ruhrchemie considered that they had made an advance and that this was the most economic line to follow.



He agreed that carbon-monoxide-rich gas should give higher olefine production and that there were no real difficulties in the technical production of such a gas.

Finally, it may be mentioned at this point that Roelen said that medium-pressure synthesis with cobalt catalysts containing 2-5% alkali resembles synthesis with iron catalysts in giving large amounts of CO<sub>2</sub>. Such cobalt catalysts have no technical interest.

Products. Iron catalysts are remarkable in producing a very much larger amount of ethane than cobalt catalysts, and frequently equal amounts of methane and ethane are obtained. They also give higher yields of wax (excepting cobalt-manganese catalysts, see p. 8) and larger amounts of branched-chain hydrocarbons.

Roelen suggested comparative figures for the hard wax i.e. material b.p. > 450°C. would be:- normal-pressure cobalt 3%, medium-pressure cobalt 25%, iron 50% of the total product. He thought that substantially the same type of fatty acids could be obtained by the oxidation of wax from iron catalysts as from cobalt. He could suggest no figure for the proportion of branched-chain hydrocarbons present in iron-catalyst wax. The presence of oxygen-compounds made the iron-catalyst waxes more plastic and more similar in properties to natural ceresin, but they had not been tested, as far as he knew, for industrial purposes.

Formation of Oxygen Compounds. It was originally thought that the high proportion of oxygen compounds in iron-catalyst products was connected with the presence in the catalyst of cerium, vanadium etc., which are known oxygen carriers, but later catalysts which did not contain these metals, were found to give a high yield of oxygen compounds. Ruhrchemie had not investigated the production of oxygen compounds systematically and the factors affecting it were not fully known. For catalysts with the composition Fe 100: Cu 5: CaO 10: kieselguhr 50 precipitation with potassium carbonate favours the production of oxygen compounds.

As an instance of the results which could be obtained, Roelen gave an account of the following experiment (Expt. 650, Appendix VI):-

The catalyst, prepared on the pilot plant scale, had the composition Fe 100: Cu 5: CaO 10: kieselguhr 5, was precipitated with sodium carbonate, and alkalisied with 3% potassium hydroxide. The iron density was 1726 g. per litre. The catalyst was reduced in hydrogen for 24 hours at 325°C. Synthesis, with water-gas at 10 atm. without recirculation, began at 140°C., conversion of CO

being 31%, conversion of H<sub>2</sub> - zero (Roelen attributed this to carbide formation). The temperature was raised slowly and at 155°C. CO conversion was 40%, H<sub>2</sub> conversion still zero. At 160-180°C. hydrogen began to take part in the reaction and CO + H<sub>2</sub> conversion reached 40%. After 50 hours the temperature had reached 205°C., M<sub>v</sub> was 13% and X, 0.67. After 100 hours, at 206°C., M<sub>v</sub> was 18%, but after 150 hours methane production increased to 76% with a rapid increase in temperature.

The product from this experiment was found to contain 61% of oxygen compounds in the fraction boiling below 200°C., 72% in the fraction < 320°C. and 63% in the fraction > 320°C. The latter (wax) fraction resembled natural waxes in being plastic and not brittle like hydrocarbon waxes. Roelen considered that the properties of this catalyst might be due in part to the reduction treatment, but the change over to methane formation he attributed to the low kieselguhr content.

When asked, Roelen said that cerium and vanadium might be of value in increasing still further the production of oxygen-compounds with these new iron catalysts. He was not sure of the structure of the alcohols obtained from iron catalyst but his opinion based on their melting points was that they were mainly primary alcohols with a fairly high proportion of branched-chain compounds.

The effect of pressure on oxygen compound production was not in accordance with Fischer's original suggestion that high pressure favoured their formation. Over the range 10 - 100 atmospheres the maximum oxygen content had been found for 20 atmospheres. At one atmosphere pressure iron catalysts give a high olefine content but practically no oxygen compounds; formation of the latter begins at about 5 atmospheres. At atmospheric pressure one iron catalyst (Catalyst 2181, Appendix VII) had given 84% of olefines in the fraction of product boiling 200 - 320°C. on the laboratory scale; this was not reproduced on the 50 litre scale, however, when the olefine content in the heavy oil was only 52%. (The difference, in Roelen's opinion, was due to the longer catalyst bed on the larger scale and hence greater opportunity for hydrogenation of the products liquid at synthesis temperature. At 10 atm. this catalyst gave a product containing equal amounts of olefines and oxygen compounds.

Research Work, other than that of Ruhrchemie. Roelen was asked for his personal views on investigations carried out on iron catalysts by establishments other than Ruhrchemie. His replies are given below.

Kaiser-Wilhelm Institute. As mentioned before, the absence of

kieselguhr in the K.W.I. catalysts would probably cause filtration difficulties on the large scale. The difference in catalysts due to the content of ferrous as against ferric iron was a question which Ruhrchemie might have investigated more closely but the difference between the results obtained by the K.W.I. with ferrous catalysts and those of Ruhrchemie with ferric catalysts was not great enough to be fundamental. No comparative experiments had been done however. Roelen considered that ferrous iron gave silicates in the presence of kieselguhr.

He did not know the composition of the K.W.I. Reichsamtversuch catalyst nor whether it contained ferrous or ferric iron.

I.G. Farbenindustrie A.G. Roelen had no knowledge of the "Synol" process, and could not remember the composition of the Reichsamtversuch catalyst. He knew, however, that it had a very high iron density, and gave so high a conversion to carbon dioxide that practically no carbon monoxide was left in the residual gas. He had seen the 100:1 recycle process in its early stages and considered it a promising development, especially for the production of olefines of low molecular weight. The catalyst bed used was 1 - 2 m. across. Roelen agreed that the method of heat dissipation was attractive, but pointed out that the chemical engineering difficulties, the large size of the gas blowers and their heat insulation, the separation of the products from large volumes of hot gas etc., would have an adverse effect on the economics of the process. He was of the opinion that the high octane number claimed for the products was mainly due to the high olefine content, but was prepared to accept the I.G. claim that iso-hydrocarbons were formed. The formation of iso-compounds under similar conditions had been claimed by Fischer at a secret conference in 1939-40.

Lurgi. Roelen thought that there was little difference in effect between aluminium oxide as used by Lurgi and lime as used by Ruhrchemie as an iron catalyst promoter. Ruhrchemie had persevered with lime partly from the patent standpoint and partly to keep one of the variables constant. Roelen would give no opinion as to whether Lurgi or Ruhrchemie were further ahead in the development of iron catalysts, but the Reichsamt trials had shown there was no great difference in the performance of their catalysts.

Roelen stated that Lurgi always added alkali silicate to their catalysts in place of alkali. They claimed that the use of water-glass decreased methane formation without changing the utilisation ratio X, and also that X could be changed by washing alkali out of the catalyst without change in Mv or U. Ruhrchemie had made some trials in which the presence of silicates was ensured

without adding water-glass (which Lurgi had patented) by heating 10% of the kieselguhr with the alkali before precipitation of the catalyst and adding the rest afterwards. It was finally decided to abandon such a procedure, as it led to unknown contents of alkali, silicate etc. There was a definite difference in effect, as found experimentally, between alkali added as potassium hydroxide and as potassium silicate. Despite the use of alkali silicate, Lurgi had not succeeded in raising X above a value of 1.0 - 1.1 and Roelen thought the advantages Lurgi claimed for water-glass could now be obtained in other ways, although addition of water-glass might still prove convenient in the technical scale preparation of catalysts.

Rheinpreussen. Roelen said he knew little of Rheinpreussen developments as Dr. K lbel was very secretive; K lbel's claims to have obtained results similar to those from cobalt catalysts were based on the use of extreme conditions of gas rate and multi-stage working. A catalyst of the composition Fe 100: Cu 5: CaCO<sub>3</sub> 120 had been tried but was probably only one of several lines of development. Calcium carbonate was originally added as solid, but was later precipitated. Powdered dolomite was also tried. The catalysts were usually reduced with hydrogen but Roelen thought the use of water-gas pretreatment was being investigated.

Roelen gave some data for the Rheinpreussen catalyst used in the first Reichsamtversuch but he did not know its composition. The catalyst was difficult to "run-in" and four attempts had to be made before satisfactory results were obtained. Total conversion (U) was 58.8%, Mv was 7.4 and the utilisation ratio X, 1.09, the latter being the highest value recorded in the first Reichsamtversuch, but lower than that given by Ruhrchemie's catalyst in the second Reichsamtversuch.

Brabag. The catalysts used were of approximate composition Fe 100: Cu 80-90: Zn 80-90. Zinc oxide was added as such or was co-precipitated with the other components. Such a catalyst was very expensive and gave a low X value but was very active. Roelen believed that Brabag tried a carbon dioxide pretreatment (though this was probably not their regular method) followed by a reduction treatment with hydrogen or carbon monoxide.

Present Status of Iron Catalysts. When asked whether he thought an iron or a cobalt catalyst would be chosen for a new technical-scale plant, Roelen replied that at present the choice of cobalt would be safer, but thought that the future lay with iron catalysts. The decision depends on whether iron catalysts already made and tested on a small scale can be made and used on the large scale. The manufacture of iron catalysts had been carried out in the catalyst

factory at Holten and therefore Roelen thought that there would be no difficulty in making the catalysts with fair reproducibility. Iron catalysts are less sensitive than cobalt to variations in the purity of the constituents, but there are more factors in the preparation requiring care. They are more flexible in the sense that a wide variation in operating conditions and type of product is possible. This flexibility is to some extent a source of difficulty where a definite product of constant composition is desired. As Roelen put it, "iron catalysts possess the disadvantages of their virtues".

The costs of manufacture of iron catalysts had been reduced by the use of sodium carbonate as precipitating agent in place of potassium carbonate but they were still approximately the same as for cobalt catalysts, depending on the amount of kieselguhr incorporated, increase in kieselguhr content increasing the cost of iron catalysts. A less pure kieselguhr might however, be used, as the impurities (e.g. Fe, Ca,) obviously have no deleterious effect on iron catalysts.

It was intended to regenerate iron catalysts by a wet process, which would dissolve the copper and 80 per cent. of the iron, using dilute nitric acid, but the process had not been fully worked out, particularly from the point of view of the impurities likely to be present (Al, Pb etc.), but no great difficulties were expected. The regeneration would be worthwhile for the sake of the copper, and also for the ease of solution of most of the iron in the finely divided state. Solution of the last 20% of the iron would probably be uneconomic. It was also proposed to recover the calcium. The use of water-gas pretreatment instead of hydrogen reduction would further cheapen iron catalysts as compared with cobalt.

