

II. THE FORMYLATION PROCESS (OXO-PROCESS)

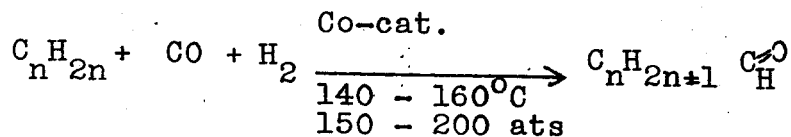
I. G. FARBENINDUSTRIE A. G. (Badische Anilin und Soda Fabrik) Ludwigshafen - Oppau, May 22, 23, 28 and 29, 1947.

Ludwigshafen: Dr. Kurt Schuster
Dr. Eilbracht

Oppau : Dr. Nienburg

A. Introduction

The Oxo-process



has been described in some detail by various previous investigators. ¹⁾ However, so far nothing has been reported on the Oxo-studies as carried out at the Ludwigshafen - and Oppau-laboratories of I.G. These institutes have no doubt contributed largely to the development of the process from the processing point of view as well as with respect to the clarification of the kinetics of the reaction. Therefore, the information collected when visiting these I.G.- works will be reported here in detail.

¹⁾ C.I.O.S. Item No.22, File No. XXVII-18:
"The Oxo-plant, Ruhrchemie Oberhausen-Holten"

C.I.O.S. Item No.30, File No. XXXII-96:
"Ruhrchemie A.G. Sterkrade-Holten" (pp.17-19)

B.I.O.S. FR No. 747, Item No.22:
"Acetylene by the arc; also the Oxo-synthesis at Ruhrchemie, Holten" (p.2)

B. General considerations

Whereas Ruhrchemie, the original inventors of the Oxo-reaction, had only carried it out as a batch-reaction and had accordingly designed the commercial plant of the Oxo-Gesellschaft m.b.H. at Holten, I.G. Farben did not consider this as the best possible technical proposition, and had started work on the possibilities for continuous operation at an early date.

The solution as proposed by I.G. Leuna consisted of passing a slurry of cobalt-on-guhr catalyst in the olefine-feed together with watergas through a series of reactors whereupon the slurry was to be treated with hydrogen in a subsequent series of reactors, first to decompose dissolved carbonyls and next to hydrogenate the aldehydes formed in the first stages, without intermediate separation of catalyst. Finally, the catalyst was to be recovered from the alcoholic product by filtration.

On the other hand, I.G. Ludwigshafen followed a completely different course in their researches. The essential point in their work is the application of the so-called "Rieselfverfahren" (trickle-phase- or drip-phase-operation) to the Oxo-process.

This specific way of carrying out liquid-gas-reactions had been developed at the "Hauptlaboratorium" by Dr. Walther Reppe and his co-workers. It is characterised by the fact that the liquid feed is charged to the top of a reactor filled with catalyst and flows downward concurrently with the gas feed. As the catalyst is always covered with a thin layer of liquid, diffusion of gas to the catalyst-surface will be relatively easy, thereby providing a high rate of reaction. Moreover, high gas velocities may be maintained without risk of "flooding" the column, and this opens the possibility of removing the heat of reaction by the application of a high rate of circulating gas, no other cooling of the reactor being provided for.

This reaction system has successfully been applied in commercial hydrogenation processes (e.g.

in the hydrogenation of "aldol" to "butol" at the Huls butadiene factory. ')

When applying this technique to the Oxo-reaction it was realized that provisions should be made for replacing the cobalt removed from the solid cobalt catalyst in the reactor in the form of carbonyl in the products to which end cobalt-fatty acid salt was added to the feed in adequate amounts.

The reaction product from the Oxo-stage was treated with hydrogen in a subsequent reactor, filled with pumice; the carbonyls present in the product were thereby decomposed and the cobalt-metal formed was deposited on the pumice, from which it could be recovered later in a suitable manner.

Finally, the decobalted product was hydrogenated in a third reaction system. As no cobalt was present in the feed to the hydrogenation-reactors, any suitable catalyst could be used in this stage. A copper-chrome-silicagel catalyst, prepared on a commercial scale at Ludwigshafen, was usually applied.

