II. CATALYST FOR THE SYNTHESIS REACTION

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Page No.

MANUFACTURE OF SYNTHESIS CATALYST

Catalyst Composition

The catalyst for the synthesis reaction was composed of cobalt, kieselguhr, and a metallic oxide. Formerly, thoria was used exclusively as the promoter, but more recently the thoria has to a large extent been replaced by magnesia. Not only was the magnesia catalyst cheaper to make originally, but the regeneration costs were less and the magnesia catalyst had certain operational advantages over the thoria catalyst; such as, ability to accommodate higher synthesis gas rates, less susceptibility to sintering, lower methane production, the retention of less wax and a longer active life.

The change from thoria to magnesia in the catalyst was being made slowly because it was desirable to exhaust the thoria stocks on hand, and also to avoid possible plant interruptions due to an abrupt change in the catalyst composition.

The composition of the catalyst first used was 32% cobalt, 5% thoria, 63% kieselguhr ($Co:0.15ThO_2:2.0$ kieselguhr). At the time the Holten plant was visited, the catalyst in general use had the composition: 32% cobalt, 2.5% magnesia, 1.5% thoria and 64% kieselguhr ($Co:0.08MgO:0.05ThO_2:2.0$ kieselguhr), although some of the synthesis chambers were in operation with a catalyst containing 32% cobalt, 4% magnesia, 1% thoria, and 63% kieselguhr ($Co:0.13MgO:0.02ThO_2:2.0$ kieselguhr). The dried, formed but unreduced catalyst contained about 24% cobalt by weight, and the corresponding reduced catalyst, as mentioned above, about 32% cobalt. The apparent density of the reduced catalyst was about 0.28 in the particular apparatus used for the measurement.

Catalysts with other ratios of promoters had been prepared and tested in the laboratory. The thoria or magnesia could be varied within the limits of 10 to 20% on the cobalt without affecting the activity of the catalyst or the products formed. The use of an amount of thoria greater than 20% led to an excessive production of solid hydrocarbons at the expense of liquid hydrocarbons, while the use of less than 10% thoria gave catalysts with inferior activity. The corresponding effects of changes in the magnesia concentration had not been definitely ascertained.

Catalyst
Preparation

Much of the information in regard to the catalyst preparation was largely concerned with small details. In an effort to simplify the description of the preparation, a brief summary of the major operations involved will be given first, followed by a schematic flow sheet of the catalyst plant, and these general descriptions will then be supplemented by a more detailed outline.

Summary of
Catalyst
Preparation

Since the preparation of the catalyst consisted chiefly of the use of materials reclaimed from spent catalysts, the preparation of fresh solutions will be omitted from the summary. The procedure given will, of necessity, be that followed at Holten, and this may not conform, in certain instances, to the latest ideas on catalyst preparation.

The spent catalyst from the synthesis plant was treated in order to destroy its activity to the extent that it would no longer be pyrophoric upon exposure to the air. The catalyst was placed in a digester and treated with nitric acid to dissolve out the cobalt, magnesia and thoria and thus make possible their separation from the insolublo kieselguhr. Under close control of the temperature during solution, practically no nitric acid was lost through decomposition to the gaseous oxides of nitrogen. The solution obtained from filtration from the kieselguhr contained impurities which it was desirable to remove before using the solution in the preparation of a new catalyst. Any iron, aluminum or nickel was removed by precipitation by partial neutralization of the solution with soda. The thoria was simultaneously removed from the solution at this point and, consequently, the precipitate was sent to the thoria recovery plant. The partially purified solution was treated with enough sodium fluoride to precipitate the calcium completely, together with about half the magnesia. Since the magnesia was inexpensive, it was discarded with the calcium precipitate. The purified solution was transferred to an adjusting vessel, wherein the desired concentrations of each catalyst component were regulated by the addition of fresh solutions. Soda solution was prepared in a separate vessel, transferred to the precipitation vessel and heated to boiling. A carefully measured amount of the adjusted cobalt nitrate solution was preheated almost to boiling and added to the hot soda solution. After stirring for about one minute, the kieselguhr (fresh, unused material) was added, and the stirring continued for about one-half minute, whereupon the precipitated mixture was filtered and washed as quickly as possible. It was regarded as highly important that all operations be performed as rapidly as possible after mixing the two solutions until the precipitate had been washed, in order to

