CHAPTER III.

MANUFACTURE OF RUHRCHEMIE CATALYST

Visit to and discussions on their catalyst
plant on 31/10/1938, 14/11/1938, 17/11/1938,
18/11/1938, 21/11/1938, 30/11/1938.

A. Manufacture of fresh catalyst.

B. Regeneration of spent catalyst.

A.   The various steps are:

1. Dissolving Co and Th and/or Mg in nitric acid.

2. Mixing the above solution with an equal volume
   of sodium carbonate solution containing 103 g
   Na_2CO_3 (water-free) per litre.

3. Addition of Kieselguhr.

4. Filtration and washing of the precipitated catalyst.

5. Addition of dust.

6. Further filtration and extruding of catalyst.

7. Drying of catalyst.

8. Screening and granulation.

9. Reduction.

See Annex A, fig. 4, for the flow of materials from
points 2 - 9.

B.   The various steps are:

1. Dissolving of spent catalyst in nitric acid.

2. Filtration of solution to remove Kieselguhr.

3. Addition of so much Na_2CO_3 until all aluminium,
   iron and nickel are precipitated (these latter
   impurities result from the fact that part of the
   Kieselguhr dissolves in the nitric acid).

4. Filtration of solution.

5. Addition of NaF to remove calcium as CaF_2.

6. After filtration the solution contains about 45 g Co per litre. Magnesium and/or thorium nitrate are added and so much water that the final solution contains 40 g Co per litre. This solution is further treated in the same way as described under A.

See Annex A, fig. 5 for the flow of materials from points 1 - 6.

Discussions of the various steps.

As fresh catalyst is only made once when starting up a new plant and from that time onward the catalyst plant will treat spent catalyst only, we are starting our description with the much more complicated production of catalyst mass from spent catalyst. Make up for Co losses is added to the spent catalyst.

1. Dissolving spent catalyst.

This is done in sichromal containers, having a volume of 32 m3, with technical nitric acid of technical strength (about 620 g per 1). These containers are equipped with cooling coils and, although they do not contain indirect heating coils, facilities for adding direct steam are installed. In newer catalyst plants indirect instead of direct steam is used for heating. The dissolving procedure is as follows:

About 12 - 15 m3 $Co(NO_3)_2$ solution having a concentration of 55 - 65 g Co/litre is introduced into the tank. Then alternatively batches of about 100 kg of spent catalyst and nitric acid are added. The addition of nitric acid is measured by rotameters and so much is added each time that the free acid content never rises above 5 %. This is done to prevent

the formation of a metal oxide difficult to dissolve
and, further, to prevent too great formation of NO
and NO_2. During the dissolving process spent catalyst
and acid are mixed by a stirrer having a V_2A-lined
shaft and V_2A-propellers. The stirrer is driven by
a 20 kW motor. As mentioned above, the solution is
heated with direct steam. In the beginning the
temperature is kept at about 55 - 60°C. From time
to time a sample is taken and filtered, the Kiesel-
guhr being analyzed on its Co content.

As dissolving proceeds, the temperature
is gradually raised until the undissolved Co on
Kieselguhr is less than 0.1 % of the total Co.
Normally the final temperature should not exceed
80°C.

Duration: 20 to 24 hours.

In Ruhrchemie's catalyst plant there are
10 such containers, each having a capacity of 1 oven-
filling or about 3 tons of catalyst giving about
25 - 30 m3 nitrate solution on dissolving. During
this dissolving procedure about 4.5 % HNO_3 of the
acid added (calculated as N_2) is lost to NO and NO_2.
In the beginning these vapours were let off into the
atmosphere outside the catalyst building. After some
experimenting, e.g. trying to remove these vapours
by injecting steam into the vapour lines, they are
now installing the following equipment. Each of the
dissolving containers is connected with a header,
through which all vapours formed during the dissolving
step are carried away by a V_2A blower after passing a
spray vessel, which is meant to remove most of the NO
and NO_2 vapours by water, the vapours entering this
vessel at the bottom, water being introduced at the
top through nozzles and continuously withdrawn.

After all Co has been dissolved, the solution contains 70 - 80 g Co/l and this solution + Kieselguhr is run off into wooden tanks, in which the slurry is stirred continuously (20 r.p.m.). These tanks are not necessary from a chemical point of view, but are merely hold-up tanks to allow smoother operation.

<u>2</u>. Filtration of Kieselguhr.

From these tanks the solution is pumped to filter presses with pitch pine frames. There are 16 of these filter presses at Holten, 12 of which are in operation. As filter material cotton is used, which apparently lasts very long. Since starting operations only 80 frames have been fitted with new cloth.

The filter cake of Kieselguhr is washed with tap water. About 30 m3 water is used per ton Co. The first part of the wash water leaving the filter presses is added to the filtered solution of $Co(NO_3)_2$. When a concentration of 21 Bé is reached the rest of the wash water is run off into precipitation tanks in which various wash waters are collected. By adding Na_2CO_3 the dissolved Co is recovered as carbonate. After filtration this carbonate is added to the spent catalyst in the dissolving tanks. About 6 % of the total Co recirculates in that way all the time.

The mixture of the first part of the wash water and the filtered solution has a concentration of 55 - 65 g Co/l. From this solution a small quantity is introduced into the dissolving tanks before starting dissolving spent catalyst in nitric acid as mentioned under <u>1</u>.