This general set-up offers a number of advantages over the Leuna operational scheme, viz.:

- a. No suspension of solid catalyst in the olefine-feed need be prepared, maintained and pumped, only clear solutions being handled.
- b. The filtration of the very small-sized catalyst particles from the final product is eliminated.
- c. No provision need be made for building sufficient cooling surface inside the reactors, the heat of reaction being removed by the gas.

1) C.I.O.S. Item No.22, File No. XX11-21
"Synthetic Rubber Plant Chemische Werke -
Huls" (p.39)

- d. The hydrogenation can be carried out with catalysts less sensitive to CO than cobalt.

However, the Leuna-system was considered to require considerably less reaction-space than the Ludwigshafen-operation. Since, on the other hand, feed stocks different both as regards molecular weight and olefine content were used at the two research-centres, the discrepancy in the allowable space-velocities may be partly attributed to this point. (Dr. Eilbracht).

At Ludwigshafen the process had been operated on a pilot plant scale by Dr. Schuster and Dr. Eilbracht of the "Hauptlabor". This plant had been removed to Gendorf in 1944 and had only partly come back after the capitulation. With the pumps and circulation-compressors missing, it could not be operated.

At Oppau research work had been carried out by Dr. Nienburg of the "Ammoniaklabor" mainly in small-scale equipment; moreover, a pilot plant had been erected in 1944, which was then damaged by bombing and had not come into operation until recently.

C. Information on the processing at Ludwigshafen

The Ludwigshafen pilot plant consisted of two reactors, each of which was 70 mm ϕ and 9 m high, made of Ni₈-chrome steel and provided with electrical heating. The first reactor was charged with 25 l Co-on-pumice (1% Co) catalyst and was used for the formylation-step. The second reactor was charged with 25 l. pumice and served for decobalting the Oxo-stage product. This was finally hydrogenated in separate equipment.

The plant was further equipped with pumps for the olefine-feed, a separate pump for injecting cobalt-fatty acid salt-solution, and with gas circulating compressors.

The arrangement of the plant, located in Lu#115, is shown in the attached diagram and photos (fig.11-1-4).

The following operational conditions were given by Dr. Schuster and Dr. Eilbracht:

	O x o	Decobalting
Feed	Michael-benzin	Product from Oxostage
Cobalt solution	Cobalt-fatty acid salt 10% Co in Oxo-alcohols	-
Feed rate	5 - 20 kg/h olefine feed 0.05 - 0.2 " Co-solution (0.1% Co on feed)	10-40 kg/h product (containing 0.1% Co)
Reaction gas	Watergas CO/H ₂ abt.1/1	H ₂
Total gas rate *	10 st.m ³ /kg feed	-
Temperature	160 - 180°C	120 - 150°C
Pressure	200 ats (grid)	180 ats (grid)
Oven charge	25 l catalyst 1% Cobalt on pumice	25 l pumice
Conversion reached	abt.95% olefine-conversion	90-99% cobalt removal
*The HP circulation gas was found not to contain any volatile cobalt compounds.		

The feed stock generally used at Ludwigshafen was Michael-benzin, the gasoline produced in the Michael-modification of the Fischer-Tropsch-process for which they had a pilot plant in operation. This feed stock contains about 60-70% of olefines,

which are mainly single-branched. Usually a fraction with 100-150°C boiling range (C_8-C_{10}) was used, but other ranges were also investigated (e.g. 100-200°C corresp. to C_8-C_{12}).

The cobalt-solution was originally obtained from hexahydrobenzoic acid or from naphthenic acids, but as forerun-fatty acids were readily available and as the latter cobalt salts were better soluble, they were later exclusively used for this purpose. The salts were obtained by reacting cobalt acetate with the fatty acids at abt. 150°C, distilling off the acetic acid formed under vacuum.

Ludwigshafen had actually run their reactor once for a total duration of 3 months with many interruptions, the conversion remaining constant all through this period.