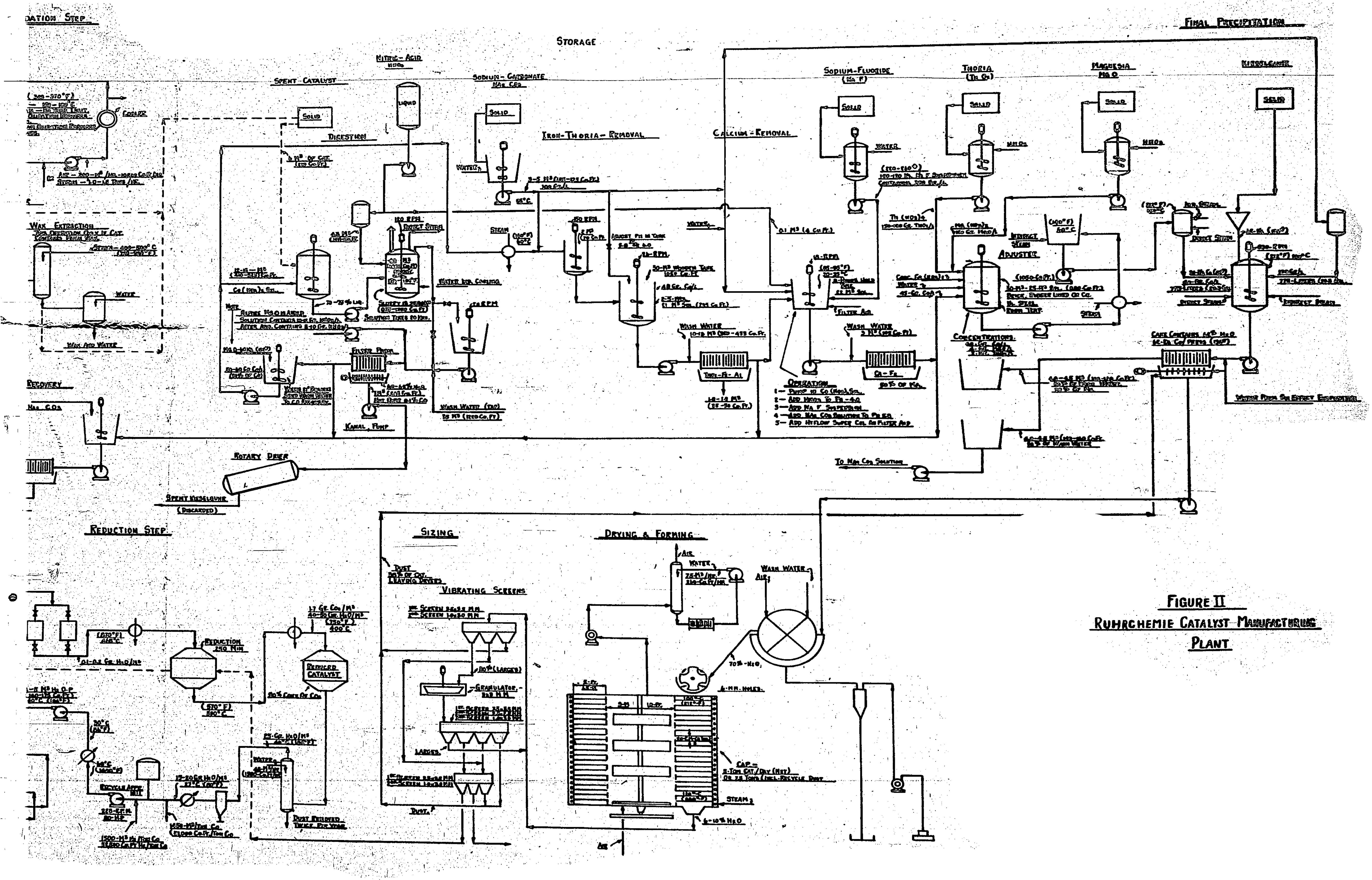

FIGURE II

RUHRCHEMIE CATALYST MANUFACTURING PLANT

time in which the kieselguhr was in contact with the

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hed filter cake was mixed with some of the dried
ines, extruded, dried and screened. The fines from
g were returned to fresh, wet, washed catalyst.
ized catalyst was transferred to small vessels built
or reducing the catalyst. The catalyst was reduced
en at about 850°F. (450°C.) and transferred hot into
sport vessel. The catalyst was cooled in the trans-
by a stream of nitrogen and when cool was treated
dioxide to protect the catalyst against oxidation by
h air. The catalyst could be poured directly from the
ssel into the synthesis reaction chamber.