3. Precipitation of impurities (Fe, Al, Ni).

The above solution is run off into wooden tanks with stirrer. MgO, which is lost later on in the process of regeneration, generally is added at this point. From these tanks the solution is pumped via storage tanks made of sichromal and via a heater, where its temperature is raised to 60 - 70°C, into a small (2 m3) wooden tank together with a Na_2CO_3 solution containing 103 - 104 g water-free $Na_2CO_3/1$ and having a temperature of about 50°C. This temperature is obtained merely by means of the dissolving heat of the Na_2CO_3.

The Co solution still contains some nitric acid from the dissolving step. So much Na_2CO_3 is added in the small wooden tank that a pH = 4 is obtained.

The operation is carried out in such a way that measured streams of the two solutions come together just before entering the small tank, the contents of which are stirred vigorously. Excess Na_2CO_3 at any point of the solution must be avoided in order not to precipitate any Co, which will then be lost together with the impurities. From this tank the solution runs into large wooden tanks where some more Na_2CO_3 solution is added until a pH of 5.8 - 6.0 is obtained. The pH is checked by means of paper slips impregnated with indicators and each showing 6 various colours for compairing the indicator colours at 6 different pH values, for instance at pH values of 3.9 - 4.2 - 4.5 - 4.8 - 5.1 - 5.4 or at pH values of 5.2 - 5.5 - 5.8 - 6.1 - 6.4 - 6.7. These papers are, for instance, manufactured by Dr Kloz (Leipzig) and called "Lyphan". Then the solution is left in the tank for about one more hour, while being stirred,

and is thereafter immediately filtered. For this purpose a large filter capacity was installed at Holten. This procedure is discontinuous.

Most important during this purification step is to obtain a precipitate which can be readily filtered. Conditions as regards temperature, concentration, degree of stirring should be very carefully supervised in order to obtain good filterable crystals.

Annex A, fig. 14 shows a sketch of this arrangement.

The amount of Na_2CO_3 added in this step is about 15 - 20 % of the total quantity of Na_2CO_3 used in the manufacture of the catalyst. Besides the impurities all thorium is precipitated in this step.

The wash water used for washing this filter cake is taken from the second part of the wash water used in a further stage for washing the final catalyst after being precipitated on Kieselguhr. The amount of filter cake being small, all wash water used for washing this cake is added to the filtered solution, which reduces its concentration from about 55 to about 48 g Co/l.

4. The filtered solution is run off into a wooden tank and stirred slowly by a stirrer with 18 r.p.m. NaF dissolved in water is then pumped into this solution. As NaF does not dissolve well in water, it forms a suspension (which is pumped through iron pipes). So much NaF is added that all calcium and about 50 % of the magnesium is precipitated. This precipitation of Mg is necessary in order to obtain a precipitate which can be filtered well. As this magnesium is lost, it, therefore, has to be added somewhere before the removal of the calcium, i.e.

either before the precipitation step of Fe, Al, etc.,
as already mentioned, or before this step. It is
evident that the amount of magnesium which has to be
supplied for this precipitation will depend on the
amount of calcium present. The ratio MgO : CaO should be
at least 3 : 1. If the catalyst contained already Mg,
which all newer catalysts do, then the Mg lost in this
precipitation step can also be added afterwards.

The final solution should not contain more
than 0.2 % by weight Ca calculated as CaO.

The precipitation was formerly done at
a temperature of about 55 - 60°C. Now the temperature
is kept about 30°C and should not rise above 40°C. It
was stated that this decrease in temperature was effected
only to obtain better crystals.

Per ton Co about 100 -120 kg NaF are added
at Holten.

The addition of NaF is controlled by
analysis.

Just before filtering the CaF_2 and MgF_2
a small amount of filter aid, such as, for instance,
Hyflocel, is added.

Duration of precipitation: 12 hours.

As formerly no good precipitate was ob-
tained when adding NaF to the solution with pH = 5.8,
HNO_3 was added first to the solution before introducing
NaF, in order to lower the pH to 3.8.

Towards the end of this precipitation step
Na_2CO_3 solution was then added to the mixture in order
to raise the pH again to 5.8. Introducing HNO_3 has
only been omitted for a few weeks past.

Filtration is done by means, of a filter press which is made of iron. The filtering material is cotton, covered with paper, the reason for this paper being only to save the cotton, as now paper plus filter cake are thrown away, whereas otherwise scraping the filter cake from the cotton would smear the jelly filter cake into the cotton openings.

The filter cake is washed with the second part of the wash water used for washing the final catalyst after its precipitation (see further on). Amount of wash water used: 3 m3 per ton Co.

Lately experiments have been started in order to see whether the removal of CaF_2 can be accomplished by decanting. No results are known as yet.

5. Not absolutely necessary, but more as a check on its final purity the solution, after being purified from Ca and having a pH = 5.8, is run off into wooden tanks of 30 m3, where a very small additional amount of Na_2CO_3 is added to precipitate any impurities which still may be present in the solution. The pH is thereby raised to 6.1. The solution is then once more filtered through a filter press and run off into so-called adjusting tanks, discussed further on under point 10.

6. Dissolving of fresh Co.

Attached is Ruhrchemie's prescription with specifications for Co. (Annex E N° 3). In no case should zinc and lead be present therein as they apparently cannot be removed; at least Ruhrchemie do not know any method of doing this.

When buying the oxide one has to be ex-
tremely careful, as oxides which have been heated at
high temperatures do not dissolve or dissolve only
partly and slowly in nitric acid. In such a case
diluted nitric acid works better than the concentrated
acid. At Prof. Fischer's laboratory in Mülheim it
was found that when dissolving spent catalyst in strong
nitric acid, a black substance was formed, which, on
analysis, proved to be CoO. This oxide could only be
dissolved very slowly , and was found to dissolve better
in diluted acid.

