H. THE PROCESS FROM THE ENGINEERING STANDPOINT

Unfortunately, the microfilm reel #14 now available does not depict all the documents which were originally seized. Some of the unavailable documents are believed to give considerable information on the engineering features of the process. Only fragmentary information can be given here, mostly taken from the preliminary reports.

As previously stated, the OXO Gesellschaft's plant in Ruhrchemie was to operate batch-wise, but the continuous process was more or less agreed upon as most advantageous. Consequently,

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it will be described more in detail later in this report. It
is, however, of some interest to note the date and kind of
information which was being obtained in semi-technical scale
at Leuna for the benefit of the design or redesign of larger
equipment at the OXO Gesellschaft. The information is given in
about the same detail as appears in the seized documents, since
it might serve as a guide for orientation experiment by others
on the OXO process.

Semi-Technical Scale Experiments (14-514 to 05516)
        Letter dated February 5, 1942.

        To see what was required for larger scale work (at
Ruhrchemie), Leuna used the following apparatus in a test
reported on above date.

Vertical Reactor   200 mm ID, length 8000 mm. High pressure
                        tube. Cooling surface total 360 cm^2/liter
                        of contents comprising welded jacket surface,
                        210 cm^2/liter and tubular surface (tube size
                        not stated) of 150 cm^2/liter of contents.
                        Cooling method not clearly stated, but by
                        inference consisted in releasing pressure and
                        thus allowing vaporization of water in jacket
                        and tubes. Temperature measurement made at
                        0.5, 1.0, and 4.0 meters above bottom flange
                        by thermocouples.

Method Used   (Translation of German follows.)
                        Reactor filled by injecting "Maische" (i.e.,
                        suspension of catalyst in liquid) from below
                        against 200 atm. pressure of gas (synthesis
                        gas in plant network). 140 liters intro-
                        duced cold, then heated by jacket steam to
                        reaction temperature. Gas pressure then
                        reduced to 150 atm. and regulated thereafter
                        by hand operation of valve. Temperature-
                        controlled by steam release in part and by
                        steam condensation in condenser above appa-
                        ratus. Gas flow through reactor held at
                        60 m^3/hr. or 190 normal liters per cm^2 free
                        cross section and hour. Gas was heated to
                        temperature before introduction "but effect
                        was insignificant" in the batch operation.
                        Gas flow maintained 65 minutes, but on

account of stoppage in outlet line the vessel
contents remained in reactor without gas flow
(but presumably under temperature and pres-
sure -- translator's note) for another 45
minutes.

Charge   "Maische" or liquid suspension consisted of
C_{12} olefin fraction with proportion of 4 kilos
Ruhrchemie Contact to 100 liters actual olefin.
The C_{12} fraction was sp. gr. 0.762, boiling
range 206°-216°C., S.P.L. 67%. Olefin content
about 65%.

Gas Reagent. Winkler water gas desulphurized
over special "Crude" (i.e., coke from low
temperature carbonization) to 2 milligr. S per
cu. meter gas. Composition of gas:

           42% CO
           52% H_2
           4.5% CO_2
           1-2% N_2 plus CH_4

Conclusions from the experiments were noted for the
benefit of Ruhrchemie to be:

1. It is possible to hinder, that is, control, the com-
pletion of the reaction by expanding steam out of the
heating system. (Presumably the water jacket, etc.,
which served as heating system at first and later
during reaction as cooling facility.)

2. One must carry out the expansion carefully, other-
wise the reaction may cease in the bottom part of
vessel.

3. It was not possible to control the reaction by steam
release so that temperature was equalized throughout.
A difference of 15°C. was noted between the upper and
lower thermocouples.

4. Due to cooling, the reaction ceased in the lower part
of reaction chamber, and it was accordingly not possi-
ble to complete the reaction in the time demanded of
20 minutes (probably specified by someone, based on
Ruhrchemie design).

5. In spite of the long time at temperature of 65 minutes with gas passing through the reaction mixture, the conversion was only 80% as determined by distillation. About 30% of the olefins which were transformed were in the form of "thick oil", i.e., were polymerized.

6. It appears, therefore, that the provisions made in the large equipment at Holten (i.e., Sterkrade) to regulate the reaction will indeed make it possible to control same, but it also appears that it will not be possible to hold constant temperature throughout the reactors; hence it will be difficult to find the proper position for temperature controllers..... Also, we question if it will be possible to get the production which has been foreseen, especially in view of the difficulties of temperature equalization.