Iron Catalyst Atmospheric-Pressure Synthesis. Attempts were also made to produce an iron catalyst which would work at atmospheric pressure and at a sufficiently low temperature to be used in the atmospheric-pressure plants instead of cobalt catalysts. It was not too difficult to produce catalysts which were active under these conditions but X was always too low, on account of excessive formation of CO<sub>2</sub>. One of the better of such catalysts had the composition Fe 100: Cu 5: CaO 10: kieselguhr 100 and contained 240 g. Fe/l., but Roelen could not remember the exact details of the preparation. When reduced with hydrogen this catalyst gave a large amount of methane, but pretreatment with water-gas improved it in this respect. Synthesis began at 140°C. and U was about 50% with X = 0.8 - 0.9, and the products had a low boiling range. Values of X higher than 1 had not been obtained at atmospheric pressure. Roelen was of the opinion that atmospheric-pressure iron catalysts were feasible but pointed out that it might be difficult to develop one which would give satisfactory values for U, M<sub>v</sub> and X.

## 2. Liquid-Phase Synthesis

About 1940 Roelen said that he put up a simple apparatus (c.f. Figure 1) consisting of a 5 m. tube, 0.2 - 0.3 m. diameter fitted with a water jacket, to investigate liquid-phase synthesis from the chemical point of view. Earlier experiments had been done from the engineering standpoint and he felt that too much attention had been paid to elaborate devices for ensuring intimate mixing of the liquid, catalyst and gas and not enough to the fundamentals of the process. At first he used a glass sinter at the bottom of his reaction tube to distribute the gas but later this was found to be unnecessary. The level of liquid in the tube was maintained constant by removing excess, as it was made, through a filter stick so that no catalyst was removed from the system. Volatile products were continuously removed as vapour.

Using a cobalt catalyst at atmospheric pressure, conversion was poor, and iron catalysts at atmospheric pressure needed mechanical stirring to give as high an output as in vapour-phase synthesis. With pressures of 10 atm., the results were as good as for ordinary synthesis. The catalyst had as long a life and the plant could be run for months without trouble.

Using iron catalysts of normal composition, at 240°C., and with water gas, he found that there was an upper limit to the amount of catalyst that could be usefully employed, determined by the solubility of the synthesis gas in the liquid medium. Using this amount of catalyst, the slurry flowed quite freely. As a run proceeded the concentration of wax in the liquid medium gradually increased, till, after about a month, only wax hydrocarbons were present. It was found quite feasible to start with wax as the liquid medium and this was later adopted as standard procedure. The catalyst can be added after reduction with hydrogen or in the unreduced form. If normal hard wax is used as suspension medium it becomes more plastic during the course of the reaction. There was some tendency for the catalyst to settle out of the suspension but this could be overcome by using several short tubes in series in place of one long one.

The throughput was the same as for ordinary synthesis per unit weight of catalyst, but lower per volume of catalyst space.

Recycling of gas was tried and found to give successful results; it made a considerable improvement in the stability of the catalyst suspension.

Using a normal iron catalyst, Roelen had found that the utilisation ratio X was decreased by adding alkali to the system. Addition of acids increased X. Fatty acids could be used but the effect wore off as these acids were gradually destroyed. Roelen found a suitable acid was boric acid, which was not a poison and was not destroyed under the synthesis conditions. Acids or alkalis could be added as solids, and changes in X could be correlated with the amounts added.

Evacuation of the oil withdrawn from the reaction vessel had shown that carbon monoxide was more soluble than hydrogen; the ratio of the gases in the liquid phase was therefore different from their ratio in the synthesis gas. Since the gases are not perfect, the ratio may vary with pressure and this factor may have a bearing on the best pressure for liquid-phase synthesis (Roelen agreed that this factor may be of importance in ordinary synthesis when the gas solubilities in the oil films are considered).

Asked about methane production in liquid-phase synthesis Roelen said that although it may have been lower than for ordinary synthesis in the past, more recent catalysts would give a methane production of less than 5% for ordinary synthesis; i.e. approximately the same as for liquid-phase synthesis.

Roelen had no knowledge of Rheinpreussen liquid-phase synthesis developments and he did not think that circulation of the oil and catalyst mixture as practised by Bamag materially affected the fundamental reaction.

A subject closely related to liquid phase synthesis is the use of an oil spray over a fixed bed of catalyst to control the temperature and remove wax continuously. Roelen said that investigations of this were interrupted by bombing before results were available, but it had been found that the catalyst granules were robust enough to allow oil spraying to be used without breaking down to give large amounts of dust. Brabag had tried continuous oil dewaxing in a laboratory (glass) reaction tube, but Roelen did not think that any advantages were found.

### 3. Iso-Synthesis

Roelen said that he wanted to investigate the possibilities of the K.W.I. Iso-synthesis process but was unable to obtain the necessary alloy steel or labour to construct a reaction vessel. He proposed to use a bath of molten salt to regulate the temperature. He felt that the feasibility of the process depended to a great extent on the development of a suitable reaction vessel, and thought

that it might be practicable to use gas circulation to control the temperature, as the heat loss by radiation would be high at the temperature used. The risk of carbon deposition was obviously high and it might be that only a few of the possibilities successful on the laboratory scale would be worth considering technically. He knew of no plant which had been set up apart from the original one at the K.W.I. In his opinion it was much too early to judge the value of the process.



### III Other Developments

#### 1. Synthesis with Ruthenium.

The ruthenium catalyst developed at the K.W.I. has the advantage of giving a very low yield of methane and a high yield of higher hydrocarbons; temperature control will also be easier and it might be possible to use a simpler type of reaction vessel. The high yield of hard wax need not make the process less attractive, as a large proportion of this could be cracked without giving an overall yield of methane as high as is normally got from the cobalt catalyst process (without cracking of wax). The catalyst has a long life and should be easy to regenerate. No experiments had however been carried out apart from those on the laboratory scale at the K.W.I., owing to the scarcity of ruthenium.

#### 2. Incorporation of Acetylene

Roelen had carried out some investigations on the addition of acetylene to the synthesis gas used for both cobalt and iron catalyst synthesis. Using a cobalt catalyst of composition Co 100: ThO<sub>2</sub> 5: MgO 8: kieselguhr 200 with 90% water-gas and 10% acetylene at 10 atm., considerable amounts of oxygen compounds were formed although the total yield of products was low. The variations in the products with synthesis temperature were studied. Increase in temperature decreased the yield of olefines and increased the yield of oxygenated compounds, while also increasing the yield of alcohols at the expense of aldehydes. Comparable figures were:-

at 155°C.	70% olefines 33% aldehydes 10% alcohols	} in spirit, b.p. < 180°C.
at 170°C.	37% olefines 15% aldehydes 15% alcohols	} in spirit, b.p. < 150°C.
at 185°C.	27% olefines 7.0% aldehydes 48% alcohols	} in spirit, b.p. < 150°C.

Spirits with an octane number of as high as 80 were obtained.

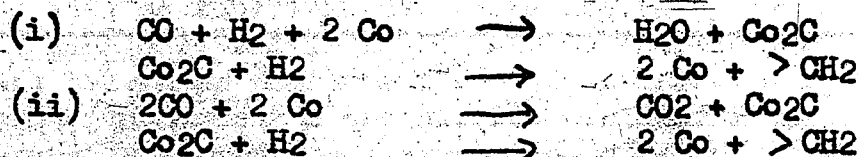
In a similar experiment, an iron catalyst of composition Fe 100: CaO 10: kieselguhr 100: precipitated with KOH to pH 9.3 and pretreated with water-gas at 250°C. at atmospheric pressure, was run

at 200 - 212°C. and 10 atm. with a synthesis gas containing 90% water-gas and 10% acetylene. The total yield was 26g. / Nm<sup>3</sup>, UCO:H<sub>2</sub> being 8; the residual gas contained 4% unchanged acetylene. The spirit fraction boiling below 100°C. amounted to 39% of the total product and contained 65% olefines and 19% total oxygenated compounds. The olefine content rose to 100% in the higher fractions including the wax boiling above 320°C. This wax was soft and in Roelen's view probably contained a large proportion of iso-compounds. Roelen considered that these results, which were obtained in about 1940, were promising and further investigation would be desirable especially if a supply of cheap acetylene were available.

Dr. Tramm, of Ruhrchemie, claimed that if acetylene were mixed with the synthesis gas used with a cobalt-thoria catalyst supported on a mixture of kieselguhr and pumice high yields of olefines were obtained at atmospheric pressure without producing oxygen compounds. This was investigated by Roelen but was not confirmed, as up to 8% of oxygen compounds were obtained, with an olefine content in the spirit boiling below 155°C. of about 50%.

### 3. Reaction Mechanism

The first step in the synthesis is, in Roelen's opinion, the formation of carbide. The decomposition of the carbon monoxide with the removal of the oxygen is the rate-determining step, and not the desorption of the products. The reaction could take place by either of two routes:-



Roelen thought that both reactions may occur but prefers (i) as the main reaction. On the basis of experimental work showing that drying the synthesis gas increases output and adding steam decreases output, Dr. Ritter of Krupp Treibstoffwerk argues that the water-gas shift reaction is taking place under synthesis conditions, thus accounting for CO<sub>2</sub> formation without postulating (ii).

In Roelen's view the CH<sub>2</sub> groups are formed at the more active spots on the catalyst (i.e. the corners and edges) and then migrate to the less active areas (planes). A considerable number of CH<sub>2</sub> groups in juxtaposition then react simultaneously, activated by an increase in energy above the mean level at some point which passes through the group as an energy wave causing union of the CH<sub>2</sub> groups to give an olefine molecule. Roelen

considers the mobility of a hydrogen atom under such nascent conditions sufficient to give the necessary rearrangement. The  $\text{CH}_2$  groups are not linked in any way before this coalescence, and the size of the hydrocarbon molecule formed is determined only by the number of  $\text{CH}_2$  groups which are in close juxtaposition. The preferential formation of normal straight-chain hydrocarbons is a result of the probability that the energy wave will not branch along two separate routes and not of any special mechanism.