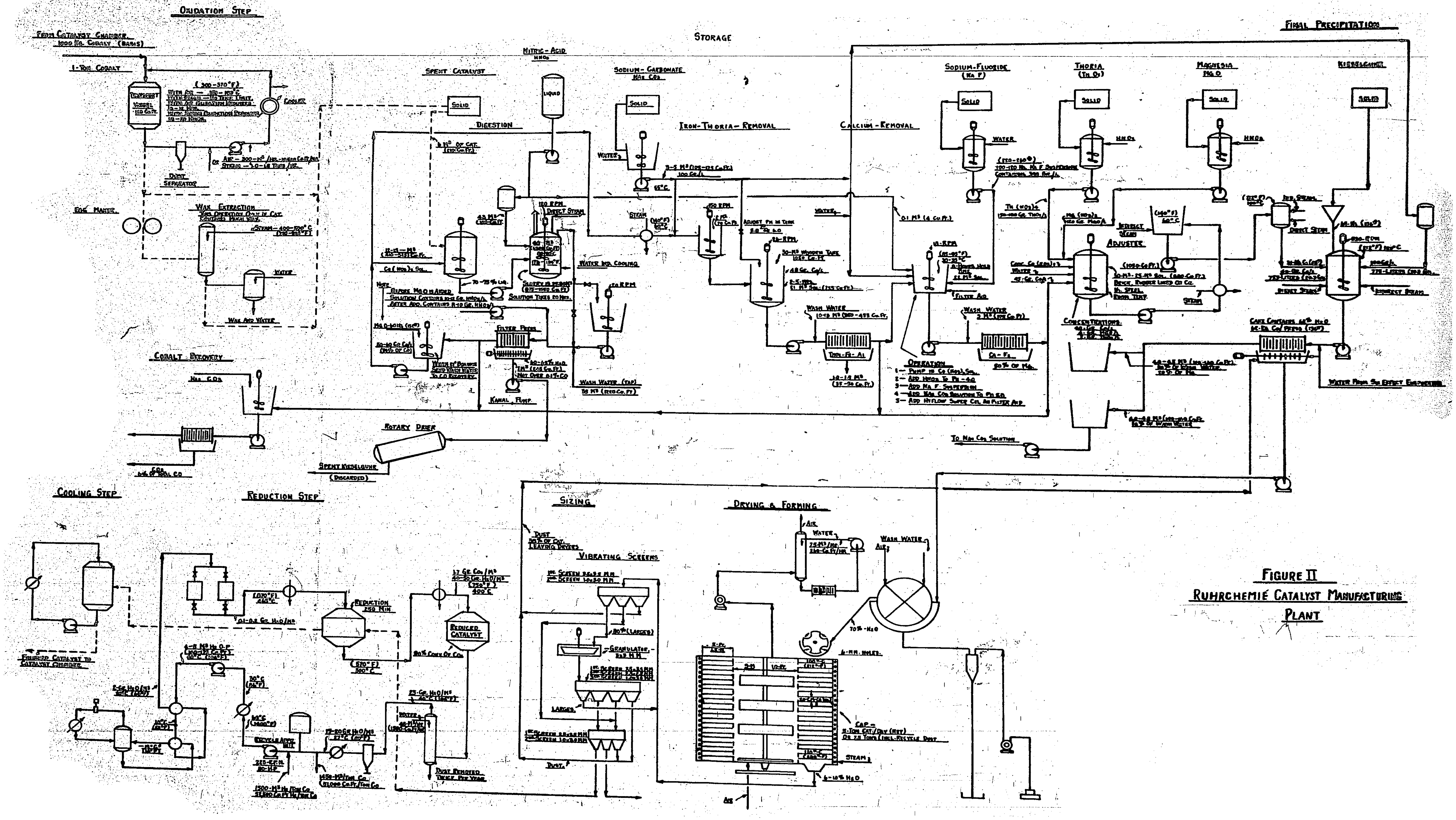

FIGURE II
RUHRCHEMIE CATALYST MANUFACTURING PLANT

Catalyst Plant Flow Sheet

Figure II

Figure II represents a schematic flow sheet of the catalyst manufacturing plant, showing the various steps involved in the regeneration of spent catalyst. The spent catalyst from a reaction chamber was first mildly oxidized to render it non-pyrophoric. If the catalyst contained less than 25% by weight of solid paraffins it was next digested with nitric acid. If the catalyst contained more than 25% solid paraffins, it was steam-extracted before being sent to the digesters. The digestion process consisted in the solution of cobalt, magnesia and thoria from the relatively insoluble kieselguhr. Due to the several impurities present in the kieselguhr, a part of the latter was simultaneously dissolved with the catalyst components which it was desirable to recover.

