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BRITISH INTELLIGENCE OBJECTIVES SUB-COMMITTEE.

Interrogation of:- Dr. Roelen.

On:- 20. 21st December 1945

Target No. C30/5.0 1(a)

MAIN INTEREST:- OXO Synthesis.

INTERESTED MINISTRY:- Ministry of Fuel & Power.

The meeting was arranged subsequently to the preliminary and more general interrogation held on 14/12/45 with the object of gaining more detailed information on certain aspects of the OXO synthesis and of CO reactions, and further to try to get some knowledge of the research back-ground.

1. OXO Synthesis

(a) Type of Catalyst

The principle catalysts contain either cobalt or iron; nickel must not be used. Roelen was of the opinion that almost any form of cobalt was satisfactory so long as it could give cobalt carbonyl. He did not think that ThO_2 or kieselguhr were really necessary, but as the standard Fischer-Tropsch catalyst was quite satisfactory and easily available, not a great deal of work was done by him on alternatives. Cobalt carbonyl could be used, and even basic cobalt carbonate. Care was necessary in comparing catalysts since traces of CO left on the walls of the autoclave had pronounced catalytic effects. Iron requires a higher operating temperature than cobalt. He thought that the degree of reduction of the catalyst was not as important as in the Fischer-Tropsch synthesis.

(b) Suspended vs Fixed Bed Catalyst

Roelen had tried the standard Fischer-Tropsch catalyst in a fixed bed but had failed; whether the process is liquid phase or vapour phase, the cobalt is dissolved out by the reaction products and removed to some extent as carbonyl, the products being seriously discoloured, and after some hours catalyst activity fails. He stated that the IG had done much work on a semi-continuous process in which cobalt was injected into the reactor with the feed as a solution or suspension of a fatty acid salt and deposited on pumice. He saw no difficulties beyond mechanical ones, e.g. with pumps and valves, in turning this semi-continuous process into a truly continuous process.

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Roelen was pressed for his views whether ultimately fixed bed catalysts would displace continuous suspension injection. He was very vague here; the Italian Plant proposed to use suspension catalysts as there was insufficient experience with other types. He thought the choice might depend on the type of olefine to be reacted, higher olefines being preferably treated with suspended catalyst in the liquid phase.

(c) Purity of Gas

Ruhr-Chemie did all their work on water gas purified to Fischer-Tropsch standards; if cobalt well in excess of the sulphur present in the gas were continuously injected, sulphur might be tolerated.

(d) Type of Reactor

Roelen was vague whether reaction with the lighter olefines such as ethylene or propylene could in any circumstances be described as vapour phase reactions; the usual conditions involved cobalt catalysts suspended in toluene in which the olefine would dissolve. The bulk of his work had been done in small autoclaves, but he had used various types of small scale reactors and he promised to supply us with more detailed information and sketches. He hinted that if we were interested in developing the OXO-reaction we should find it most convenient and economical to start up plant at Holten (making use of his know-how).

(e) Scope of Reaction

Besides the usual hydrocarbon solvents, Roelen stated that the reaction could be carried out in water, at least in the case of ethylene where he quoted a product consisting of a 3-4% solution of propionaldehyde, the yield being 70-80% under the best conditions. He maintained that 70-80% yields could be obtained with most olefines. A yield of only 40% butanols from propylene with by-product C_7-C_8 alcohols and higher alcohol esters was quoted to him. He considered that this low yield was due to operation under non-optimum conditions; probably in attempting to get the alcohol in one stage from the olefine. For example, in making n-propanol from ethylene in one operation, 40% ethane is produced as a by-product. He preferred two-stage operation through the aldehyde. He did not know why the Italians were building a large plant for propionaldehyde using the OXO process. He had not done much work on propane as it was not available.

Asked about the relative amounts of isomeric aldehydes formed from a given olefine, Roelen stated that they were roughly equal. He did not think they were affected by pressure in the small range he had studied. He said that complex molecules were relatively unreactive, probably due to steric hindrance. Olefines prepared by polymerising olefines with $AlCl_3$ react with only half the CO/H_2 corresponding to the double bonds present. Some terpene hydrocarbons did not react as expected though limonene (dipentene) reacted smoothly. There were other reactions with which he would supply us. The long list of substituted olefines given in USP.2327066 had been included for patent purposes. The work had been done by an assistant and Roelen did not recollect the results; he thought that CO/H_2 was absorbed but that the products had not been thoroughly examined.