Batch Producing Plant - OXO Gesellschaft

The OXO Gesellschaft's batch process production plant at Ruhrchemie consisted of nine units, each with two reaction vessels for first and second stage. These reaction vessels were all fitted with tubular heat exchange surfaces for control of the reaction. The notes of interview give the following data, which should, however, be checked by drawings. These, it is believed, will be available later in microfilm form.

"Reactors - Intervolume 1.2 m³

> ⌀ O.D. 570 mm
> ⌀ I.D. 400 mm
> Length - 12,000 mm

"Reactor Cooling Surface

> 31 tubes 38 mm O.D.
> Length - 8,000 mm"

Operating Conditions

Temperature first stage   - 120°-140°C.
Temperature second stage   - 180°C.
Pressure both stages   - 150 atms.

The operation of the equipment was simple, consisting in the water-gas treatment in Vessel No. 1 then pumping the reaction product containing catalyst into the second vessel, where hydrogenation was caused to take place. Both the water-gas and the hydrogen were continuously circulated through the reaction vessels to insure good contact and to keep the solid catalyst syspended.

The exit hydrogen from the second stage in the recirculation circuit was passed through an iron catalyst to reduce the carbon monoxide content arising from solution of carbon monoxide in the liquid and decomposition of cobalt carbonyl from about 2.0% to 0.05%. The hydrogen purified in this way was pumped back into the second stage. No details of the operation are available, but microfilm Reel 14 contains a memorandum showing what was planned for the batch operation production of phthalic acid ester of a C_7 to C_{10} cut. The work was to be done at Leuna by a method presumably quite similar to that projected for the large plant at Ruhrchemie.

The document is translated with rearrangement here because of interesting sidelights which it contains. File memorandum dated October 20, 1942 (14-668):

"Sufficient alcohols in the middle range of chain lengths (say from C_8 to C_{12}) are not available for the manufacture of Palatinol as plasticizer for rubber in cables to withstand cold temperatures and for shoe soles."

"Since the OXO plant in Holten cannot be put into operation before 1943, and since then the production of middle-length chain alcohols will be at the cost of reducing production of alcohols for washing media, we will consider in what follows whether it is possible in the OXO plant at Leuna to make about 2,000 tons per year of middle-length chain alcohols.

"Kogasin I from Ruhrchemie will be cut so as to give the boiling range of 80°-175°C. (C_7-C_{10} hydrocarbons). The raw materials will be delivered to the plant at Leuna in a form and with a boiling range which makes it unnecessary to distill them.

"Form of the OXO Process to be Used

"The olefin raw material will be mixed with 3% to 4% of finely divided reduced cobalt catalyst, and the suspension

will be continuously treated first with water-gas and
then with hydrogen at high pressure and at the required
temperatures.

"The 'Maische' or suspension will be expanded to atmos-
pheric pressure after the first stage to remove the
carbon monoxide before injecting into the hydrogenation
stage. Filtration to separate the solid will be done
after the hydrogenation stage. The catalyst will then
be stirred up with the fresh olefin (for reuse).

"The filtrate will generally be clear and of light yellow
tone. It will contain the desired alcohols and also
unreacted constituents, such as the paraffins, and up to
10% of the original olefins. Perhaps up to 10% of the
alcohol formed will be present as higher boiling viscous
oil obtained by aldolization and a ketone reaction.

"The present picture of the esterification by phthalic
acid to make Palatinol is as follows: in spite of the
large amount of neutral oils, namely, from 65% by volume
in the case of these alcohols from primary olefins, the
esters formed are not lost in the neutral oil. Return
of the neutral oil after separation of the water is not
necessary, and the neutral oil acts very satisfactorily
as water-transporting media (translator's note: Refer-
ence must be had to azeotropic removal of water in con-
tinuous esterification). An addition of 10% of the
viscous oil to Palatinol does not act deleteriously.

"According to the present viewpoint, the crude filtered
product from the second stage of the OXO process can be
sent through to esterification. If, for any reason,
distillation of the crude product and a concentration
of the alcohols are necessary, such distillation can be
carried out in the existing distillation plant ....."

"Throughput Required of the Plant

"On the assumption that the alcohol yield will be one-
third of the product introduced, the required capacity
of the plant will be 3/4 ton of charge stock per hour
or 6,000 tons per year. This will mean that 1,050
liters/m of charge stock, sp.gr. 0.72, will have to be
introduced into reactors.