The formation of metal carbide from CO is a slow reaction but it may be increased by local increases in the catalyst temperature due to synthesis also taking place on neighbouring atoms. When water-gas is passed at a very slow rate over a fresh catalyst, oxygen is removed from the gas before synthesis starts, but Roelen could not suggest what reaction was taking place although it might be concerned in carbide formation. With the normal gas rate, hydrocarbon synthesis starts almost immediately.

It was an experimental fact that alkali present in the catalyst increased the production of carbon dioxide. This could be accounted for as follows, without the need to postulate reaction (ii). Alkali can combine with carbon monoxide to give formate which then decomposes to formic acid. It has been shown experimentally that under synthesis conditions in the presence of catalyst formic acid is decomposed with formation of carbon dioxide although it is stable at  $200^\circ\text{C}$ . in the absence of catalyst. If no alkali is present the metals cobalt and iron themselves can function in a similar way although to a smaller extent.

Roelen considered that metal carbonyl took no part in the reaction. The OXO-reaction was not catalysed by nickel since the latter forms no hydrocarbonyl. Since nickel catalysed the Fischer reaction, the latter did not include hydrocarbonyl formation and therefore probably not carbonyl formation as a normal stage.

Formation of high-molecular-weight hydrocarbons could not be due to polymerisation of olefines, since the hydrogenating power of nickel was so great that olefines formed would be hydrogenated before polymerisation could occur. In this connexion, Roelen mentioned that the presence of ammonia in the synthesis gas increases the yield of wax. The reason was not known, and the effect was too small to be of technical interest.

The production of methane is probably due to the breaking away of single  $\text{CH}_2$  groups from the catalyst surface, but there was also some tendency for higher hydrocarbons to decompose with production of methane. Roelen was questioned about the reverse

reaction to this, namely, the incorporation of methane or higher paraffins in the synthesis, but he said that he had never observed it and that he was ignorant of Dr. Velde's proposed work on it. In general, however, he expressed the view that a number of side reactions might take place to a small extent during synthesis which could not be realized separately.

Asked about the results obtained by replacing ordinary hydrogen by heavy hydrogen in the synthesis, Roelen said that Ruhrchemie had carried out such experiments. With a cobalt catalyst the reaction was slower than with ordinary hydrogen but the products were similar. He thought it would be possible to utilize heavy hydrogen in elucidating the reaction mechanism, in particular, the sequence of stages in the synthesis.

#### 4. Experimental Plant

Pilot-Plant Scale. Although Ruhrchemie operated experimental plants varying in catalyst capacity up to 1000 l. ( $1/10$  full-scale), the bulk of their process development work was carried out in 5 l. converters. The reaction vessel and experimental arrangements used are shown in Figure 2. The reaction tube could be either a single or a double tube. The thermo-regulator operating a relay connected to the electric heater gave a temperature variation of not more than  $\pm 0.3^{\circ}\text{C}$ . Spirit was usually collected in active carbon, a large excess being used, but refrigeration was used in special cases. Direct condensation with a water spray was never used on the pilot-plant scale. The same reaction vessel was used for normal and medium-pressure work. At medium pressure only one input meter was used for several plants, being connected in the gas line before the compressor and measuring the input to the common pressure reservoir. For the individual plants the gas rate etc., was calculated from the residual gas rate, measured at atmospheric pressure, and the process and residual gas analyses. When recycling experiments were being carried out, the recycle gas was usually metered at atmospheric pressure and recompressed. Recycling had been done, however, without decompression by using orifice meters but these were very inaccurate. Pressure meters consisting of an ordinary atmospheric-pressure dry meter in a pressure case had been used.

At medium pressure the wax issuing from the reaction tube was kept fluid by an electric heater. A double separating vessel was used, the lower section being under atmospheric pressure.

If any blockage occurred in the catalyst bed the practice was to shut down and start with fresh catalyst. If the gas flow had to be stopped for a short time the outlet might be shut and

the catalyst left under pressure of process gas, but it was preferable to replace the gas with hydrogen.

In the pilot-plant laboratory the night shift consisted of two workmen in charge of eight 5-litre plants and one liquid-phase plant, who took one set of readings per hour per plant. All active-carbon steaming etc., was done during the day shift when more staff was present.

Laboratory Scale. The design of apparatus used is shown in Figure 3. The heating furnace was built up from lengths of drawn aluminium of suitable section to take four or eight glass or metal reaction tubes, each with a catalyst capacity of 50 ml. in a 50 cm. bed. The main work done was the testing of the activity of new catalysts, so the reaction tubes were arranged at a slight inclination to the horizontal to avoid blockages due to dust or swelling. Temperature was regulated automatically to within  $\pm 0.5^{\circ}\text{C}$ ., and a separate alarm, set to ring a bell if the temperature rose  $2^{\circ}$  above the desired value, was fitted to give warning of the failure of the thermostat due to changes in the electricity supply or to other causes. Two hundred and forty experiments could be carried out simultaneously, flow meters being used to measure the gas rates. An accurate yield, calculated from the gas analyses, was determined about once a week for each experiment. Four assistants per shift formed an adequate labour force; gas analyses were carried out in a separate laboratory.

Experiments at medium pressure were done in a similar apparatus using metal tubes but the scale was slightly increased by increasing the tube diameter.

For analysis of the gasol by low-temperature fractionation a Podbielniak or similar type of column was available. Roelen knew of no other way for the accurate determination of the yield and composition of the gasol fraction. For distillation of the liquid products many different columns had been tried. That normally used for exact fractionation had a platinum spiral packing and was fitted with a vacuum jacket. The capacity of the boiling flask was 100 ml. Roelen could give no figure for the column efficiency.

Sulphur Estimation. The pilot and laboratory plants used purified gas drawn from the works supply to the large-scale Fischer-Tropsch plant. On the technical scale two or three estimations were done per day, the gas being burnt and sulphur estimated as  $\text{SO}_4$ . I.G. had developed automatic sulphur recorders but Ruhrchemie had not found them necessary.

#### IV. The OXO - Synthesis

Roelen stated that he first predicted the possibility of the OXO-synthesis in 1938 but realisation of the reaction had to wait on the development of suitable plant. At atmospheric pressure with a cobalt catalyst very little OXO-synthesis takes place even with ethylene although aldehydes can be detected in the products. At a pressure of 50 atm. the OXO-synthesis goes well, but further increase in pressure (to 100-150 atm. or higher) is really necessary. The smallest-scale apparatus used by Roelen was a steel, tubular autoclave, total liquid capacity 50 ml., which could be shaken within a aluminium block electric furnace (of design similar to the small-scale synthesis apparatus, Figure 3). The next large scale was a 4-5 litre autoclave, liquid charge usually 2 litres, fitted with a stirrer. Both these plants were connected to a static water-gas supply at a suitable pressure. The smallest apparatus with gas circulation was a water-jacketed tube, of 10-litre capacity, using a liquid charge of 5 litres. (The design followed the lines of the hydrocarbon-synthesis pilot plant, Figure 2). A larger 90-litre capacity plant with a vertical tube was also used. The length/diameter ratio for the tubular plants is not critical.

In all these cases the finely powdered catalyst was kept suspended in the liquid contents of the autoclave either by shaking or by the gas circulation. The heat evolved per unit volume of reaction space is slightly greater than for hydrocarbon synthesis so that normally this heat cannot be removed by the circulating gas, although by using a fixed bed of catalyst in a more complicated apparatus I.G. had had some success with this method of cooling. Ruhrchemie had investigated the possibilities of catalysts in a fixed bed, with single passage of gas, recirculation of gas, circulation of gas and liquid, etc. The best method depended on the olefine used, but in all cases cobalt is removed from the catalyst. I.G. counteracted this by addition of cobalt in the form of fatty acid salts, and obtained good results with fixed-bed catalysts for propyl aldehyde synthesis.

Roelen agreed that the reaction had to be done in the liquid phase. With gaseous olefines such as ethylene a liquid medium must be used e.g. water or toluene, as otherwise the concentrated aldehydic product tends to polymerise and the polymers dissolve out cobalt from the catalyst in large amounts. Temperature control did not have to be so accurate as for hydrocarbon synthesis. The optimum temperature varies from 115°C. for ethylene up to about 140°C., depending on the molecular weight of the olefine, using normal cobalt: thoria: magnesia catalyst, reduced with hydrogen at

350°C. and powdered under oil. A reaction temperature lower than the optimum favours the production of by-products. Pressures above 150 atm. were found by Roelen to offer no advantage. The catalyst can be regenerated by filtering it out of solution and then reducing it with hydrogen in the filter. The useful life of the catalyst before regeneration was necessary, depended on many factors - olefine used, type of plant etc.

1. Production of Propyl Aldehyde. I.G. carried out the synthesis of propyl aldehyde with a fixed-bed catalyst in an aqueous system. The gas used contained equal volumes of carbon monoxide, hydrogen and ethylene. Reaction temperature was 150 - 200°C. and pressure 150 - 300 atmospheres. The rate of water circulation was adjusted so that the issuing solution contained 2 - 3% of propyl aldehyde which was removed by distillation and the water recirculated. For complete conversion of the ethylene the products consisted of 65% propyl aldehyde, 20 - 25% ethane and 10 - 15% of by-products (propyl aldehyde polymers etc.). The cobalt concentration in the catalyst, which Roelen thought contained 0.5 - 1% cobalt with pumice as support, was maintained by the addition of cobalt salts of fatty acids to the ingoing water.

Ruhrchemie prepared propyl aldehyde in the presence of toluene chosen as solvent because it was easy to separate from the products. At the optimum temperature, 115°C., the yields were, for complete conversion of ethylene, 70 - 80% propyl aldehyde, 15% other products including ethane, methyl ethyl acrolin and diethyl ketone, and 5% loss. The reaction mixture used contained 5 l. ordinary cobalt: thoria: magnesia: kieselguhr catalyst in 30 kg. toluene; this will give three times its volume of product without complete loss in activity. An account of the method of working is given in Appendix VIII.

2. Catalyst. Roelen's opinion was that the reaction mechanism involved the formation of cobalt hydrocarbonyl(s) as the active catalyst. This was partly based on the fact that nickel does not catalyse the OXO-synthesis and it is known that nickel does not give hydrocarbonyls. It had been found that the cobalt could be introduced in several forms and reduced cobalt metal was not necessary. Thus cobalt carbonyl, prepared separately, was a good catalyst for all olefines, and fatty acid salts of cobalt were also used successfully. Even basic cobalt carbonate could be employed without preliminary reduction. Roelen had used the cobalt catalyst from the catalyst factory as his standard mainly because it was readily available, and frequently more catalyst than was really necessary was used.