Dissolving fresh Co for making the first
batch of catalyst is done with about the theoretical
amount of nitric acid, e.g. 1.05 - 1.1 parts per part
Co.

The procedure is as follows: All HNO_3
needed for one batch is introduced into a dissolving
tank and then the total amount of Co is added either
as powder, in which case 35 % HNO_3 is used, or in
melted form, which allows the use of 50 % HNO_3. The
dissolving tank is equipped with cooling coils, where-
as heating can be done with direct steam. The temper-
ature is kept at a maximum of about 90°C. At the end of
the dissolving process some more Co and then Na_2CO_3 are
added to raise the pH to 6.1, which will precipitate
any dissolved impurities. Maximum 10 - 15 kg Na_2CO_3
should be used per 4 tons Co. The contents of the
tank are then sucked up by means of a vacuum and pumped
via a filter press into storage tanks. Some undissolved
Co will also be carried along by the solution, which
will be removed, together with the impurities, by the
filter press.

The filter cake is washed with distilled
water and the wash water added to the mother liquor in

the storage tanks.

After about 10 - 15 of such dissolving
tank batches have been filtered, the entire filter
cake is returned to the dissolving tank and the Co
dissolved in diluted (35 %) HNO_3. The material which
finally remains undissolved in the tank at Holten is
returned to the manufacturer from whom Ruhrchemie
buy their Cobalt.

The excess of Co in the dissolving tank
and the Co on the filter press will remove any Cu
which might be present in the Co metal and which
otherwise would remain in the $Co(NO_3)_2$ solution
after being dissolved in the HNO_3 together with
the Co.

In the step of dissolving spent catalyst
some Co is added from time to time as make-up for
unavoidable losses in preparing and handling the
catalyst.

7. Dissolving of magnesium.

There are no special prescriptions for
the magnesium. Various market products have been
investigated at Holten, i.e. cheap, expensive, pure
and impure ones. After having started with pure ones,
it was found that impure magnesium products could
also be used. However, in general it can be said that
the purer the magnesium, the better the catalyst.

Most important is that no impurities are
present in the magnesium which cannot be removed in
the purification step. Calcium should not be present
when preparing the first batch of catalyst, as this
is about the worst impurity conceivable. The SO_4
ion might be present.

Dissolving of magnesium compounds in nitric acid is done in a separate step in wooden tanks without any difficulties. The usual concentration at Holten is about 120 g MgO/l. However, this concentration does not matter very much.

8. Dissolving of thorium.

Thorium has been obtained thus far from the Auer Company in sufficient purity. The amount of SO_4 ion should be limited and can be controlled by the washing when manufacturing this metal, as it is made via the sulphates. In the beginning the thorium contained too much SO_4 but since discussing this problem with the Auer Company a sufficiently pure metal has been obtained. The reason for limiting the SO_4 content is because thorium sulphate will precipitate when heating the nitrate solution, which apparently causes trouble by deposits in pipelines and valves. Furthermore insoluble K or Na-Th double salts can also be formed.

Zinc and lead should not be present, for the same reason as mentioned above when discussing cobalt.

The thorium compound bought from the Auer Company is a basic carbonate. However, as nitrate it can be used just as well. The first thorium bought by Holten did not contain enough water, which apparently is important in dissolving the thorium. Holten now buy a product with so much thorium that the basic carbonate contains about 70 % thorium calculated as ThO_2.

Also in this case it can be said that the purer the thorium compound, the more active the final catalyst.

Another compound which should not be present from an economical point of view is iron. It does no harm in the catalyst when freshly made, but one pays the thorium price for the total amount of metal present in the thorium compound; moreover, the removal of the iron in the first precipitation step costs sodium carbonate.

The concentration of ThO_2 in the nitrate solutions made at Holten is about 150 g/l.

The price of pure thorium in Germany is about RM 18.- per kg thorium calculated as ThO_2, i.e. RM 18.- for so much thorium as would give 1 kg ThO_2.

9. Kieselguhr.

Some general prescriptions will be given for the Kieselguhr. It should be

a. as pure as possible;

b. available in large quantities of uniform structure;

c. as light as possible;

d. as cheap as possible.

A heavy guhr can give a good catalyst, but a light guhr will give a better one. Some guhrs are heavy because the total composition is heavy, whereas others are heavy because, notwithstanding the fact that they contain good diatoms, up to 30 % sand is mixed with the guhr. Dr Reulen suggested that we should send about 10 l of various types of Kieselguhr available in the U.S. to Ruhrchemie to be investigated there.

10. Adjusters and measuring tanks.

At Holten the adjusters are tanks of 32 m3 each, into which the 3 solutions of magnesium, thorium and Co nitrate are run to obtain a final solution having

the right concentration of 40 g Co/l. It is not
implicit to adjust this concentration to exactly
40 g. In that case, however, one should know the
exact concentration of the solution before using it
for precipitating the catalyst in order to adjust the
amount of Na_2CO_3 solution to be added. It facilitates,
however, the operation if always the same amount and
concentration of Na_2CO_3 solution can be used, for
which reason the nitrate solutions are adjusted to an
exact concentration of 40 g Co per litre.

Five such tanks are available at Holten,
four of which being made of iron, lined with acid-
proof brick, and one having rubber coating.