Some confusion exists as to the allowable feed rate to the reactor: as a representative figure Dr. Schuster stated that the production of alcohols amounted to about 0.35 kg per litre of reaction space ("8 kg Alkohol pro Liter pro Tag"), which figure would correspond to a total feed rate of abt. 0.5 kg/l.h. However, Dr. Schuster was convinced that a higher rate would be allowable, provided that sufficient gas-circulation is maintained for removing the heat of reaction.

The pre-treatment of the fixed catalyst used is not critical: pumice was impregnated with cobaltnitrate and the catalyst was thereupon ignited in order to decompose the nitrate. It was subsequently reduced with hydrogen, but it is also active without previous reduction.

As a representative product-composition the following figures were stated:

from 1 kg olefine feed, fraction 100-150°C,
olefine content 67%

were obtained: 350 grams forerun paraffin-
fraction,
700 " Oxo-alcohols C_9-C_{11}

were obtained: 110 grams thick oil boiling >
120°C at 10 mm.

The product-distribution therefore is

abt. 85% alcohols

and 15% thick oil.

The thick oil contains esters and higher alcohols as well as aldol-type condensation products; however, no ketones were found in the thick oil of this type of feed stock.

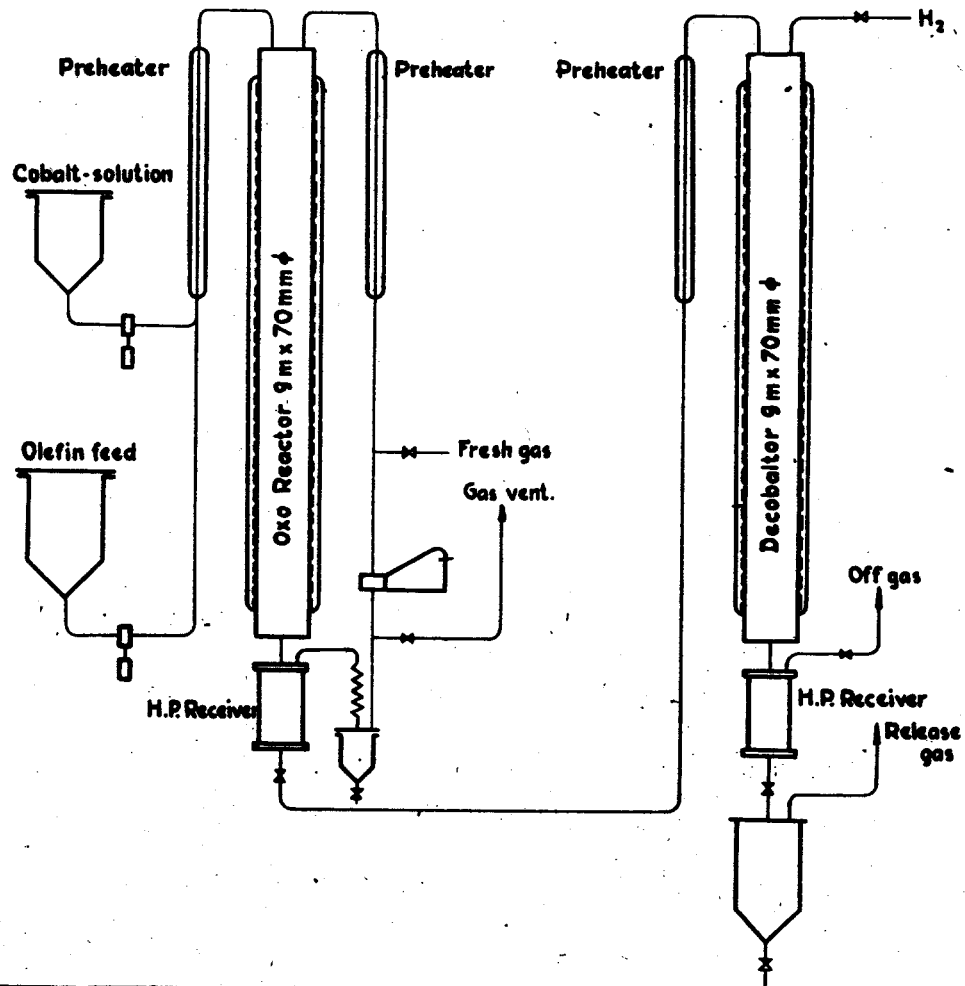
The feed rate in the decobalting step may easily be chosen twice or more times as high as in the Oxo-step. The pressure is not critical: good results were obtained at lower pressures (100 ats) as well. The use of hydrogen seems to be rather essential: with nitrogen a certain decomposition of the cobalt-carbonyl-compounds was reached, but decobalting remained less complete than with hydrogen. The total amount of cobalt metal to be "stored" in the decobalting reactor could not be given. The system had once been in operation continuously for a period of over two months and was then still operating satisfactorily. This would correspond to a total quantity of about 15 kg Co per 25 l of pumice.