A proportion of the cobalt goes into solution as cobalt carbonyl, some of which may be carried away in the gas stream, from which it can be recovered by scrubbing with synthetic hydrocarbons or OXO-process alcohols. The loss of cobalt due to its solution in the reaction products, and particularly in their polymers, was much more serious, but this cobalt could also be recovered and regenerated by reduction (cf. Appendix VIII).

On the laboratory scale (50 ml.) the process was usually run to give alcohols as final products, the aldehydes formed being reduced with hydrogen in the same reaction vessel. The hydrogen used simultaneously reduced any cobalt in solution to cobalt metal which was deposited on the undissolved catalyst, affording practically complete recovery of the cobalt in a form suitable for further use as an OXO-catalyst. Using this technique a single charge of catalyst could be used several times.

Iron carbonyl can also catalyse the OXO-reaction but its activity is much lower than that of cobalt carbonyl. During reaction with cobalt catalysts a certain amount of iron carbonyl is formed, (from the walls of the reaction vessel) and contaminates the catalyst. The effect of the accumulation of iron in a catalyst which had been regenerated several times had not been determined, but Roelen expected that a complete recovery of the cobalt might be necessary at some stage to free it from iron. This point would have arisen if the project for a large scale plant, using a charge of 1000 kg. of cobalt catalyst, had been further advanced.

3. Starting Materials. A wide range of olefines had been converted to aldehydes by the OXO-process. There was no apparent limit to the molecular weight of the olefine; all straight chain olefines up to and including waxes could be used. The reaction had been successful with turpentine, oleic acid esters, linseed oil, which gave very viscous products, and rubber. Aromatic compounds containing an olefinic link in a side chain reacted in the side chain, although difficulty was sometimes experienced due to polymerisation of the olefine, e.g. with styrene, but the aromatic ring did not react. Partly reduced aromatic rings, however, did react. Thus cyclohexene readily gave hexahydro-benzaldehyde, which polymerised to a crystalline compound or could be reduced to hexahydrobenzyl alcohol; the unsaturated hydro-naphthalenes reacted in similar fashion.

Synthetic lubricating oils had been used and found to react to an extent of only 50% of that expected; the extent of reaction was measured by the volume of water-gas absorbed. This was considered a steric hindrance effect. A similar effect was sometimes found when cracked petroleum fractions were used; in this



case the non-reactive unsaturated hydrocarbons were probably aromatics. Conjugated olefines give unsaturated aldehydes which usually polymerise so that it is difficult to isolate the simple compounds.

4. Products. Since the CO may react with either of the doubly-linked carbon atoms of the olefine, the products obtained from an  $\alpha$ -olefine may be either straight- or branched-chain compounds or a mixture of both. For propylene it had been found experimentally that the product consisted of equal amounts of butyraldehyde,  $\text{CH}_3\text{CH}_2\text{CH}_2\text{CHO}$ , and dimethyl acetaldehyde,  $\text{CH}_3(\text{CH}_3)_2\text{CHO}$ . In the case of ethylene only n-propylaldehyde is possible.

For higher olefines Roelen said the exact nature of the products obtained was doubtful. The position was complicated by branching present in the hydrocarbon chain originally and the position of the double bond. Even starting with a pure n- $\alpha$ -olefine he could not say that any straight-chain aldehyde would be formed. It had been found that cobalt carbonyl catalysed movement of a double bond, and this is bound to happen during the OXO-synthesis since cobalt carbonyl is present in large amounts. Ruhr-chemie had not done much work on the actual constitution of the products; their main concern was to get as complete a conversion to aldehydes as possible, but from the properties of the aldehydes, and the alcohols and acids derived from them, it was known that a high proportion of branched-chain compounds was present.

In addition to the aldehydes the OXO-synthesis gives a mixture of polymerisation and condensation products as by-products, which in Roelen's opinion may prove to have technical applications (as solvents, plasticisers etc.) which may make them more important than the aldehydes themselves. Ketones are also produced as by-products. The yield of diethyl ketone made from ethylene can be increased by working at a lower reaction temperature, but Roelen had been unsuccessful in attempts to increase the yield of ketones from other olefines.

If the temperature was increased in the propyl aldehyde synthesis a certain (small) amount of Fischer synthesis took place, but the main change was the production of propyl alcohol in place of the aldehyde. Roelen said that this direct alcohol synthesis could be carried out with water-gas/ ethylene mixtures by passing them over a fixed cobalt catalyst supported on pumice at a temperature of ca.  $210^\circ\text{C}$ ., the products being ethane and propyl alcohol only. No cobalt carbonyl appeared in the products. He did not give the working pressure. (I.G. did not get alcohol at  $200^\circ\text{C}$ . because they had a less active catalyst). The catalyst life was at least 1000 hours without fall in activity. A direct

alcohol synthesis of this type can be carried out with higher olefines but the proportion hydrogenated directly to the hydrocarbon increases with molecular weight.

5. Secondary Products. As mentioned above, the OXO-aldehydes can be converted to the corresponding acids by oxidation with air at room temperature in the presence of alkali. The acids are suitable for the production of soaps. A special case of this reaction was used in the preparation of cutting oils which were used successfully by Ruhrchemie. Synthetic Diesel oil was treated by the OXO-process, and any cobalt present in the product washed out with acid. Lime was then added and the aldehydes oxidised. The solution of calcium salts of the fatty acids in the Diesel oil paraffins could be used alone or emulsified with water. A similar process was applied to synthetic lubricating oils, the acids being converted to the calcium or aluminium salts and the product being used in the preparation of special lubricants. The aluminium salts had the property of forming long fibres.

The OXO aldehydes are also readily reduced to alcohols. These could be combined with fatty acids (also derived from OXO-products) to give esters by heating in nitrogen, the small amounts of cobalt present in the products acting as a catalyst. The esters could be purified by vacuum distillation if required. They had good lubricating properties, the viscosity pole height being below 2, and, due to their predominantly branched-chain structure, their setting points were very low, i.e. of the order of  $-70$  to  $-80^{\circ}\text{C}$ . The esters prepared from acetic and higher acids were also valuable as solvents, plasticisers etc.

Conversion of the alcohols, in a suitable hydrocarbon - alcohol mixture obtained by the OXO-process, to nitric acid esters by treatment with nitric acid had given a Diesel oil with the extremely high cetane number of 280. As far as Roelen could remember the nitrate content was about 40%. This material was tested for aircraft use and was being considered as a cold-starting fuel. Later, samples were made from iron-catalyst-synthesis product with a suitable alcohol content.

The formation of products by aldol condensation of the OXO-aldehydes had received some attention. By this reaction followed by dehydration Roelen had prepared a synthetic drying oil from propylaldehyde, but even with catalysts present this oil was too slow drying to be satisfactory. Roelen was convinced that OXO-products could be used as a source of unsaturated long-chain aldehydes, alcohols and acids by controlled polymerisation. He pointed out that the possible applications in the field of synthetic chemistry were very numerous. Dr. Reppe of I.G., had prepared aldehydic perfumes by the OXO-synthesis, and it might prove possible

to make synthetic terpenes and camphors. Synthetic hydrocarbons could be made as final products. I.G. had already found that a gasoline fraction, after conversion of the olefines present to aldehydes and hydrogenation of these to the corresponding hydrocarbons, showed a substantial increase in octane number, presumably due to the introduction of branches in the carbon chains. At present Roelen agreed that the OXO-process formed a source of mixtures of compounds of a certain type rather than of pure individual compounds.

Finally Roelen said that he did not know if the OXO-process would be an economic proposition in peace time, but it was possible that it would, since Germany had to import large quantities of natural oils for production of soap and detergents.

#### Further Information.

During the course of the interrogation a considerable number of questions were asked which Roelen could not answer. Most of these he thought he could deal with after his return to Oberhausen-Holten by consulting documents available there or interviewing his colleagues.

Any additional information which is received in this way will be reported separately.

Appendix I

Otto Roelen, Dipl. Ing., Dr. Ing., Professional Career.

Born 22nd March, 1897, Mülheim-Ruhr.

1914 Technische Hochschule, Munich.

1919-1921 do do Stuttgart, obtained Diploma.

1922 Working for Doctorate under Geheimrat F. Fischer,  
Kohlenforschungs - Institut, Mülheim - Ruhr. (K.W.I.)

1923 Assistant in laboratory of Prof. Bucherer,  
Technische Hochschule, Charlottenburg.

1923 Graduated at Technische Hochschule, Stuttgart.

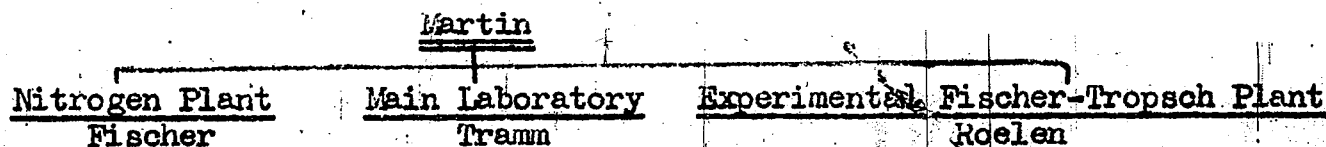
1924-34 Kohlenforschungs - Institut, Mülheim - Ruhr.  
At first Assistant, later constructed and was in  
charge of the experimental plant for Fischer-  
Tropsch Synthesis.

1934-1945 Ruhrchemie A.G., Oberhausen.  
At first in charge of the experimental Fischer-Tropsch  
plant, later in charge of the research department.