The solution obtained from filtration of the digested material was subjected to two purification steps. The first purification step consisted in a partial precipitation with sodium carbonate. This left the desired cobalt and magnesia and the undesired calcium in solution, while the precipitate contained the thoria, iron, aluminum, copper, etc. The precipitate was treated to recover the thorium. The partially purified solution was then subjected to treatment with sodium fluoride in a second purification step. The solution from the latter step contained the cobalt and a part of the magnesia, while the precipitate contained practically all the calcium, together with about half the magnesia. The precipitate was discarded since the magnesia was not worth recovery. The solution of cobalt and magnesia was ready for reprecipitation, after the concentrations of catalyst components had been adjusted to the desired values.

The adjusted solution of cobalt, magnesium and thorium was precipitated with a slight excess of sodium carbonate solution at a temperature near the boiling point. After the two above solutions had been mixed together, the requisite amount of kieselguhr was quickly added and the resulting mixture quickly filtered and washed.

The washed precipitate was made into a slurry with water and the fines from the screening operation, refiltered, extruded, and simultaneously dried and formed. The dried material was separated into particles 1-3 millimeters in size and fines. The fines were returned to freshly precipitated catalyst and redried and reformed.

The sized particles of catalyst were reduced with hydrogen at about 840°F. (450°C.) in shallow beds. A large part of the equipment shown on the flow sheet for the reduction step had the purpose of purifying the hydrogen which was to be recycled. The reduction reaction itself was very simply accomplished, but the removal of all water and carbon dioxide from the recycled hydrogen entailed the use of considerable equipment.

The reduced catalyst was transferred to transportation vessels, cooled, treated with carbon dioxide, ~~and~~ was then ready to be placed in the synthesis reaction chambers.

With the preceding brief summary, it appears that the flow sheet should be self-explanatory. All the details obtained in connection with the catalyst manufacture at Holten have been included on the flow sheet.

Details of Catalyst Manufacture

The details regarding the catalyst manufacture will be outlined in the paragraphs immediately following.

Material Specifications

The specifications for the raw materials to be used in the preparation of the synthesis catalysts were not very rigid, since certain impurities were inevitable, some of which could be removed by simple purification procedures, and others could be tolerated to a certain extent.

Cobalt

The materials found in technical cobalt metal were divided into three groups:

1. The non-harmful metallic constituents were cobalt and nickel. The cobalt should amount to at least 98%. No more than 0.7% nickel should be present.

2. The harmful constituents were all metals other than cobalt and nickel, in addition to silica. The total amount of the constituents of this group should be less than 1%. The least desirable constituents were copper, zinc, and lead. An analysis of the cobalt should show the amounts of iron, manganese, copper, zinc, lead, silver, aluminum, calcium, magnesia, and silica.

3. Other constituents included non-metallic impurities such as oxygen, sulfur, carbon, etc., as well as material insoluble in nitric acid. The constituents of this group should be kept at a minimum.

Cobalt oxides which can be dissolved in nitric acid may be used in place of the metallic cobalt. Similar specifications were required for the cobalt oxides.

Magnesia

At first, chemically pure magnesia was used; later, magnesia of medium purity, and finally magnesia of a technical grade. From the standpoint of the catalyst activity there was no choice as to the source of the magnesia. Magnesia was avoided which contained materials which did not drop out in the regeneration procedure. The most common impurity to be avoided was calcium carbonate, since this substance was removed only with difficulty and a large loss of magnesia occurred in the removal. The particle size of the magnesia was of no consequence except insofar as it affected the rate of solution in nitric acid. Small amounts of iron sulfate were not harmful.

Thoria

The chief sources of thoria in Germany were sulfate residues and consequently there was danger of sulfate contamination. The difficulty with sulfate impurities was the deposition of double sulfates of thorium and calcium (or sodium) in the lines used for preheating the solution for the catalyst precipitation. No harm was done to the catalyst, but there was a loss of thoria and a plant interruption, due to the necessity of cleaning the lines.

The thoria used at Holten was bought as a pure basic carbonate from Auer. This basic carbonate contained 70% ThO_2, and was very readily soluble in nitric acid. The dry, normal thorium carbonate was very difficultly soluble in nitric acid. In the absence of a nitric acid plant, it was recommended that thorium nitrate be bought in place of the basic carbonate. The presence of ceria in the thoria was apparently without effect upon the catalytic activity. When other impurities were present, the thoria was subjected to a purification procedure. The cost of thoria was 18-20 RM per kilogram, based on ThO_2.

Kieselguhr

The cheapest, purest (especially calcium-free) and largest sources of the lightest kieselguhr of constant quality were sought. The selection of the best kieselguhr was still an art and was largely done on an empirical basis. Two types of kieselguhr were available in Germany and both could be used:

1. Guhr, which had been heated to 1100°F. (600°C.).
2. Guhr, which had been heated to 2200°F. (1200°C.).

The latter type was treated with hot gases in a rotary furnace and Ruhrchemie preferred this type. The apparent density of the guhr was only of interest in that the lighter the guhr the easier it was to handle. Sand in the guhr was to be avoided.