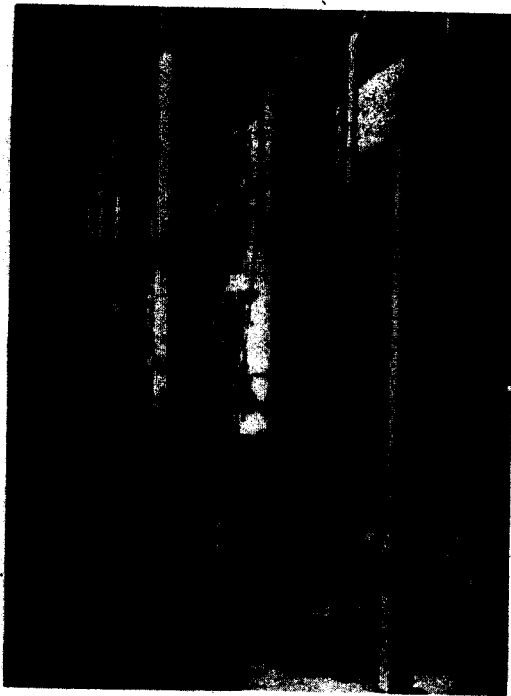
The cobalt is not distributed evenly throughout the column, some accumulation taking place near the feed-side. This can, however, be improved by applying a sufficiently high gas circulation rate and by a proper choice of the temperature distribution.

It has been proposed to convert the cobalt, accumulated in the decobalter, into a solution of cobalt-tetracarbonyl by feeding Oxo-alcohols and carbon monoxide under pressure (as available at Ludwigshafen) to the reactor, after this should have been loaded to capacity. Dr. Eilbracht, however, does not consider this to be a practical proposition: as the decobalter can be run for months on end, the cobalt-carbonyl-solution would have to be storable for the same period, and he

Fig. II-1

Note: The decobalting is operated at a pressure about 20 atms lower than that of the oxo-stage and the oxo-product was run without intermediate depressuring into the decobalator.