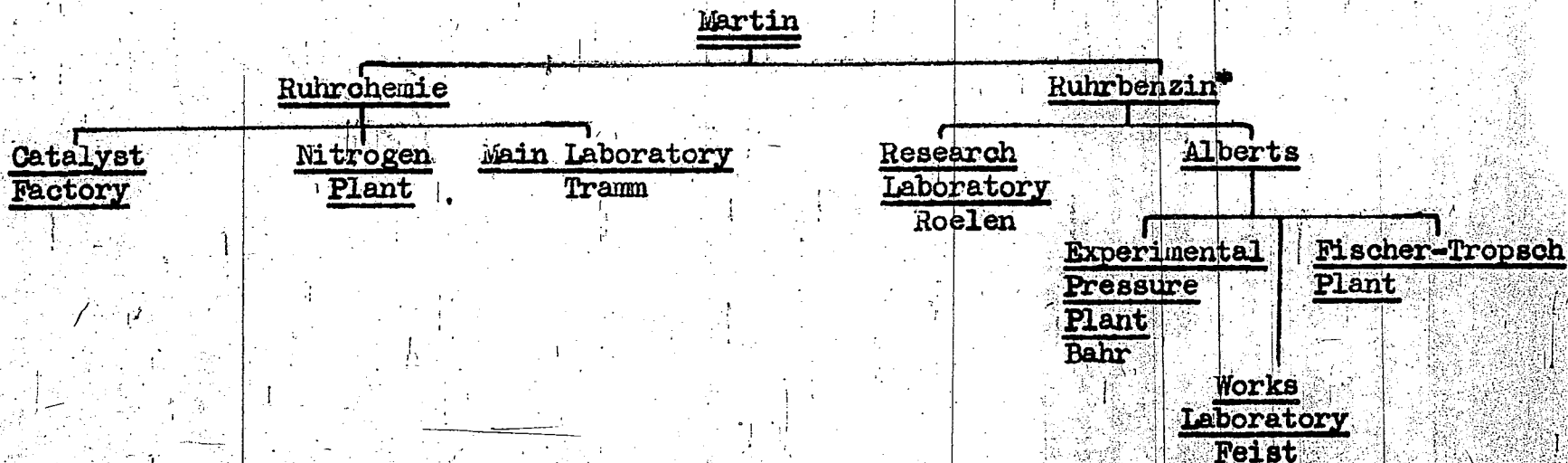
ca. 1939 (40?) Member of the advisory council to the OXO-  
Gesellschaft, Oberhausen.

Appendix II  
Organisation of Ruhrchemie

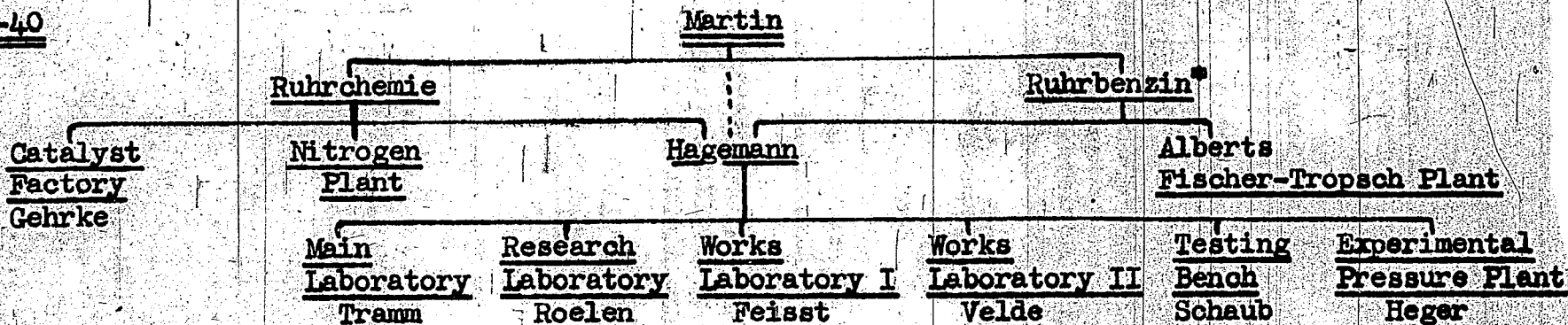
1934



ca. 1937

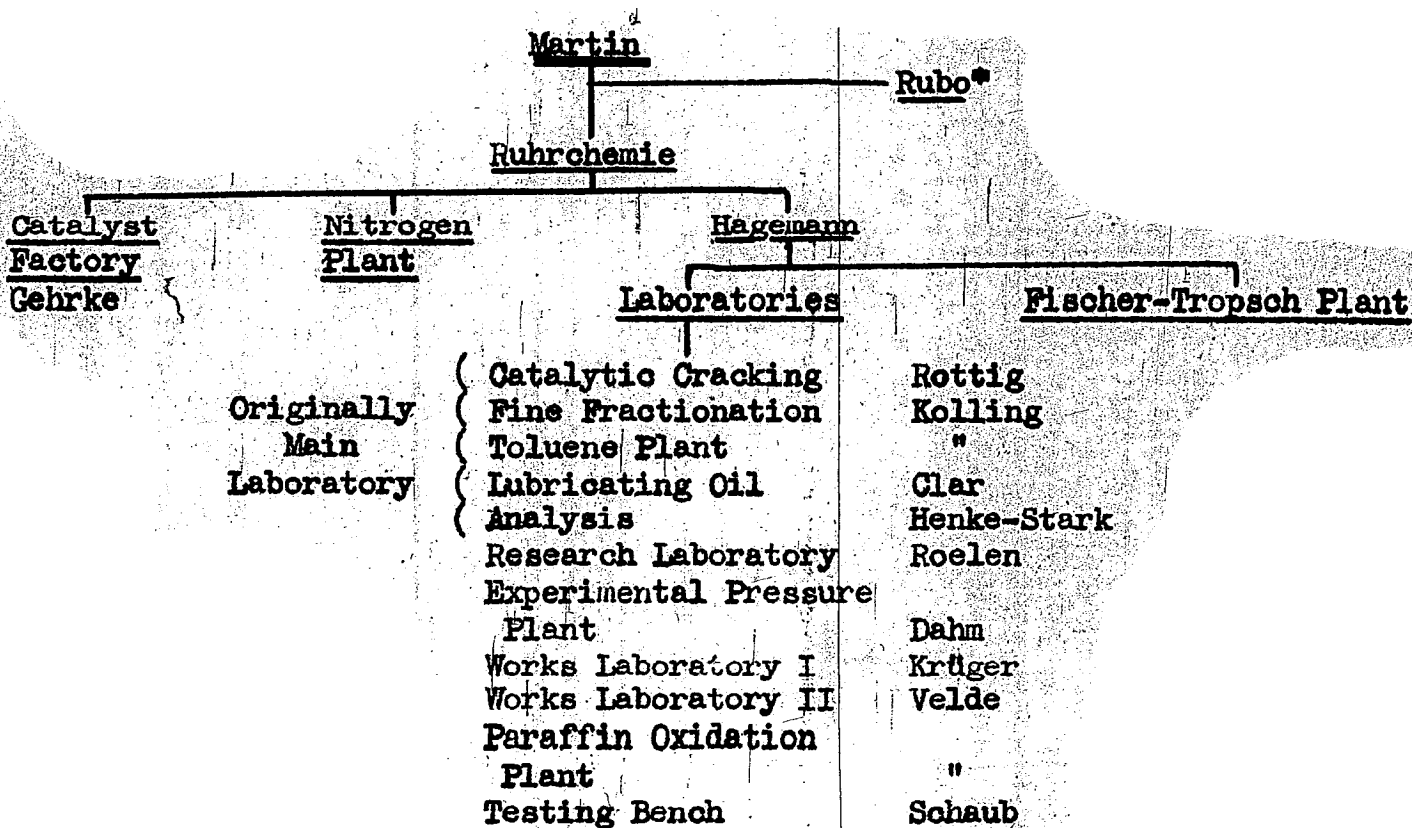


1939-40



\* Ruhrbenzin A.G. amalgamated with Ruhrchemie A.G. in 1942.

ca. 1945



\* Ruhrbenzin Oberhausen G.m.b.H., founded 1942 (new lubricating oil plant in course of erection).

### Appendix III

#### AN ACCOUNT OF THE DEVELOPMENT OF COBALT-THORIA- MAGNESIA CATALYSTS

(1) When the synthesis was taken over from the K.W.I. in 1934 the best cobalt catalysts were considered to be those containing thoria as activator, prepared by precipitation as carbonates on to kieselguhr. In addition, copper might be added or not. The advantage of the copper lay in the possibility of reducing the catalyst at such low temperatures that the reduction could be carried out in the synthesis vessel. Such reductions were carried out successfully in Holten in 1934-35 in reactors containing 1 cu.m. of catalyst and with 400 m<sup>3</sup> gas throughput per hour. However, the disadvantages of using copper with cobalt were found to outweigh the advantages. Copper is one of those metals which particularly favours the sintering of the finely-divided cobalt, and on this account it has never been possible to obtain catalysts containing copper with any length of life. They had already been abandoned in 1935 and as far as it is possible to say, permanently (at least as far as cobalt is concerned). Another effect in the same direction, namely, the shortening of catalyst life in normal-pressure synthesis, is the effect of copper in favouring the formation of high-molecular-weight hydrocarbons and hence the more rapid saturation of the catalyst mass with wax.

It is on account of the sintering of reduced cobalt that, in the preparation of normal cobalt catalysts, the cobalt solutions have to be carefully freed from copper (e.g. by means of metallic cobalt).

(2) The catalyst composition taken over from the K.W.I. contained 18 parts of thoria. Researches were at once begun in Holten in 1934 on the suitability of this thoria content, on the one hand because it seemed to us possible to obtain longer life, and on the other hand because the preparation and continuous regeneration of such large quantities of thoria was fairly costly.

It was soon found that the thoria content could be reduced without disadvantage to 15 parts, this giving, in fact, a slight increase in the activity. At this optimum thoria content changes in the kieselguhr content had no great effect; at least no such effect was observed.

This position was fundamentally changed when magnesia was introduced into the mixture. In the presence of magnesia the thoria content can be very considerably reduced. For large scale preparations I decided after many and extensive investigations on a thoria content of 5 parts. If one could be certain that the nitrate solutions used in the precipitation were always very pure, one could work equally well with a thoria content of, e.g. only 2 parts. The excess over this figure is added as a safety measure because the thoria has the special property of reducing to a certain extent the harmful effect of impurities such as copper, calcium and aluminium. Thoria also reduces the deleterious effect of vigorous mechanical treatment of the wet catalyst cake (after filtration and washing) e.g., a wet cake of catalyst containing thoria can be thixotropically liquefied without any reduction in catalytic activity. With, for example, catalysts containing only magnesia, this is not the case.