The C_9 alcohol had been made from diisobutylene (source ?); the I.G. had examined similar alcohols for plasticiser intermediates. Roelen showed little knowledge of Reppe's work on CO reactions. Asked his views on operation at higher pressures, e.g. 1000 ats., he thought this would only be helpful in making unreactive olefines respond.

2. Detergents

Roelen explained that the Holten factory of the OXO-Gesellschaft was erected to make detergents from the primary alcohols made from Fischer-Tropsch C_{11}-C_{17} olefines only after the most careful calculations had shown that direct sulphonation of these olefines was less advantageous. He thought that this was because the olefine sulphonates were inferior detergents. He promised to supply a history of the OXO-plant at Holten with a flow-sheet. He again suggested that this plant could be used as the nucleus for further development.

In the process, the olefines were fractionated at least to two molecular sizes so that the alcohols formed could be separated from the associated saturated hydrocarbons. The alcohols would be obtained better than 98% pure (calculated on -OH groups) and had outlets in other fields than detergents, e.g. for plasticiser intermediates.

He understood the washing properties of the sulphates from the OXO-alcohols were at least as good as the sulphates from the C_{16} saturated or C_{18} unsaturated straight chain primacy alcohols derived from natural fats and the wetting properties were better. The physical form of the final product was not quite the same and Henkel had had to carry out a little work to solve packing problems.

The intermediate C_{12} - C_{18} aldehydes had also been oxidised to fatty acids; these were better washing agents (on cotton ?) than the sulphates from the alcohols, but were obtained in somewhat lower yield. In reacting CO/H_2 with the olefine, some dimer was formed which was split on hydrogenation but not on oxidation. The yield of alcohol on olefine was 85%. The dimers were of considerable interest as textile assistants, but only small samples had been examined and he did not know by whom and for what. They were not employed to make wax emulsions. The detergents had been assessed by Henkel, I.G. and Bohme. Roelen obviously did not know much of this side of the work but he mentioned that he had heard of a so-called "super soap" of which the course of the war had prevented development.

The olefines obtained by cracking paraffin wax were also suitable for making detergents via the OXO-synthesis. These latter had a disagreeable odour which Roelen found could be removed by drying in air at 140°C for several hours in a finely divided form.

Roelen was not aware of the IG work on alkyl phenols from C_{12} olefines. He knew that they drew diesel oil fractions from Fischer-Tropsch plants other than those of Ruhr-Chemie for their Mersol process.

3. Fischer-Tropsch Process

(a) Catalysts

Roelen would supply a document explaining why iron was adopted in place of cobalt for the medium pressure Fischer-Tropsch process. We explained that our particular interest was its use for olefine synthesis. This document would also deal with the substitution of some of the ThO_2 by MgO in Fischer-Tropsch catalysts. A detailed comparison had been made in Schwardzheide (east of the Elbe) of iron vs. cobalt in the conventional Fischer-Tropsch process by the firms interested (Ruhr-Chemie, Lurgi, Fuel Research - Mulheim-Ruhr, Rhein Preussen, I.G.) I.G. had been developing a heavy fused iron catalyst but this had not been taken on to the large scale. The advantages were (i) no cobalt required; (ii) little methanation (iii) better control over M.W. The main drawback was increased CO_2 formation.

Direct Alcohol Synthesis

In the course of the work in displacing cobalt by iron, during which he had examined over a thousand catalysts, Roelen had discovered that certain iron catalysts gave mainly alcohols. Under the best conditions, over 70% oxygenated compounds were present in the product (was this the yield?). High pressure was not essential, most of the work apparently being done at 10-15 ats., although there is some information that 200 ats. has also been used. Conditions of making the catalysts were more important than catalyst composition. The product contains little methanol and consisted of primary alcohols over the whole range. Only about 10% methane on CO/H_2 reacted was formed. This process had only been worked on a very small scale. Roelen would supply us with details of this work. He was not aware of the I.G. "Synol" process which he confused with their higher alcohol synthesis based on methanol.

4. Research Background

(a) Staff

Roelen was in charge of CO-hydrogenation and OXO-reaction research for Ruhr-Chemie, having a staff of 8-10 graduate chemists and a total staff, including girl assistants, of 140. Shortly after his discovery of the OXO-reaction, Ruhr-Chemie and I.G. formed a purely financial Company - "Chemo" - to exploit the process. With the inclusion of Henkel, "Chemo" was transformed into the "OXO Gesellschaft". This Company was formed solely to manufacture alcohols for detergents and did not have a research staff.