"Requirements for the Reaction

"Assuming an average molecular weight of 155, an olefin
content of 35% for the charge stock, and the introduction
of 750 kilograms of liquid/m, the OXO reaction will
require per hour 58 m³ of carbon monoxide and 58 m³ of
hydrogen. Both figures are reduced to 0°C. -- 760 mm Hg
pressure -- as are all subsequent gas figures.

"For hydrogenation of the aldehyde in the second stage,
there will also be required 58 m³ of hydrogen.

"The following amounts of gas will be dissolved from each
of the circulating streams per hour:

> "42 m³ of CO + H₂   - first stage
> 26 m³ of hydrogen   - second stage

"Accordingly, the total usage of the two gases will be
160 m³/hr. of water-gas and 85 m³/hr. of hydrogen.

"Heat of the Reaction

"1. OXO stage - 100 kilogram calories per kilogram of
      liquid introduced, under the assumption that 40%
      of the total hydrogenation will occur in the OXO
      stage, hence 75,000 kilogram calories/hr. for the
      750 kilograms introduced.

"2. Hydrogenation stage - 50 kilogram calories per kilo-
      gram of liquid introduced, hence 37,500 kilogram
      calories/hr. for the 750 kilograms of liquid intro-
      duced.

"Methanization of the Carbon Monoxide to Purify
 the Hydrogen Circulating Stream (Second Stage)

"Under the assumption that about one-third of the cobalt
contained in the catalyst mass will be present as dis-
solved carbonyl after the OXO reaction, one calculates
a content of bound carbon monoxide in the form of $Co(CO)_4$
of 1/5 gram mole per kilogram of product, equals 4.5 liters
carbon monoxide per kilogram of product. With the intro-
duction of 750 kilograms of liquid, the methanization
reaction, to form methane out of carbon monoxide, must
therefore handle an amount of carbon monoxide equal to
3.4 N m³/hr. The heat quantities to be removed by the

reaction will be 3,000 kilogram calories/m^3 of carbon
monoxide, equal to about 10,000 kilogram calories/hr.
0.8 liters of water will be produced per m^3 of carbon
monoxide; hence in our case 2.75 liters H_2O/hr."

Translator's Note:

The very substantial degree in which the Fischer catalyst
is formed and reformed in the reaction itself is evident
from the above. It will be clear why the plan was to
release the pressure from the products after the first
OXO stage, thus freeing the mixture of dissolved gases
before passing to the hydrogen stage. This materially
reduces the load on the purification of circulation
hydrogen by removal of carbon monoxide, as just mentioned.
The manuscript then considers the amount of loss of prod-
uct which will be involved in this release of pressure
from the reactants.

"Product Loss Through Release of Pressure on
Products -- After First Stage

"Not inconsiderable amount of product loss will result
from the release of pressure on the product gases.
These losses will be as follows (translator's note:
conditioned by the vapor pressure, hence temperature at
which the gas is released):

"Temperature, °C.	Loss/m^3 of Released Gases
50	500
30	200
15	100
0	50

"With product gases, from both stages, in the amount of
70 m^3/hr., the product losses will be as follows,
expressed as a function of temperature:

"Temperature, °C.	Percent of the Raw Material Introduced
50	4.5
30	1.85
15	0.93
0	0.47

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"As may be seen by the above tables, it proves to be
necessary to extract liquids from the expansion gases,
either by cooling the gases or by raising them through
an active charcoal plant.

"## Catalyst Requirement

"In a plant of the size of that in ME 458A (translator's
note: this is a building number), a circulation volume
of 4 m^3 of liquid suspension or 'Maische' can be
expected. To begin the experiment, catalyst in the
amount of 120 kilograms is required for a concentration
of 3% catalyst in the liquid. The catalyst will circu-
late about six times per day with an injection of about
1 m^3/hr. of liquid suspension.

"If one reckons according to present experience, with a
catalyst application of 50 to 60 times, then the total
amount of catalyst must be renewed every ten days.
Since, however, the catalyst will be renewed continu-
ously, a daily introduction of about 12 kilograms of
catalyst will be necessary. As a safety measure, it
will be advantageous to hold in storage an amount of
catalyst equal to the requirements for two to three
months. Accordingly, the amount of catalyst necessary
will be as follows:

"Store house   - 1 ton catalyst
 For initial experiment   - 120 kilograms catalyst
 Daily catalyst requirement   - 12 kilograms

"These data are on the basis that Ruhrchemie's Fischer
synthesis catalyst will be used.