(3) The catalyst composition taken over from the K.W.I. contained 100 parts of kieselguhr to 100 parts of cobalt. This ratio was not the result of exhaustive researches in this field, but merely the most favourable result of a few series of experiments. Researches were at once put in hand at Holten which showed that it would be better to increase the kieselguhr content. As a result of numerous life tests over long periods, Ruhrchemie finally introduced cobalt catalysts with 200 parts kieselguhr. The desirability of this measure was contested by Herr K lbel of Rheinpreussen. He thought that by simply turning over to concentrated cobalt catalyst (e.g. with 100 parts kieselguhr) the yield of the synthesis plants could be increased to twice the actual output. Thereupon the Licensees decided to repeat the laboratory experiments on a large scale. The result of these costly investigations was a confirmation of the earlier results of Ruhrchemie. This would seem to establish fairly firmly the inferiority of catalysts richer in cobalt.

The ratio 200 kieselguhr to 100 cobalt is not absolutely constant. The catalyst factory has to prepare catalyst of constant cobalt density (e.g. 80 g. cobalt per litre catalyst). To obtain this, the weight of kieselguhr to be added must be suited to the actual quality of the sample; a smaller weight of a light kieselguhr must be taken than of a denser one. The maintenance of a constant cobalt density is necessary not only on general grounds, but also because it is one of the main factors controlling the reducibility. The higher the cobalt density the more easily the catalyst is reduced.

The part played by the kieselguhr in the satisfactory functioning of the catalyst consists principally in establishing and



maintaining the porosity of the individual granules. This point of view is supported by many observations, above all by those concerned with the building up of wax on the catalyst.

With both the more finely divided, "loose", kieselguhrs and the heavier samples obtained by sintering them, the initial wax build-up under parallel conditions is approximately the same. On dewaxing with hydrogen however, considerably more wax can be removed from catalysts prepared with the lighter kieselguhrs than from the others. Correspondingly, the latter have always a higher residual wax content than the former, e.g. 300% as against 200% after 1,200 hours and 400% as against 280% after 2,700 hours.

These differences can be explained by saying that the lighter kieselguhr, by giving a looser structure to the catalyst mass, favours the movement of the reactants and the products through the interior of the granule. It is probably permissible to regard the ease of removal of the catalyst wax as a measure of this interior penetrability.

(4) — The catalyst, as taken over from the K.W.I., contained only thoria as activator. This too was not the result of exhaustive investigations, for which much greater resources would have been necessary than were available at the Institute. On account of the unsatisfactory life of the catalysts of that date we therefore began at Holten in 1934 systematic investigations of the effect of the most varied range of additives. We found inter alia that manganese showed a similar effect to thoria. It increased the activity and directed the synthesis to the production of higher-molecular-weight hydrocarbons. A cobalt catalyst containing manganese later showed the highest activity of all, measured at the very low reaction temperature of 165-170°C. At the same time large quantities of solid wax were formed. The use of catalysts containing manganese on a large scale was avoided, however, as difficulties were to be expected in the regeneration of the cobalt solutions. Magnesia had already been used at the K.W.I. as an activator without any special effectiveness being observed. We found, however, a favourable effect on the addition of magnesia. Systematic investigation showed that magnesia was one of the best activators available for cobalt catalysts. This probably depends on the fact that MgO has almost the same molecular volume as CaO (11.3 and 11.6 respectively) and forms a continuous series of mixed crystals with it.

In contrast to thoria, magnesia directs the synthesis towards the formation of lighter products. Not only is the total amount of high-molecular-weight hydrocarbons generally less with

magnesia than with thoria or manganese, but also the amount of residual wax after hydrogenation is vanishingly small, e.g. after 2,300 hours the residual wax not removable by hydrogenation was for a cobalt-thoria catalyst 500% (reckoned on weight of cobalt) and for a cobalt-magnesia catalyst only 25%.

Thoria, manganese and magnesia show basically the same effect with nickel catalysts. With these, magnesia exhibits its effect on the reaction direction so markedly that a nickel-magnesia-kieselguhr catalyst can be developed which gives the maximum activity for the synthesis of methane. Since all other considerations are favourable to the use of magnesia, e.g. price and availability, and its behaviour in the regeneration of the solutions, there is nothing against its introduction on the large scale.

Initially we had difficulty in reproducing cobalt-magnesia catalysts of different composition. We found that the reason was that the magnesium was incompletely precipitated under the preparation conditions for cobalt catalysts and was more or less readily washed out of the precipitate. It is therefore necessary to start with nitrate solutions containing a corresponding excess of magnesium.

(5) Thoria and magnesia each individually have a very great activating effect on cobalt catalysts. The question arose whether their effects were additive in mixtures. To a certain extent this is in fact the case, and therefore cobalt-thoria-magnesia-kieselguhr "mixed catalysts", are among the very best.

The particular advantages of such catalysts are set out below. They show, as against catalysts containing thoria and magnesia only,

- (a) the maximum catalytic activity
- (b) the lowest reducibility
- (c) the least readiness for oxidation to  $\text{Co}^{\text{III}}$
- (d) the greatest volume after precipitation and reduction.

Like all other catalysts containing thoria, those containing both thoria and magnesia have the advantage of being relatively insensitive to impurities and rough treatment of the wet filter-cake. The presence of magnesia also reduces the amount of catalyst wax formed in atmospheric-pressure synthesis, as compared with the amount formed on a catalyst having thoria as the only activator. The boiling range of the products lies between that for a catalyst containing thoria alone and one with magnesia as the only activator. The presence of magnesia makes the

wet regeneration easier than for catalysts with thoria as the only activator, and also cheaper on account of the reduction of thoria content from 15-18 parts to 5 parts. The limits defining the best ratios of the four constituents are not narrow, so that variations in composition of catalysts prepared on a large scale, which are inevitably larger on account of the special properties of the magnesia and the kieselguhr, are practically of no importance. The most favourable composition is Co 100: ThO<sub>2</sub> 5: MgO 10: kieselguhr 200 (the figures for Co, ThO<sub>2</sub> and MgO refer to the solution of the mixed nitrates) and the catalyst prepared from this mixture will be approximately Co 100: ThO<sub>2</sub> 5: MgO 8: kieselguhr 200.

(Sgd.) O. Roelen.

London, 8th November 1945.

Appendix IV \*

Ruhrchemie 2nd Reichsanversuch

Catalyst Composition. Fe 100: Cu 5: CaO 10: Kieselguhr 50

Pressure 10 Atm., Reaction Temperature ca. 220°C.

Reaction Period 0-168 hours

Process Gas 80.64 x 1000 Nm<sup>3</sup>

Residual Gas 50.94 x 1000 Nm<sup>3</sup>

Gas Analyses:	Process	Residual
CO <sub>2</sub>	0.0	9.82
C <sub>n</sub> H <sub>m</sub>	0.0	0.98
CO	39.0	28.71
H <sub>2</sub>	48.4	38.73
CH <sub>4</sub>	4.0	8.21
C <sub>n</sub> H <sub>2n+2</sub>	-	1.11
N <sub>2</sub>	8.6	13.65

Residual Gas/ Process Gas Ratio 0.632

Conversion (U) % of CO + H<sub>2</sub> 51.3

Methane (Mv) % of U 5.9

Utilisation Ratio X 1.15

Yield, (Excluding CH<sub>4</sub>) Calculated  
from gas and product analyses,  
g./Nm<sup>3</sup> process gas 87.9

Maximum Yield for U = 100%, g./Nm<sup>3</sup> 164

\* This and subsequent Appendices are abstracts of documents which Koelen brought with him.

Appendix V

Synthesis with Iron Catalyst

Experiment No. 595

Catalyst No:- F 2093a

Composition:- Fe 100: Cu 5: CaO 10: kieselguhr 30

Precipitated by  $\text{Na}_2\text{CO}_3$ . Impregnated with 3% KOH

Preparation in Catalyst Factory. Form:- F.-L., 2.5 mm. Fadenkorn.

Reduction:- 1 hour, 300 l.  $\text{H}_2/\text{N}_2$  per 60 ml. catalyst.

Catalyst charged 5040 ml. = 3077 g. Iron density 270 g./litre

Reaction conditions:- 10 atm., 200-220°C., Recycle 1 + 2.2 with water-gas.

Duration of Test:- 160 days

Catalyst removal:- easy after wax removal with hydrogen.

[Note. According to Roelen the precipitation had been carried out in small batches, and the exact quantities were found which would give a  $\text{pH}$  of 9.0 immediately before adding the kieselguhr. Washing was done with hot water, 4.6 litres per 25 g. iron. This had been found sufficient to remove all alkali. (Attempts to wash to a suitable final  $\text{pH}$  were not reproducible). Impregnation was done by stirring the catalyst (gently, to avoid damage to the gel structure) with a sufficient amount of a 10% solution of KOH over a period of 30 minutes. The reduction was carried out at atmospheric pressure and 300°C., the hydrogen rate being normal (space velocity 5000).

(The full description of the preparation of an iron catalyst in the Holten catalyst factory as reported by W.S. Faragher et al. in the Field Team report entitled "Supplementary Report on Ruhrchemie A.G., Oberhausen - Holten", File No. XXXII -96, is believed to refer to the above catalyst).

## Results

Mean values over 30 working days (5th month over 40 days)

Month		1.	2.	3.	4.	5.
CO+H <sub>2</sub> conversion	U %	63.4	64.1	65.7	63.5	61.5
Methane yield	Mv %	7.0	6.6	6.8	8.8	8.9
	MCO %	3.6	3.5	3.7	4.6	4.7
Reaction Temp.	°C.	200 - 218	218 - 220	220	220	220
Utilisation Ratio						
1 CO : X H <sub>2</sub>	X	1.04	1.14	1.17	1.11	1.12
Yield g./Nm <sup>3</sup> water-gas (C <sub>2</sub> and higher)		105	107	111	104	102

### Distribution of Liquid Products:

Spirit to 200°C.%		16.5	15.4	13.3	19.8	25.1
Diesel Oil 200-290°C.%		11.8	5.9	7.5	8.5	11.8
	290-320°C.%	4.1	3.7	4.6	3.8	6.0
Wax	320-460°C.%	27.9	27.2	22.9	22.3	25.5
	above 460°C.%	39.7	47.8	51.7	43.6	31.6
Wax above	320°C.%	67.6	75.0	74.6	65.9	57.1
Wax above	290°C.%	71.7	78.7	79.2	71.7	63.1

### Soluble in Sulphuric - Phosphoric Acid Mixture

Spirit to	200°C.Vol. %	44.8	30.9	28.0	48.7	66.3
Diesel Oil	200-					
	290°C.Vol. %	46.9	42.6	38.4	52.8	64.2
	290-					
	320°C.Vol. %	44.7	44.6	39.0	54.5	66.8

If reduced with water-gas it gives an improved Utilisation Ratio.