Oxo
Reactor

Decobalter

FIG. II-2



FIG. II-3

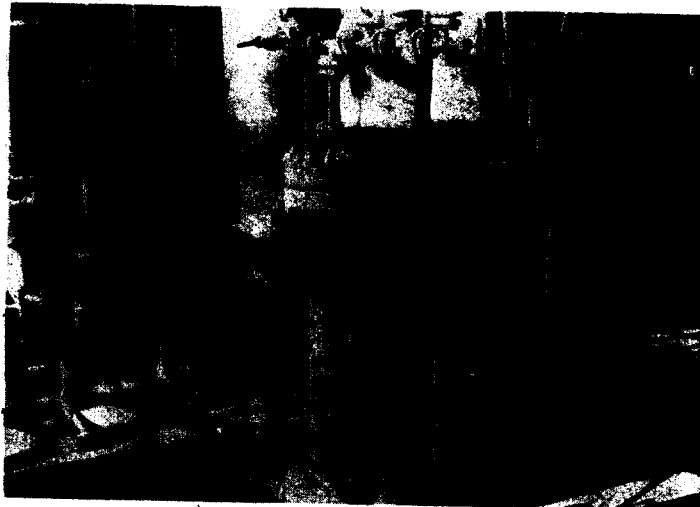
Decobalter

+

Preheater

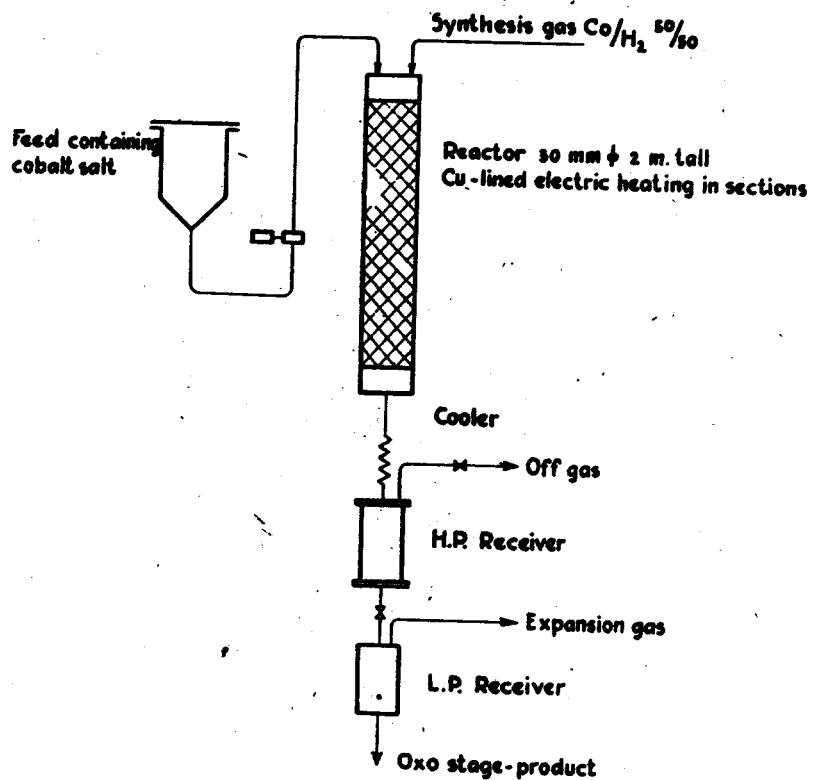
H.P. Separator

FIG. II-4



Bottom-end of
Decobalter with
H.P. Separator

Fig. II-5



OXO LABORATORY REACTION SYSTEM

Op # 140

FIG. II-6

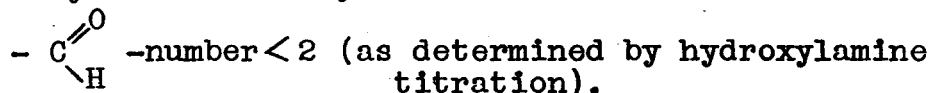


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2 Oxo
reactors Decobalter Hydro-
reactor

does not consider this to be feasible. Accordingly, in Dr. Eilbracht's opinion, the reconversion of the cobalt into the fatty-acid salt is the preferable proposition for the recovery of this material.

The hydrogenation of the decobalted product has been effected with different catalysts, as e.g. 5% Co on silicagel, 5% Ni on silicagel, Ni on pumice or Cu-Cr on silicagel (B.B.E. catalyst). The latter was generally used for aldehyde-and ester-hydrogenation and being available from large scale production it was later used exclusively. Complete hydrogenation could be reached in one pass in a trickle-phase system. The final product was said to contain only very little aldehyde:



Finally it should be noted that in the early stages of their work Dr. Schuster had used small-scale apparatus in which liquid olefine-feed (obtained from wax-cracking) and water gas were passed up-flow through a catalyst bed. Although no direct comparisons between this system and the trickle-operation were made, the latter was generally preferred, primarily because of the supposed better contact between gas and liquid and catalyst, but also in view of the small liquid hold-up in the trickle-system. This will offer a definite advantage in case a reactor should have to be disconnected in a large-scale plant.

D. Information on the processing at Oppau

1. Laboratory studies

The small scale equipment as in use at Oppau 140 is shown in the attached flow diagram (fig.II-5) and photograph (fig.II-6). It consists of 4 reactors, two of which are used for the formylation proper, one is used for decobalting and one for hydrogenating.