The solution in these adjusting tanks
still contains some free acid, e.g. 10 - 20 g/l.
This is due to the fact that an excess of acid is
necessary to dissolve thorium. Magnesium can be
dissolved with the theoretical amount of acid. From
these adjusters the solution is pumped via a heater
into tanks in which the solution is heated to exactly
60°C by means of indirect steam, as the concentration
has to be kept entirely constant during this heating,
and then run into measuring tanks. Measuring is done
at exactly 60°C. This temperature itself is not important,
but a certain temperature should be adhered to rigidly,
in order to measure always the same amount of same
specific gravity. As, after the measuring, dilution
of the solution is immaterial, it is further heated
with direct very pure steam - which is specially
purified over filters - to 98°C and then run off into
the precipitation tanks.

11. Preparation of sodium carbonate solution.

This is done in the same kind of dissolving
tank as used for dissolving Co in HNO_3. Calcined Na_2CO_3

and water are added into this tank and stirred while
the dissolving procedure is going on. The solution
should be made to an exact concentration of 103 -
104 g Na_2CO_3 per litre. Water for dissolving is
again taken from the second part of the wash water
used for washing the final catalyst after its
precipitation on Kieselguhr.

12. Precipitation of catalyst.

Co, Th and Mg are precipitated as car-
bonates on Kieselguhr. Sodium carbonate solution is,
therefore, heated in a tank to 60°C and then measured
at exactly this temperature for the same reason as
explained for the nitrate solutions. After being
measured, the carbonate solution is run off into
the precipitation tank, where it is heated further
to almost its boiling point by direct specially
purified steam before addition of the hot, almost
boiling, solution of the nitrates. These high temper-
atures must be adhered to closely, as 10°C lower
temperature will result in much inferior catalysts
being obtained. As mentioned under 11, the sodium
carbonate solution contains 103 - 104 g water-free
Na_2CO_3 per litre. During the precipitation step the
contents of the precipitation tank are stirred
vigorously. After addition of the nitrate solution,
which is done very quickly, e.g. in 1 - 1.5 minutes,
stirring is continued for 30 seconds longer and
thereafter Kieselguhr added. This latter addition
takes 80 - 90 seconds. Again stirring is continued
for 30 seconds longer, the total contents of a
precipitating tank being then pumped quickly via a
screener to the filter presses. The reason for the
screener is to remove any large undesired particles
which may have been added with the Kieselguhr. Size
of screen 10 mm.

After precipitation, the mother liquor will contain about 2 g Na_2CO_3, 6 - 7 g $NaHCO_3$ (Mg titrates as bi-carbonate) and 70 g $NaNO_3$ per litre.

There are sets of 4 precipitating tanks at Holten. One floor above the precipitating tanks are sets of 4 measuring tanks for the nitrate solution, 4 measuring tanks for the sodium carbonate solution and further 4 hoppers for the Kieselguhr, arranged as shown in figure 15, Annex A.

Into the precipitating tanks are run per charge:

a. 750 l nitrate solution, containing 31 kg Co;

b. 750 l Na_2CO_3 solution;

c. 62 kg Kieselguhr.

Belonging to a set of four precipitation tanks are four filter presses for filtering these solutions, each filter press having a capacity of 2 precipitating tank charges containing 62 kg Co. Each filter press is able to handle 18 filter press charges or 18 x 62 kg Co per day. In all there are 12 filter presses at Holten, 6 of which are in use.

After filtration the filter cake, having a thickness of 22 - 25 mm (this depends on the Kieselguhr, as some Kieselguhrs allow a thicker cake) is washed with 8 - 9 m3 distilled water. This water should be as pure as possible and only contain the least possible amount of salts, as otherwise the activity of the catalyst will be impaired. The first part of this water is added to the mother liquor, consisting of sodium nitrate solution, and dumped. The second part is used for dissolving sodium carbonate, or used as wash water for the Fe-Th filter cake. However, at Holten this latter part can also be used

for the first washing of the next filter press charge. The most efficient procedure of washing seems to be washing alternatively backwards and forwards, in which way the total quantity could be reduced to 130 - 160 tons water per ton Co.

Filtering and washing should be done quickly, as otherwise the $NaNO_3$ will attack the Kieselguhr.

Washing is done with hot water having a temperature of over 85°C, but not above 95 - 100°C. This washing takes about 25 minutes with new filtering cloth and about 35 minutes with old cloth.

The Na-concentration in the washed filter cake amounts to 0.009 % by weight, with a maximum of 0.015 % by weight, on Co. This amount should be kept as low as possible.

In this step 20 % MgO is lost; for instance, if the charge to the precipitating tank should contain 15 g MgO per 100 g Co, then the precipitated washed catalyst would only contain 12 - 13 g MgO per same quantity of Co.

The filter presses used now are so-called "Kammer filter presses"; formerly so-called "Rahmen filter presses" were in use. The first-mentioned ones, however, work much faster.

The final cake, after washing, still contains about 70 % water.

13. Addition of dust.

After dropping the filter cake on the mixer beneath the filter-press, dust (obtained further on in the process when granulating the catalyst) is added with so much water that the mixture of filter cake, dust and water is easily pumpable. About 30 - 40 - 45 %

(at present at Holten 38 %) on total catalyst to be dried is added as dust.

It has been found that the catalyst becomes harder when dust is added.

Formerly dust and water were added separately to the filter cake. At present dust and water are first mixed together, the slurry being added to the filter cake. After this addition, the mixture of filter cake, dust and water contains about 83 % water.

14. Further filtration and extruding of catalyst.

The above mixture is then pumped to a rotating vacuum filter working under a vacuum of 60 cm Hg, by which the amount of water is reduced to about 65 %. On this filter the catalyst is again washed with hot distilled water. Depending on the Co and NaNO$_3$ content the recovered water is either used for making the dust slurry mentioned above or run off into the general precipitating tank for the recovery of Co.