Sgd. Dr. Heckel,  
22.2.44

## Appendix VI

### Direct Alcohol Synthesis

#### Experiment No. 650

Catalyst used: Fe 100: Cu 5: CaO 10: kieselguhr 5,  
precipitated with  $\text{Na}_2\text{CO}_3$ , impregnated with 3% KOH.

#### Preparation of Catalyst:- (F. 2188)

The hot solution of the nitrates (42 kg. iron nitrate, 1.17 kg. copper nitrate, 1.75 kg. calcium nitrate in 120 l. water) was added to a boiling soda solution (24 kg. sodium carbonate in 190 l. water). 0.35 kg. kieselguhr was added, the mixture stirred for a short time, filtered in a filter press, washed (30 min.) with hot distilled water, and partially dried with air (15 mins.). The filter cake was then treated with 500 l. of distilled water in the precipitation vessel, filtered in the press, washed (10 minutes) and dried with air. This treatment was repeated twice. For impregnation, the catalyst was passed through the extruding machine three times after the addition of 0.21 kg. KOH in 1 litre water. The finally extruded catalyst was spread over sheets of ~~metal~~, dried in an oven at  $140^\circ\text{C}$ ., and granulated to 1 - 3 mm.

#### Reduction:

A charge of 5 litres of catalyst was introduced into a 6-litre reduction apparatus (R 25 a) previously filled with nitrogen, and 28 m<sup>3</sup> of hydrogen-nitrogen mixture (75%  $\text{H}_2$ ) were passed through per hour at  $325^\circ\text{C}$ . for 24 hours. It was cooled for 1 hour in a stream of nitrogen, previously freed from oxygen by passing over a sample of a reduced cobalt catalyst, and was removed in nitrogen.

Shrinkage was 30%. Bulk Density 780 g. /l. Iron Density 726 g./l. Reduction Value 85% (Fe soluble in acetic acid)

Testing of Catalyst. 4.47 kg. (ca. 5 l.) was charged into the reaction vessel (M.R.1) and was heated slowly with a low rate of water-gas at 10 atm. At  $140^\circ\text{C}$ . the first contraction was observed; carbon monoxide consumption was 31% rising to 40% at  $155^\circ\text{C}$ . with no consumption of hydrogen. In the range  $160-180^\circ\text{C}$ . hydrogen began to take part in the reaction, its consumption increasing slowly. Methane formation remained below 1%, total conversion (U) rising to 40%. At  $205^\circ\text{C}$ . after 50 hours U was 65% with Mv 13% and X 0.67. This conversion was maintained for a further 100 hours, the temperature being such that methane formation did not increase unduly (to

Mv = 18%). A large increase in methane production then set in suddenly, Mv becoming 76%, and after 15 hours the test was shut down as methane production showed no signs of decreasing.

The removal of the catalyst was made difficult by carbon deposition.

Examination of product obtained between the 81st and 152nd hour of the test.

	<200°C.	200-320°C.	>320°C.
Proportion	69.0-% by wt.	20.9-% by wt.	8.6-% by wt.
Density	0.778	0.811	0.824
Refractive Index	1.3950	1.4320	1.4471
% Acids	0.2	0.1	0.2
% Esters	3.6	14.4	25.3
% Alcohols	51.8	52.7	33.7
% Aldehydes	5.6	5.1	2.8
% Total Oxygen Compounds	61.2	72.3	63.1
% Olefines	30.0	28.5	24.2
Total S.P.L.	85-% by Vol.	82-% by Vol.	-

Valuation of Catalyst:- Conversion good at low temperatures. Pronounced tendency to methane production. Content of olefines and oxygen-compounds in product very high.

Total running period 190 hours.



## Appendix VII

### Catalyst F 2181

Composition Fe 100: Cu 5: CaO 10: kieselguhr 10 + 40.  
Precipitated with technical  $K_2CO_3$ ; 10 parts of kieselguhr were added before the precipitation, the rest afterwards. One washing only was given and no impregnation.  
Bulk density (before reduction) 580 g./l. Iron Density 229 g.Fe/l.

Normal Pressure Testing. On laboratory scale; other conditions not stated.

Products, b.p.	< 200°C.	200-320°C.	>320°C.
% by weight	42.7	19.2	37.0
S.P.L., % by vol.	89	92	-
Olefines, %	75	84	ca.72

On 50 litre scale; the same catalyst, prepared on the semi-technical scale. Reduction with hydrogen at 325°C.  
Reaction temperature 230 - 235°C. Conversion (U) = 50%.

Products, b.p.	< 200°C.	200-320°C.
Olefines, %	47	52.5

### Medium Pressure Testing.

At 10 atm., reaction temperature 230 - 235°C.

Products, b.p.	< 200°C.	200-320°C.
Olefines, %	23	26
Oxygen Compounds, %	24	26

A higher yield of oxygen compounds was given at 20 atm. pressure than at 40 atm.

## Appendix VIII

### Synthesis of Propylaldehyde at Holten

Technique in use, May 1943

#### A. Synthesis

The suspension of 5 l. of catalyst (Co 100: ThO<sub>2</sub> 5: MgO 8: kieselguhr 200) in 30 kg. of toluene was pumped into a tubular reaction vessel set at a slight inclination to the vertical, with a capacity of 90 litres. Water-gas was pumped in up to a pressure of 100 atm. and the temperature raised to 115°C. At this temperature and a pressure of 150 atm. a mixture of ethylene (1 part) and water-gas (2.5 parts) with a total composition of C<sub>2</sub>H<sub>4</sub> 25%, CO 25%, H<sub>2</sub> 35% was passed through at a rate of 18 m<sup>3</sup> per hour. The residual gas, 4-5 m<sup>3</sup> per hour, was practically free from ethylene. Conversion was maintained constant i.e. at 100% on ethylene, for 165 minutes, after which time the reaction had to be stopped as the liquid product had filled the reaction vessel. After cooling to room temperature, the product was pumped to a settling tank (capacity 80 l.). The gas evolved on releasing the pressure contained some ethylene and was recovered. The complete synthesis operation took 8 hours.

#### B. Filtration

After standing for 12 hours, the catalyst had settled sufficiently for 80% of the product to be pumped through a filter candle into the distillation vessel. The remainder was separated from the catalyst by filtration under a pressure of 2-3 atm. Two charges, 10 litres of catalyst, were accommodated on the filter at once. The catalyst was washed three times with 5 litres of toluene each time, and was dried on the filter, which could be heated electrically. The filtrate, washings, and solvent evaporated off during drying were pumped to the still.

#### C. Treatment of the Catalyst with Hydrogen

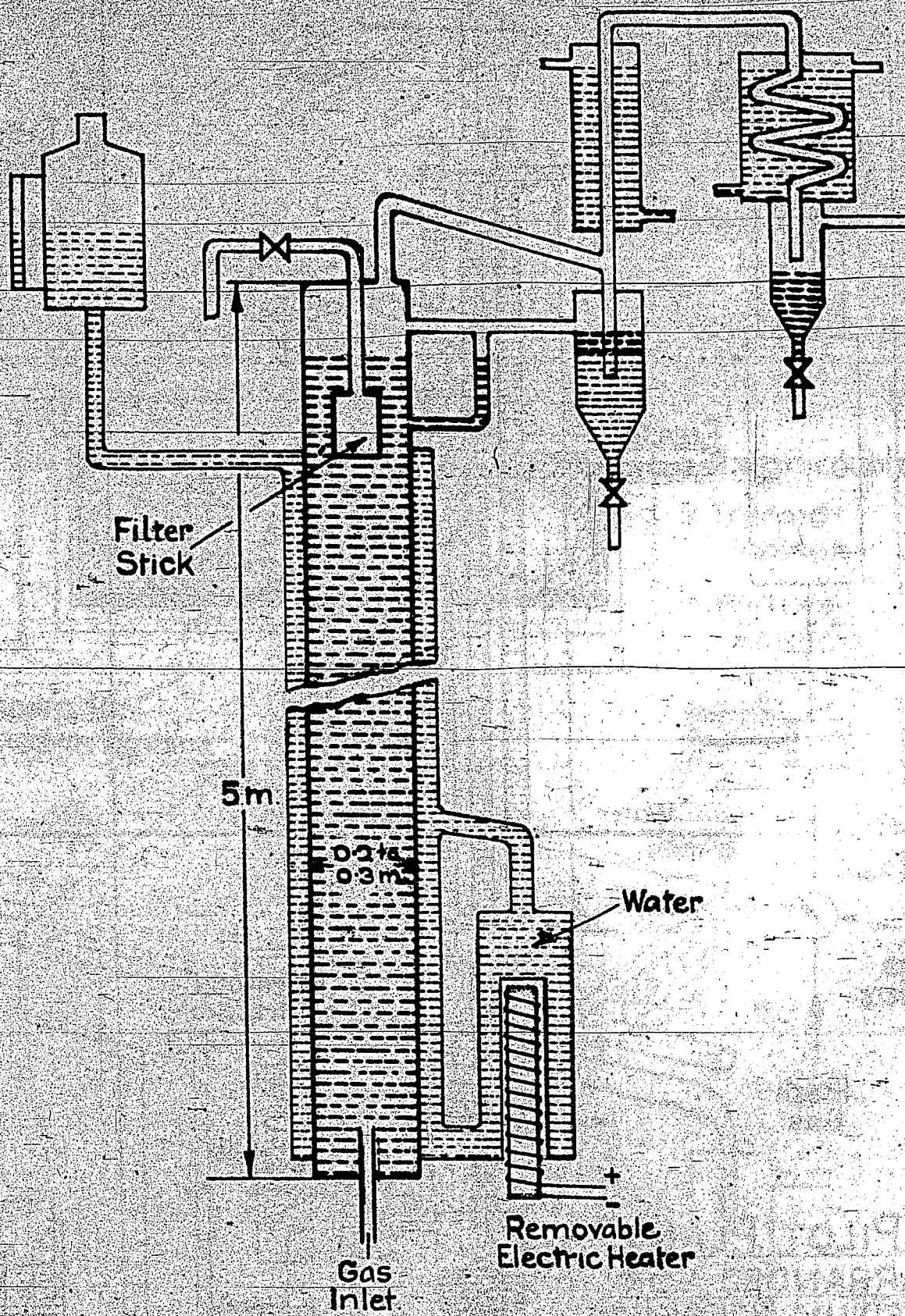
The dry catalyst without removal from the filter, was broken up by stirring, and treated for 90 minutes with hydrogen at 250-270°C. and at a gas rate of 6 m<sup>3</sup> per hour, the gas being recycled. It was then cooled and removed as a slurry in toluene and was ready for further use, after addition of the cobalt which had been dissolved out during the synthesis.