Roelen continued with Ruhr-Chemie, his staff consisting of:-

Heckel	-	catalysts
Bückner	-	analysis
Hausen	-	OXO-products
Landgraf	-	OXO-synthesis
Lenke	-	" "
Schenk	-	CO-hydrogenation

Landgraf subsequently was made OXO-Plant Manager. In addition, the following chemists worked with Roelen, but subsequently were transferred to the operating side of Ruhr-Chemie.

Lüben	-->	waxes
Feisst	-->	sulphur removal
Schaller	-->	catalyst manufacture
Schuffe	-->	main Fischer-Tropsch synthesis plant,

Other individuals of Ruhr-Chemie staff are as under:-

Gerkl	-	catalyst manufacture
Hartwig	-	instruments
Heger	-	Fischer synthesis
Henke-Stark	-	Analysis
Kolling	-	Hydrocarbon distillation
Krüger	-	Synthesis laboratory
Nebelling	-	Synthesis plant
Rottig	-	catalytic cracking
Strötgen	-	Records and documents
Velde	-	Synthesis laboratory
Von Asboth	-	Designer of Italian OXO-plant

Roelen himself acted as Liaison Officer on OXO-work with I.G., the I.G. officials being Reppe & Schuster at Ludwigshafen and Herold & Gemasmer at Leuna.

(b) Research

Roelen stated that research policy was very flexible, and he was unable to assess the amount of research devoted to the OXO-process in contrast to Fischer-Tropsch research. The emphasis in the OXO-field was very definitely on producing detergent intermediates as rapidly as possible. The bulk of the work was done on C_{10} - C_{20} olefines, comprising investigation of raw materials and separation of the product. Much work was also done on design data for the OXO-plant, design of which was started hurriedly.

Not a great deal of work was carried out on catalysts, since the standard Fischer-Tropsch catalyst was satisfactory and was available in quantity. Little work was done on regeneration or re-use of catalyst since here again the usage was small compared with that on the main plant, and if necessary, all catalyst could be comfortably absorbed in the Fischer-Tropsch catalyst recovery plant.

A good deal of research was done on sources of olefines. Those obtained from the cracking of wax and heavy Fischer-Tropsch oils were more branched than those synthesised, and olefines from the medium-pressure recycling process were preferred.

Research was also done in connection with the Italian plant to produce propionaldehyde, but the Ruhr-Chemie/I.G. split is not clear.

Roelen investigated Gasol (C_3 + C_4 olefine-paraffin mixture) polymerised olefines, oleic acid, cyclopentadiene, octenes etc., but his information was scanty.

A good deal of his effort had apparently been put into the development of the iron catalyst for Fischer-Tropsch synthesis. He was rather vague about the direct alcohols synthesis research.

In general, the impression was created that he is less expansive when talking about the research side.

(c) Apparatus

As well as the large number of small 50 ml. autoclaves, he had three or four semi-continuous units consisting of jacketted tubes (hot water cooling) which were gradually filled with reaction liquid, CO/H_2 being passed through continuously. These were up to 15-20 cm. in diameter and 2-3 metres high.

He had about 8 units which he had used for the direct alcohol synthesis, operating at 10-15 ats. and carrying up to 5 lts. of catalyst.

Several stirred autoclaves up to 15 lts. capacity and directly gas-fired were available.

He had done some work at 1000 ats., but was very vague as to its nature. He had however three Hofer type compressors.

It appeared that the semi-technical equipment was very flexible and no information was obtained of any sustained effort along the lines of developing continuous working. The development of a continuous OXO-process was largely in the hands of I.G. at Ludwigshafen and Leuna. The Leuna work was on a large experimental scale and a large pilot plant apparently was ultimately operated on a continuous basis. Pilot plants he knew of for the OXO-synthesis were:-

1) Holten (Ruhr-Chemie).
2) A large unit (10,000 t/yr.) at Holten, not yet operated.
3) Several units at Ludwigshafen (I.G.).
4) A large unit at Leuna used as a research pilot plant (I.G.).

5. Action

Dr. Roelen would supply us with the following accounts:-

1) Types of apparatus used in the OXO-synthesis, with sketches.
2) Examples of unreactive olefines and steric hindrance.
3) History of the OXO-process and plant flowsheet.
4) Iron catalysts for the Fischer-Tropsch medium pressure synthesis, with special reference to olefine synthesis.
5) Details of the direct alcohols synthesis.

R.F. Goldstein
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