The catalyst cake, after being scraped off the rotating vacuum filter, drops onto a kind of extruding machine, which presses the wet cake having a temperature of about 40°C through 6 mm holes. A cross-sectional sketch of this extruding machine is given in figure 16, Annex A.

The four blades A, B, C and D rotate in such a way that the catalyst mass is pressed through the holes. The clearance between each of the blades and the bottom plate with holes is 2 mm.

15. Drying of catalyst.

The driers used at Holten are not specially

designed for this purpose, but bought as a normally
available type. They consist of about 22 slowly
rotating horizontal discs having a radius of about
2 - 3 mm, each of which consists of segments and
each having a scraper which scrapes the catalyst
from a segment onto the corresponding segment of
the disc just beneath it. Hot air is blown over
this catalyst. This air circulates and is heated
with 18 atm. steam through steam coils arranged in
the heater alongside the walls. Fresh air enters the
drier at the bottom after being preheated with 8 atm.
steam. This is the expanded steam obtained from the
18 atm. steam used in the coils just mentioned. Wet
air is removed from the drier at the top by means
of a blower. The temperature of the air in contact
with the almost dried catalyst should not be above
110°C and not be higher than 100°C when in contact
with the wet catalyst. Otherwise the structure of
the Kieselguhr would be harmed (see fig. 17, Annex A).

The catalyst leaving the drier contains
about 10 % of water.

The air leaving the drier is washed by
water for dust recovery in a tower having trays with
holes. This water is then passed through a filter
press under its own pressure and the filtered water
returned to the wash column by means of a pump. The
recovered dust has been exposed to too high a temper-
ature and is, therefore, unsuitable as such for the
manufacture of catalyst. It is returned to the dis-
solving tanks for spent catalyst (see fig. 17, Annex A).

The total time of drying is about 2 hours.
Capacity of the drier is about 5 tons of final catalyst
per day. As about 30 % of the total dried catalyst is
returned as dust, the actual amount of catalyst passing

through this drier is, therefore, 30 % more.

Lately Holten have started to use driers which do not have a scraper for removing the catalyst from the disc segments, but which make these segments turn slightly at a certain point to let the catalyst drop onto the corresponding lower segment. It was said that this kind of drier causes less dust formation. For the same reason they intend using a continuous belt drier, in which a belt slowly moves downward through the drier, leaving the catalyst in its place on the belt during the entire time of its presence in the drier.

16. Screening and granulation.

The catalyst leaving each of the four driers is moved by a horizontal belt conveyor to a vertical bucket conveyor (elevator) which drops the catalyst onto vibrators. There are two bucket conveyors or elevators at Holten, each dropping the catalyst onto two vibrator sets, each vibrator set consisting of:

first vibrator,
granulator,
second vibrator,
third vibrator.

(See fig. 18, Annex A).

The first vibrator separates the catalyst by means of 2 vibrating screens, viz. a 2.5 x 3.5 screen and a 1 x 3 screen, into three different sizes, viz. too large size, good size (1 - 3 mm) and dust (everything passing the 1 x 3 screen). The oversize particles not passing the 2.5 x 3.5 screen are fed to the granulator, which consists of a screen and a slowly rotating arm pressing the oversize particles through

the screen. The material leaving the granulator drops
onto the second vibrator having three screens, viz.
from top to bottom:

> a 2.5 x 3.5 screen
> a 2.5 x 2.5 screen and
> a 1 x 3 screen.

The particles not passing the top screen
are returned via the elevator to the first vibrator.
The particles not passing the second screen are fed
to the third vibrator, as well as the particles not
passing the third screen. Everything passing the
latter screen is dust and drops into the dust
collector. The third vibrator consists of two screens,
viz. a 2.5 x 2.5 and a 1 x 3 screen. This vibrator
serves for removing any dust left in the good-size
particles and, therefore, receives the good particles
from the first vibrator (1 x 3 screen) and the second
vibrator (2.5 x 2.5 and 1 x 3 screen), giving, there-
fore, two different-sized particles, which is neces-
sary, as some licensees ask for smaller and some for
larger particles.

The vibrators are enclosed and work under
a slight vacuum in order to prevent dust from escaping
into the atmosphere.

Catalyst of the desired size is put into
paper bags, each containing 30 kg catalyst. This
catalyst is called "green catalyst".

17. Hereafter the catalyst is reduced with hydrogen
which is previously heated to about 450 - 460°C.

Ruhrchemie use mixed gas of their ammonia
plant for this reduction step instead of pure hydrogen.

This gas is kept in circulation. After passing through the catalyst to be reduced, it is freed from CO_2 and H_2O in various units and then returned via a heater to the reduction chambers containing the "green" catalyst (see Annex A, figs 6 and 7).

The reduction plant consists of the following parts:

a. reduction chamber,
b. conversion of CO_2,
c. spray cooler with separator,
d. Junker's cooler,
e. gasometer,
f. blower,
g. cooler,
h. blower,
i. cooler,
j. ammonia cooler,
k. Silica gel drier,
l. gas heater.

a.   A sketch of the reduction chamber is shown in fig. 20, Annex A.