"## Reduction of Catalyst

(Translator's note: Apparently I. G. was planning to have
unreduced catalyst delivered to them, since the following
is stated:)

"The reduction equipment in Building ME 458A can still be
used for the reduction of catalyst. A milling plant will
have to be provided for the catalyst."

Flow Sheet of the Continuous Equipment for
the OXO Process

The continuous process developed by I. G. was des-
cribed in interview by aid of a flow sheet given here as
Figure 1. It is not clear from the combination of documents
and notes of interview whether the I. G. actually had a plant
in this form or would suggest this form of plant for a new
installation. The writer may mention that it was often diffi-
cult to get at the facts in such cases, because bombing damage,
rebuilding of plant with slight changes, projection of new
equipment by engineers, etc., was often probably a more or less
confused mass of facts in the minds of the interviewed indivi-
duals, themselves.,

In any case, the flow diagram, Figure 1, is more or
less self-explanatory.

The notes of interviews state that the first reactor
is identical with those used in the batch process (with inner
coolers), while the second reactor of the same size does not
have coolers but disc and doughnut baffles. The hydrogenation
section is the same, except for a converter in the gas recycl-
ing line for converting the carbon monoxide to methane. This
is claimed to be essential to avoid poisoning of the catalyst.
Gas released from the products of the first stage is scrubbed
with incoming feed to the first stage, thus any special   ,
arrangement for liquid recovery from the released gas is
avoided. The gas release tank and the gas scrubber are not
shown in Figure 1.

Figure 2 shows another version of the process equip-
ment. Reaction vessels are identical, each having an annular
chamber for upflow of the liquid and catalyst suspension,
assisted by gas, and an inner cylinder fitted with cooling
tubes, down which the catalyst suspension moves against the
rising flow of gases. The inner section was baffled to pre-
vent excessive back-mixing of the catalyst and liquid reactants.
Here again the scrubbing apparatus for the released gases is
not shown. In interview it was stated that the results of this
pilot plant indicated that a throughput of 3 vol. liq. per
1 vol. react. vessel per hour could be had, and still attain
95% reaction of the olefins.

While it is to be hoped that documents which will
become available later will enable the design of the equipment
to be given more precisely, the writer is of the opinion that

the data already given, together with fundamental information
available in handbooks, would enable a reasonable design of
plant to be projected by competent engineers. It is, however,
also obvious that any group planning to use the process in this
country, hence planning to utilize different raw materials and
catalysts, would necessarily have to build a background of
semi-plant experience before a large plant could be constructed.
Substantially no data are available at the present time on the
materials of construction for these plants. It was definitely
stated to the writer that the vessels in the process were
copper-lined, and that no particular difficulty was experienced
in pumping the catalyst suspension due to corrosion of pumps,
glands, and the like. There is, however, no confirmation or
contradiction of these points in the documents reviewed.

J. ECONOMICS OF THE PROCESS

The following is copied directly from the preliminary
report of Dr. E. B. Peck:

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

REPLACE

TABLE II

Estimated Cost of Primary Fatty Alcohols by the OXO Process

	Ruhrchemie pfg/kg	I. G. Corrections
100 Kg. Olefines (for 95% yield)	38.00	–
Gases: (CO/H_2 & H_2)	1.30	–
Catalyst	0.60	–
Distillation (Feed & Product)	6.00	10.00
Water	1.50	3.00
Power for compression, etc.	2.30	–
Charges	1.60	–
Wages & Salaries	4.80	–
Amortization & Interest	15.00	
15% on RMG million	71.10	76.60"

Microfilm pages 724-736 present under date of August 4, 1944, a series of assumptions and cost calculative respecting OXO alcohols and the cost of making washing powders thereof. Pages 733 and 734 clearly diagram the chemicals required, and the process steps in such washing powder manufacture. Pages 735-736 tabulate the cost in RM of the intermediate and final products. Interested readers will probably wish to refer to these pages, some of which are, however, not very legible.

In common with all other cost figures under German war conditions, these figures are probably of value only as a rough indication of the general order of costs. The absolute figures are perhaps of much less value than the ratio of the various figures given, one in respect to the other.