#### D. Distillation

The product and catalyst washings were distilled up an 8 m. column. The first fraction consisted of practically pure propylaldehyde. This turned brown on standing due to the separation of ferric hydroxide derived from traces of iron carbonyl formed during the synthesis and volatilizing during the distillation. The second fraction, boiling between 50 and 70°C., contained considerable amounts of propylaldehyde and was added to the next batch of product being distilled. The third fraction, boiling 70-110°C., contained propylaldehyde, diethylketone and toluene. The fourth fraction was practically pure toluene. The third fraction, the toluene and the distillation residue could be used as solvents in the synthesis.

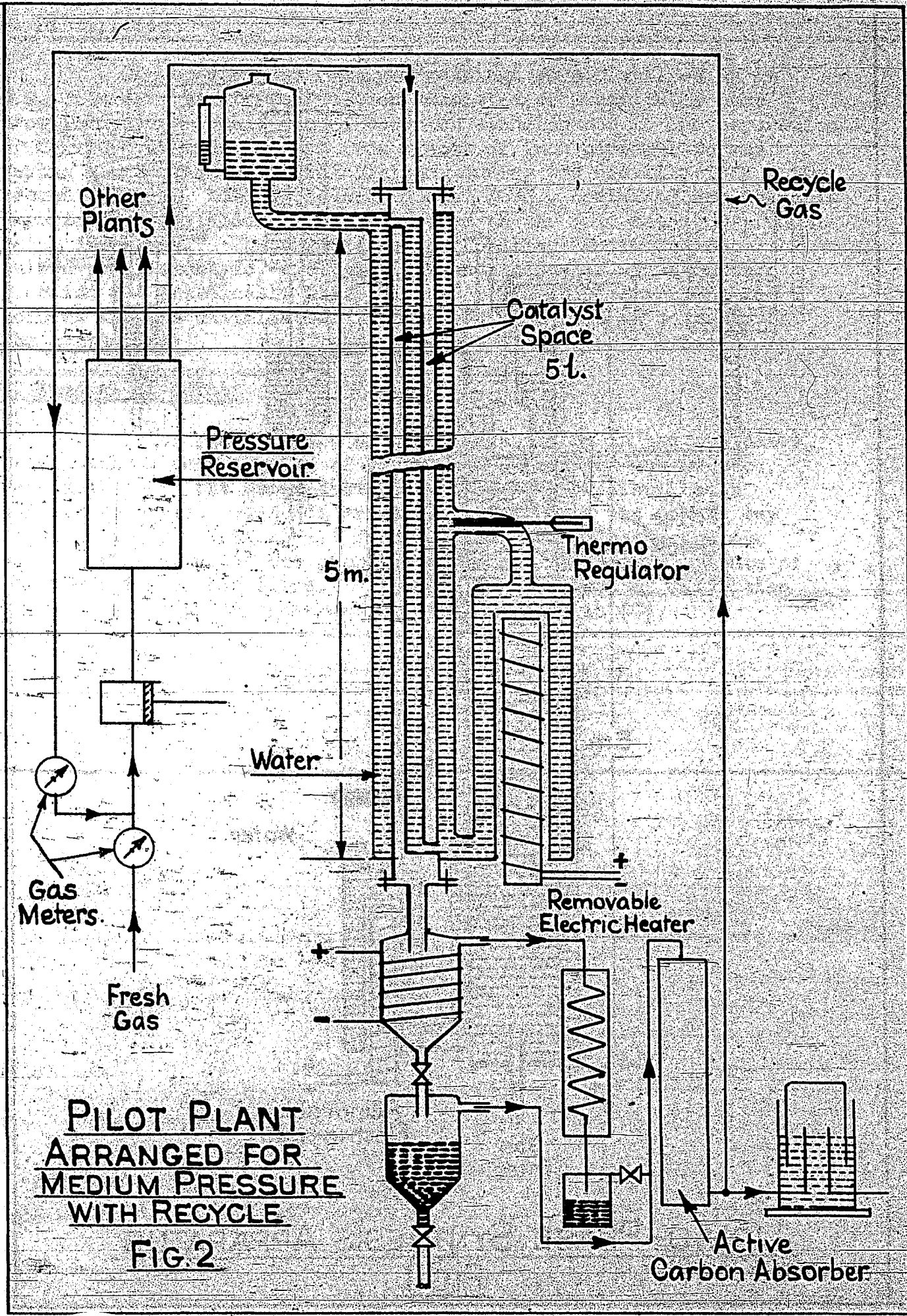
#### E. Removal of Cobalt

Using pure toluene as the liquid medium in the synthesis, only small amounts (ca. 5%) of cobalt were dissolved out of the catalyst. (If the above distillation residue or distillates containing oxygen compounds are used, up to 50% of the cobalt may be dissolved). This cobalt formed a suspension in the residue after distillation of the propylaldehyde and toluene in amounts of about 0.5-1.0 g. per litre. It could be recovered by filtration and used again after treatment with hydrogen as in (C).

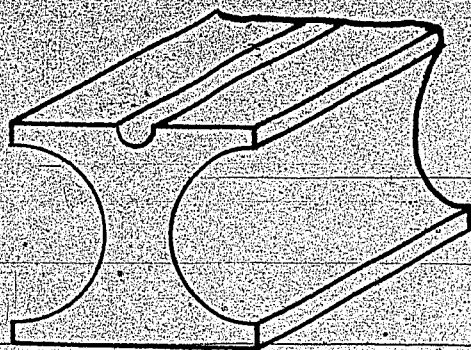


**LIQUID-PHASE SYNTHESIS APPARATUS**

**FIG. I**

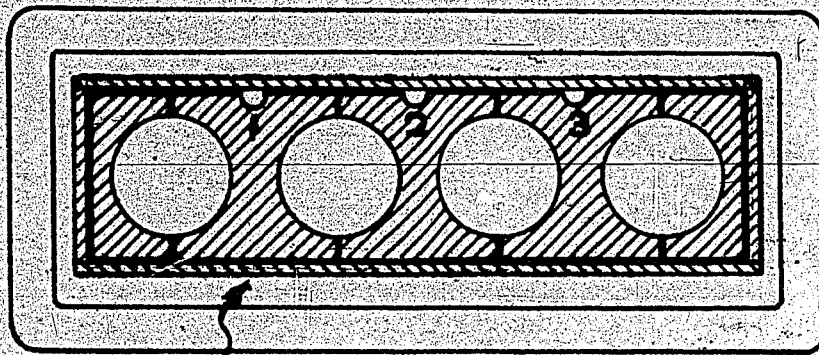


**PILOT PLANT  
ARRANGED FOR  
MEDIUM PRESSURE  
WITH RECYCLE  
FIG. 2**



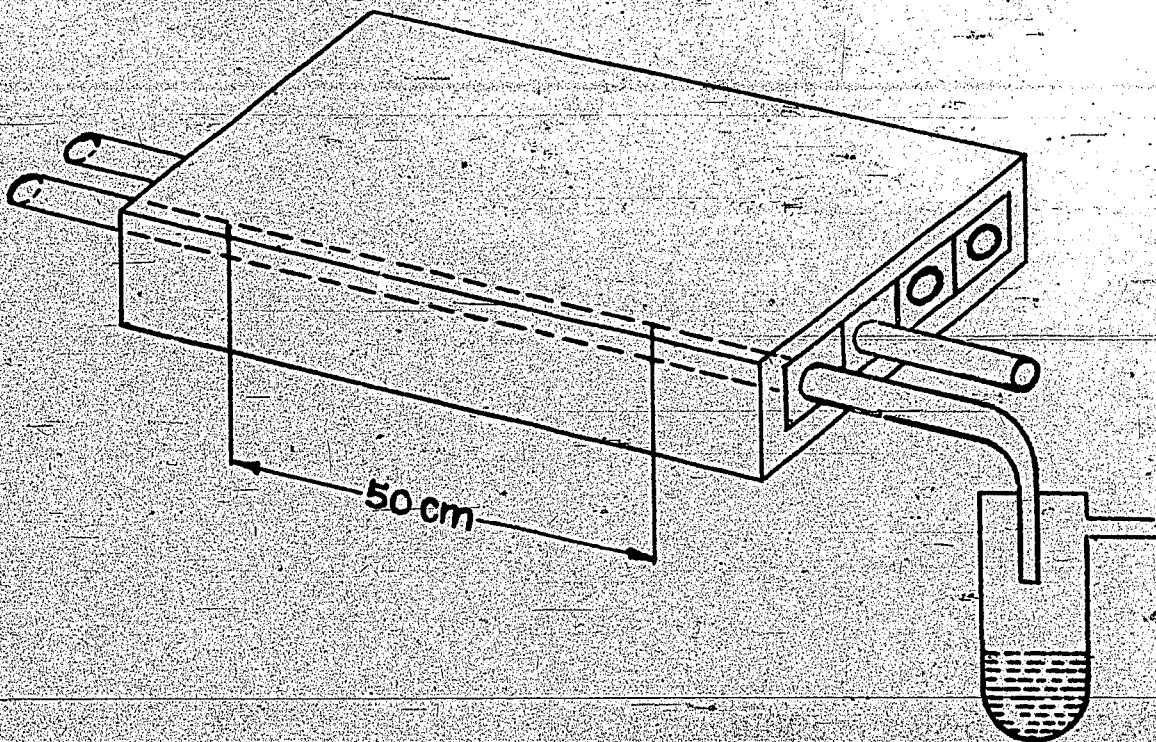
SECTION OF  
ALUMINIUM

FULL SIZE



Space for  
Electric Winding

1. Thermocouple
2. Thermo-Regulator.
3. Warning-Regulator.



LABORATORY-SCALE SYNTHESIS APPARATUS

FIG. 3