By lifting the top part, the inner basket, having a height of 35 cm, can be filled with catalyst. At Holten the depth of such a catalyst layer does not exceed 20 - 25 cm. About 8 paper bags or 240 kg catalyst are filled each time in each chamber. When reducing, the hot hydrogen passes through the "green" catalyst from top to bottom, heating it to 380 - 450°C. The following conditions are absolutely necessary for obtaining an active catalyst:

1. a thin layer of "green" catalyst;
2. high velocity of the hydrogen;
3. low vapour pressure of H_2O and CO_2, say, below 0.1 g H_2O per m3 circulating gas;
4. constancy in conditions, e.g. temperature, H_2 velocity and purity of H_2.

The catalyst is not sensitive to H_2O and CO_2 at room temperature, but very sensitive at higher temperatures.

If the vapour pressure of H_2O and CO_2 should be too high, the temperature has to be increased in order to obtain a good reduction.

However, this increased temperature, say, above 450°C, produces a considerably less active catalyst. One may expect, therefore, a still better catalyst than obtained at the moment by reducing at still lower temperatures. Holten have succeeded in reducing even at 300 - 320°C. However, the time of reduction is then about four times longer than at 380°C.

It is very difficult or even impossible to measure the actual temperature within the catalyst.

The difference in gas temperature between the inlet and outlet of the catalyst bed is about 200°C when starting the reduction. This difference decreases gradually and is usually about 80°C towards the end of the reduction. However, this temperature difference is not a guide for the time of reduction.

The amount of hydrogen used at Holten is 1200 m3/h gas ($3H_2$ + N_2 + impurities) per m2 catalyst surface. This quantity cannot be increased

much, as otherwise the catalyst will start swimming.
To prevent this, a set of distributing vanes,
having about 10 x 10 cm squares and a height of
about 10 cm, is attached to the top cover of the
chamber. When this cover is closed the distributor
is pressed about one inch into the catalyst bed.

The figure of 1200 m3 mixed gas/hour/m2
does not mean that with pure hydrogen one could
use 900 m3/hour/m2, as a certain partial pressure
of water should not be exceeded and enough gas
has to be passed through to dissipate the heat
of methane formation.

It is said that with pure hydrogen the
reduction temperature can be reduced somewhat.

At Holten there are six chambers, each of
which is connected to one hydrogen header. The
total quantity of gas passing through the chambers,
which means the total quantity of gas in circu-
lation, is 10,000 m3/h. Every 20 minutes a
chamber filled with catalyst is being connected
to the hydrogen cycle to start the reduction.
This reduction takes one hour, for which reason
all the time 3 chambers will be connected to the
hydrogen cycle and the amount of 10,000 m3 just
mentioned is, therefore, passing through 3
chambers all the time. In order not to increase
the percentage of impurities above a certain limit
about 950 - 1450 m3 gas per hour is continuously
blown off and 1000 - 1500 m3/h fresh $H_2 + N_2$
added. The six chambers together can reduce six
synthesis converter charges per day. Cross-sectional
surface of one reducing chamber is 1.4 m2.

During this reduction a small amount of
dust is formed, which is removed in the cooling

stage mentioned sub b.

After reduction is finished (this time is known by experience, and not controlled by any analysis) hydrogen is replaced by N_2. Then connections from and to the chamber are removed, the chamber turned upside down and connected to a much larger container, which can be moved backwards and forwards under each of the six reducing chambers. This latter container is filled with nitrogen and reduced catalyst is dropped into it. It can hold 15 - 17 reducing chamber charges, i.e. an amount equivalent to 15 - 17 x 240 kg "green" catalyst. Smaller containers are also in use, having a capacity of 4 - 5 reducing chamber charges.

All work in this reducing plant is manual. Time needed for the various operations in the reduction step is as follows:

60 minutes for reduction;

10 minutes for replacing H_2 by N_2, disconnecting chamber and turning it upside down;

5 minutes for emptying the chamber;

10 minutes for turning chambers, filling, reconnecting to cycle and purging with nitrogen.

In a new catalyst plant charging, discharging, etc. will all be done automatically, which will also reduce the time for the total cycle.

b. Conversion of CO_2.

As mentioned under a, it is imperative to keep conditions constant during the reduction step in order not to impair the activity of the catalyst. However, this has not been entirely possible as part of the CO_2 removed from the green catalyst

(carbonate) stayed in circulation and was converted to CH_4 when coming again into contact with the already partly reduced catalyst. This caused a continuous variation in CO_2 and CH_4 content of the recirculating gas. Moreover, everything that has been said with respect to a necessary low vapour pressure of the water also holds good for CO_2. Removal of CO_2 after the reduction chamber, therefore, was expected to give a better catalyst. Holten are afraid that this cannot be done, however, by caustic wash, as the chances are that a small part of the caustic may be carried through to the catalyst. They have, therefore, just started to reduce the CO_2 to CH_4 over a catalyst right after the reduction step.

This can be done at 180 - 250°C, when no or hardly any water is present. However, with the actual amount of water present, viz. 40 - 50 g/m3, in the gas after the reduction chamber (e.g. reaction water and moisture present in the green catalyst) a temperature of 350 - 400°C is necessary. This is somewhat higher than the average temperature of the gas when leaving the reduction chambers, for which reason a special heater is now being installed. Without this heater only 40 - 50 % of the CO_2 which is present in the gas after the reduction chamber to an amount of 1.7 g/m3 can be converted, as the gas temperature is only 250 - 300°C. As catalyst for this $CO_2 \longrightarrow CH_4$ reaction Holten use their synthesis catalyst, which they expect will last for a long time.

c. Spray cooler.

The spray cooler reduces the temperature of the gas leaving the reduction chambers from 300 - 400°C to about 40°C, at the same time

removing any dust carried along.