All reactors are operated trickle-phase and once-through for liquid and gas. The total length, 2 meters, is considered by Dr. Nienburg to be the minimum which can be used successfully in trickle-

phase operation and a greater length is certainly advisable: the contact-time in this type of processing is primarily determined by gravity-flow rather than by the throughput applied; in model-experiments carried out in glass equipment with water as the trickling liquid a contact-time of abt. 2 minutes per meter is found, independent to some extent of the throughput.

Dr. Nienburg had studied the formylation of a large number of pure olefines in this equipment (vide next section) during the war.

The following representative data were given for a recent run with cyclohexene as the feed:

<u>Condi- tions</u>	Oxo-stage	Deco- balting	Hydro- stage
Feed	{ 90% v. cyclohexene 10% v. Co-solution	product from Oxo- stage (0.1% w. Co)	decobal- ted pro- duct (0.00%w. Co)
	d = 0.805		
Cobalt solu- tion	2.2% w. Co in butanol Co as fatty acid salt	-	-
Feed rate	126 cm ³ /h mixed feed	120 cm ³ /h	100 cm ³ /h
Gas rate	20 st.l/h off gas	120 st.l/ h off gas	120 st.l/ h off gas
Cata- lyst	pumice, no Co 7 - 9 mm size 560 cm ³ = 167 grams	pumice 530 cm ³	B.B.E. ₃ 1000 cm ³ = 730 grams
Pres- sure	150 - 200 ats CO/H ₂ 1/1	200 ats H ₂	200 ats H ₂
Tempe- rature	140°C	120°C	160°C
<u>Results</u>			
Conver- sion achieved	93% olefine con- version	complete Co-re- moval	2.4% alde- hyde in main al- cohol fraction

In the Oxo-stage 113 cm³/h product (density 0.915) was obtained, yielding through rectification:

up to 90°C	10.7% wt	} butanol and unconverted olefine
90 - 120°C	2.7% "	
120 - 150°C	1.3% "	
150 - 170°C	68.0% "	aldehyde fraction
residue	17.3% "	thick oil

100. % wt.		

The composition and quantity of the reaction gases were:

Quantity	<u>Off gas</u>	<u>Release gas</u>
	20 l/h	3,25 l/h
Composition % v. CO ₂	0.6	1.4
C _n H _{2n}	0.0	1.4
CO	46.6	49.6
H ₂	45.0	40.6
CH ₄	0.8	0.8
N ₂	7.0	6.2

In the decobalting stage no aldehydes were found to be hydrogenated, no saturation of unconverted cyclohexene taking place either.

The hydrogenation of the decobalated product yielded a final product, the main distillation-fraction of which was analysed as follows:

fraction 170 - 190°C

- OH number	460	(93.6% C ₇ -alcohol)
- C _n H _{2n} O	12.1	(2.4% C ₇ -aldehyde)
- COOH	0	

saponification
number

7.2 (2.9% C₁₄-ester)

Only 30% of the cyclohexene present in the decobalted product proved to be hydrogenated in the hydrogenation stage.

2. Splitting hydrogenation of thick oil

The thick oil obtained in the Oxo-process may be converted partially into valuable alcohol by hydrogenation in drip-phase at higher temperatures:

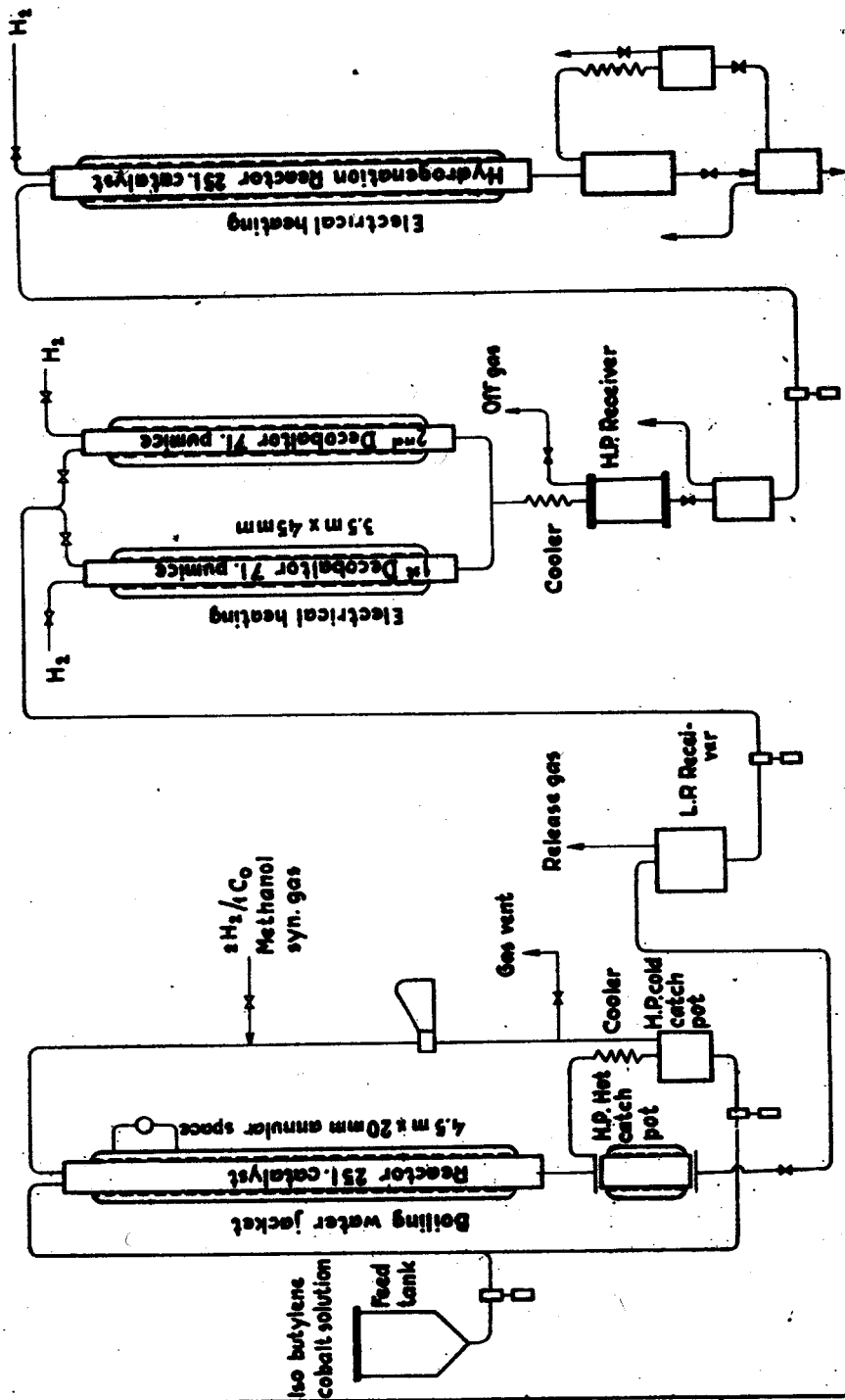
Apparatus : laboratory type
Feed : thick oil from cyclohexene
Feed rate : 100 cm³/h
Gas rate : 2 l/h H₂ off gas
Catalyst : B. B. E. 1000 cm³
Pressure : 200 ats H₂
Temperature : 280°C

Properties:

	<u>Feed</u>	<u>Product</u>
-COOH number	1.0	0.0
-Saponification number	157	0.0
-C $\begin{smallmatrix} \text{H} \\ \diagdown \\ \text{O} \end{smallmatrix}$ number	109.2	1.0
-OH "	23.8	304.3
% wt. C	77.03	76.85
% wt. H	11.00	13.01

Distillation of the reaction product yielded:
25%^{wt} fore-runings, containing water (9% on total), cyclohexane and methyl-cyclohexane and other not identified hydrocarbons.