This latter amount is very small and dust which remains in the tower is only removed from it twice a year (see fig. 23, Annex A).

d. The Junker's cooler is a tubular indirect water cooler, the temperature, after this cooler, therefore, depending on cooling water temperatures and being, say, about 25 - 30°C.

f, g, h, i. There is no reason why the 2 blowers + 2 coolers could not be reduced to 1 blower + 1 cooler. Pressure after the second blower: 4000 - 5000 mm water.

It is worth mentioning that the use of Roots blowers cannot be recommended, as such blowers give impulses to the gas-flow, and most important is that the gas should pass smoothly over the catalyst during its reduction.

j. The ammonia cooler brings the gas temperature down to -10°C. This cooler has a capacity of 150,000 kcal/h, the compressor using 80 hp, and is guaranteed to reduce the water content to below 5 g/m3 gas. Actually at Holten about 2 g H_2O/m3 or less is reached.

The equipment consists of one heat exchanger (recuperator) and 2 NH_3 coolers in parallel.

k. The silica gel plants at Holten consist of two driers, operating alternatively. Each drier has 2 layers of silica gel and switching over to the other drier is done long before the bottom layer is saturated with water. The gas entering these driers at the top contains about 2 g H_2O/m3 and leaves the drier with 0.05 - 0.1 g H_2O/m3.

Regeneration is carried out with hot hydrogen in circulation, which is heated with steam to 120°C. After regeneration is finished, the silica gel is cooled by hydrogen in circulation, this being itself cooled indirectly by water. The cycle is: one-hour absorption, one hour regeneration.

When starting operation, Holten used gel driers constructed by the Silica Corporation in the U.S.A. At that time they did not have an ammonia cooling. The gas entering this drier, therefore, contained about 25 g $H_2O/m3$, leaving the drier with about 0.2 g $H_2O/m3$. As the gel cannot stand such large amounts of water present in the fresh feed a gas volume of about 3 - 4 times the amount of fresh feed was kept in circulation to dilute the fresh feed with dried gas. Regeneration according to the Silica Corporation's method was carried out by the hot gas itself, after leaving the reduction chambers described under a and having a temperature of about 250 - 300°C. After the gas left the gel unit to be tried, its temperature was about 100°C. It was then cooled and passed through the gel-absorbing unit (see Annex A, fig. 24).

This method of drying did not prove to be very successful, as

1. the driers had too much resistance for a fresh gas rate of 10,000 m3 gas/h. With normal blowers one cannot attain much more than 6 m H_2O. Increasing this pressure, considerably increases the power consumption, e.g.

$$6 \text{ m } H_2O : 250 \text{ kW,}$$
$$8 \text{ m } " : 350 \text{ ".}$$

2. Some dust from the reducing containers accumulated on the gel. Holten installed a dust catcher, but owing to the small amount of dust and the particles probably being electrically charged this did not work well.

As a gel drying preceded by NH_3 cooling was considered to be considerably less expensive, an NH_3 cooling system was installed, at the same time replacing the gel unit just described by gel driers from Gebr. Hermann, Köln. Now the results mentioned in the first paragraph of this point k are being obtained.

1. Gas heater.

The gas heater consists of a tubular bundle through which hydrogen passes from top to bottom and is heated by hot flue gases obtained by burning rest gas with air. Also in this case the tubular bundle consists of two parts which allow independent expansion of the tubes heated by the flue gas entering the bundle (vide Chapter II). (See Annex A, fig. 19).

18. Cooling of reduced catalyst and saturation with CO_2 or oil. As mentioned before, the reduced catalyst is dropped hot into small or larger containers, holding either 4 - 5 or 15 - 17 reducing chamber charges. After being filled, these containers are cooled, which is done outside the reduction part of the plant with circulating N_2 (see Annex A, fig. 7a). Time for cooling of a large container: 5 - 8 hours; for a smaller container: about 2 hours. When a temperature below 40 - 45°C is reached the catalyst is saturated and impregnated with CO_2 by feeding CO_2 through the catalyst from bottom to top. This

saturation is continued until the gas leaving the top of the catalyst container shows a CO_2 content above 98 %. 120 kg CO_2 is used for a large container. This step takes about 10 minutes.

The circulating N_2 is cooled itself indirectly by water. The cross-sectional form of the tubes of this cooler is stream-lined. The tubes are made of aluminium and have a diameter, square to the stream-line direction, of about 1". Wall thickness 0.3 - 0.6 mm. These coolers are made by Rudolf Otto Meyer, Hamburg, and are said to be very cheap, viz. about half the price of normal tube coolers. They are also used by the German Navy and are called "aerodynamic coolers".

Instead of CO_2 also oil can be used; for instance, a catalyst charge shipped to Japan had been impregnated with oil. Although this latter procedure apparently does not harm the overall activity of the catalyst, its starting activity is somewhat lower than in case of CO_2 impregnation.

If the catalyst has to be transported over a long distance solid CO_2 is put on top of it after the CO_2 impregnation is finished.

19.   Transport of catalyst to licensees. For transporting catalyst to licensees two methods are used:

1. two large catalyst containers on a railroad car, each container having a dead weight of 5650 kg. One fresh catalyst charge weighs 3000 - 3250 kg. After use the spent catalyst might weigh up to 5000 kg, owing to paraffin absorbed in the catalyst. For this reason the Holten cranes have been amply dimensioned at 15 - 17 tons.

2. Eight small containers on a railroad car, each
weighing empty 1470 kg and each having a capacity
of 800 kg catalyst. Therefore, four such containers
just have enough capacity for one oven charge. The
form of these containers is shown on figure 21,
Annex A. Dimensions are 1570 mm long, 1420 mm
wide and 2135 mm high; total volume 3500 litres;
net volume 2500 litres. Lately these containers
have been transported to the various licensees in
upside down position, in order to facilitate
filling the synthesis converters and making it
possible to transport the containers on rails on
top of the ovens, allowing a lighter construction
of the synthesis building. See fig. 22, Annex A.

For sketch of transport cars see figure 21,
Annex A.

20.   Some remarks on equipment installed at
Holten's catalyst plant.

It may have been noticed that for all
filtering steps, except one, filter presses are
used. Ruhrchemie stated in this connection that
when designing the plant this type of press has
been chosen on purpose, as it is very flexible
and reliable for all types of precipitates,
independent of crystal size, and furthermore en-
sures effective washing of the filter cake.

Once the conditions for a certain
precipitation step are known and rigidly adhered
to, one can advantageously apply continuous
filters, thereby reducing materially the cost of
upkeep and labour.

Regarding the material for the equipment
to be used in the catalyst plant, the following

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can be said.

Iron can be used throughout the plant when no free acid is present.

———   Parts coming into contact with neutral catalyst, whether dry or wet, should not contain or be made of: copper, bronze, zinc, tin, aluminium or lead.

Whenever HNO_3 is present it is necessary to use either iron with acid-proof lining (bricks, rubber), or Cr-Ni steels, or alloys such as ascaloy or sichromal (DEUTRO 16-S made by Vereinigte Stahlwerke Thyssen, Düsseldorf, or V_{17} F.E. made by Krupp. Both these metals contain a small amount of Ti and can be welded without being annealed afterwards).

———   For the final catalyst precipitation V_2A is used. It is important for better cleaning that these containers have a smooth surface, for which reason sichromal, which, moreover, oxidizes quicker, is less desirable.

All pumps can be of normal construction. They should run at moderate speed to avoid excessive wear; for more viscous liquids open vanes should be applied. In case of acid-containing liquids, Cr-Ni or Cr-steel or stoneware is to be used. The latter material is not applied at Holten.

As mentioned in the foregoing description filter presses for acid-containing liquid are made of wood, for which pitch pine is specially recommended.

NaF is pumped through iron pipes.

In the purification steps mostly wooden tanks are used.

Iron is used in the reduction plant throughout.

As packing material rubber is mainly used,
except at hot places, where asbestos packing is applied.

The following names of manufacturers may
be mentioned:

Vacuum filter:	Maschinenfabrik Buckau R. Wolf, Magdeburg.
Extractor:	Büttner Werke, Uerdingen ("Spezial Aufgabe Apparat für Pastenförmige Produkte").
Drier:	Büttner Werke, Uerdingen.
Vibrator:	Flämrich, Recklinghausen.
Reduction step cooler:	Junker's Cooler, Dessau.
Nitrogen cooler:	Rudolf Otto Meyer, Hamburg.
Hydrogen heater:	Rekuperator, Düsseldorf.
Heater for heating the $Co(NO_3)_2$ solution before removing Fe, Al, etc.:	Fritz Scheibler.

Capital costs and utility requirements for a catalyst
plant for manufacturing Co-Mg catalysts, sufficient for
200,000 tons of liquid product per year.

This catalyst plant should have a capacity
for the re-generation of $1\frac{1}{2}$ converter fillings per 24
hours; the capital cost for such a plant built in Germany
under the present circumstances would amount to RM 2,100,000.

This includes buildings and apparatuses,
cooling water supply, purification of wash water, all
electrical equipment, settling pits, etc.

The costs for buildings amount to 25 - 30 %,
which buildings are necessary in Germany on account of
the possibility of freezing.

When built in the South of the U.S.A. it might
be possible to reduce the capital investment by omitting
or simplifying the buildings.

The above plant can normally re-work 1.3 tons

of Cobalt with a maximum of 1.6 tons of Cobalt per 24 hours.

The utility requirements were stated to be as follows:

Condensed water, 200 tons/ton Cobalt; this quantity is sufficient also for making solutions, etc.

If the costs for preparation of condensed water should be extremely high, it might be possible to reduce the above-mentioned quantity to 130 - 160 tons, replacing the balance by normal tap-water.

The latter should then be used for the washing of the Kieselguhr, diluting of nitric acid, etc.

Apart from these quantities make-up for cooling water and a certain quantity for rinsing water are necessary.

It was mentioned in this respect that the condensed water-distilling plant at Lützkensdorf is dimensioned for a quantity of 288 tons/24 hours for regenerating 3 tons catalyst per 24 hours. This must be considered to be a bottom figure.

The cooling water circulation for regenerating 1½ tons of Co is to be set at somewhat more than 200 tons per hour; the returning cooling water from the refrigerating plant is taken at 30 - 40°.

If cooling water in large quantities and of sufficiently low temperature is available (e.g. from a river), the quantity of circulation water can be reduced considerably.

The steam consumption will be from 4 - 7 tons per hour for regenerating 1½ tons of Co/24 hours.

Regarding the electrical facilities the following figures were given:

The total rated capacity of the electrical motors in a plant for re-generating $1\frac{1}{2}$ tons of Co/24 hours is about 780 kW. The actual consumption will be about 25 % of this figure, i.e. 200 kW.

The total quantity of Co tied up in the catalyst plant of the above-mentioned capacity, may be estimated at 30 tons.

This figure may be considered as ample, but when such a quantity is available, a smooth running of the catalyst plant is facilitated.