Fig. II-7



Oxo PILOT PLANT OPPAU # 266

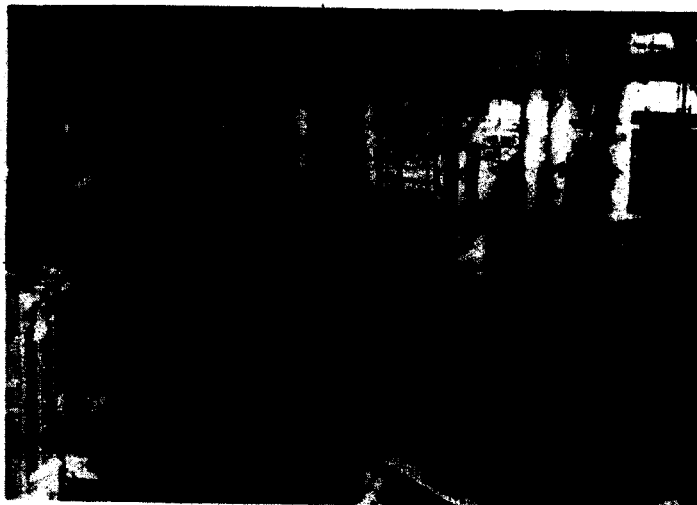
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FIG. II-8

Oxo 2 Hydro
Reactor Decobalters Reactor

FIG. II-9



48% wt. fraction 181-186°C corresponding to cyclohexyl-carbinol.

27% wt. residue.

The residue may well contain C₁₄-alcohol. In the case of cyclohexene-thick oil its constitution was not determined. With isobutene as the feed, however, a similar residue was analysed to contain C₁₀-alcohol.

3. Semi-scale experiments

In view of the availability of propene from propane-dehydrogenation Oppau started erection of a semi-scale Oxo-plant during the war (Oppau 266). This plant was damaged by bombing but has since been repaired. Operations had recently been resumed. With a view to obtaining products useful for the manufacture of pharmaceuticals, the plant is now being run on isobutene as the feed. As the isobutanol-manufacture was in operation, isobutene could easily be obtained via dehydration of the isobutanol.

Dr. Nienburg intends to run the plant applying a hot separator (the product from which will be the main product) followed by a gas cooler and cold separator, the product collected in which will consist of unconverted isobutene and therefore will be recycled. Moreover, as during the reaction a volatile cobalt compound obviously is formed, assumed by Dr. Nienburg to be cobalthydrocarbonyl, this cobalthydrocarbonyl may be expected to be trapped in the cold catchpot from which it will be recycled to the reaction zone. This way of operation is expected greatly to reduce the amount of cobalt required to be fed in with the fresh feed to the plant. ¹⁾

¹⁾ This conception does not seem to be completely new: a similar arrangement was proposed by Ludwigshafen accordingly to T.O.M. Microfilm Reel 134, Section VII, Item 17, page 7. (FD 2161/48) Available at:- Technical Information & Documents Unit, Board of Trade (German Division), 40 Cadogan Square, London, S.W.1.

So far, operations had not been successful, as the iso-amyl alcohol formed was not trapped in the hot catchpot but distilled to the cold separator.

The plant consists of one reactor for the formation proper (being 4.5 m high and having an internal diameter of 91 mm with a 45 mm central displacer, leaving a free annular space of 200 mm). provided with a jacket for boiling water, the temperature being controlled by the pressure. The reactor can be operated either drip-phase or "sump-phase" and is provided with a gas circulation system. It is charged with abt. 20 l of catalyst, consisting of 2% wt. Co on silicagel.

The product from the Oxo-stage will be decobalated, "prehydrogenated" as it is called in Oppau, in either one of two decobalting ovens, 3,5 m high and 45 mm wide, provided with electric heating and filled with pumice (7 litres). No provisions for recirculation of gas have been made.

Finally, the decobalated product will be hydrogenated in a reactor of similar size as the Oxo-reactor. It is, however, not fitted with a constant temperature jacket but is heated electrically. The gas system is for once-through operation.

For the sake of completeness reference is made to the attached flow scheme and pictures of the plant (fig.II-7 -9).

Oppau intend to run the installation at a feed rate of 10 l/h isobutene, a solution of 2% wt. Co (fatty acid salt) in butanol being added to the feed. The life of the solid catalyst in the Oxo-stage is expected to be very long, as the small-scale reactors have been run for several months without decline of conversion.