Dr. Roelen offered to give his opinion as to the usefulness of any American kieselguhr if a 10-liter sample were sent to him.

<u>Soda</u>

The chief impurities avoided in the selection of soda were chlorides and sulfates. Neither chlorides nor sulfates were detrimental to the catalytic activity, but the chlorides gave a very corrosive acid solution, and the sulfates, as mentioned previously, caused the precipitation of thoria complexes in the preheater lines.

Preparation of Fresh Cobalt Solution

A digestion vessel of about 1100 cubic feet (32 cubic meters) capacity was about half-filled with cobalt nitrate solution and cobalt and nitric acid (50%) added in such proportions that there was 5% excess acid in the solution. Additional cobalt was added in 200 pound batches, followed by adjustment of the nitric acid concentration until the digestion vessel was filled with solution. At the end of the digestion the pH of the solution was usually about 4. The pH of the solution was raised to 6.1 by the addition of soda solution and the solution filtered to remove iron and copper and sent to cobalt nitrate storage. The desired temperature for the digestion was 160 to 175°F. (70 to 80°C.), although some variation in the temperature was inevitable. In the absence of higher temperatures, the reaction in the solution step was a displacement of the hydrogen of the nitric acid by cobalt. Side reactions accounted for a loss of nitrogen of the order of 4.0% for a carefully controlled digestion. The time required for the preparation of 1000 cubic feet (28 cubic meters) of solution, containing from 160 to 180 grams of cobalt per liter of solution, was 12 to 13 hours. The rate of solution was affected, to some extent, by the particle form in which the cobalt was added.

The above description was for the use of pure cobalt. When impure cobalt was used, the cobalt was added to the digestion mixture in which the spent catalyst was being extracted. In the latter instance, fresh cobalt would undergo the usual purification steps for the solutions reclaimed from the spent catalyst. When especially large amounts of copper were present in the cobalt, the solution was passed through a tower filled with small particles of cobalt, whereupon the copper was displaced from the solution and plated out on the cobalt packing. The same end could be accomplished by having an excess of cobalt present at the end of the digestion step.

Preparation of Fresh Solutions of Magnesium and Thorium

Solutions of magnesium and thorium nitrates were prepared separately by the respective treatment of the oxide and carbonate with nitric acid (50%). The magnesium nitrate solution was made up to contain 120 grams of magnesia per liter and the thorium nitrate solution to contain 150 grams of thoria per liter.

Treatment of Spent Catalyst

As will be described under the heading "Synthesis", a catalyst which had reached the end of its useful life was subjected to one of the several possible treatments for removal of the solid paraffins accumulated on the catalyst.

Deactivation of the Dewaxed Catalysts

When the spent catalyst was still pyrophoric after the removal of the solid paraffin, it was deactivated by a mild oxidation. Catalyst containing thoria as a promoter had to be much more carefully handled in the oxidation step than catalysts containing magnesia as a promoter.

Deactivation of Thoria Catalysts

The thoria promoted catalysts were usually deactivated by treatment with steam for a period of about one day, in much the same manner as in the removal of the solid paraffin. The thoria catalysts could also be deactivated by oxidation with diluted air, care being taken that the temperature did not exceed 300°F. (150°C.). If the temperature exceeded the above limit, the thoria was very difficult to extract from the kieselguhr in the subsequent digestion step. The deactivation with steam required about 35 pounds of high pressure steam per pound of cobalt, while the air deactivation required the circulation of about 65 cubic feet of gas per pound of cobalt (4200 cubic meters of gas per ton of cobalt).

Deactivation of Magnesia Catalysts

The magnesia catalysts, or the mixed catalysts containing large amounts of magnesia in relation to the thoria content, were deactivated by oxidation with air. Practically no temperature control was necessary during the oxidation and the deactivation could be completed in a period of about 10 hours.

At the time the plant was visited, a system was being installed to handle the pyrophoric catalyst without the necessity of the oxidation step. The spent catalyst was to be transferred from the transport vessel, in a stream of inert gas, to a mixing vessel wherein the spent catalyst was to be made into a pumpable slurry with cobalt nitrate solution. This slurry would then be pumped directly to the digesters.

Digestion of Spent Catalyst

The spent, dewaxed, non-pyrophoric catalyst was placed in a digester, stirred with cobalt nitrate solution and nitric acid added, with stirring, at such a rate that about 5% free nitric acid was in the solution. The digester was started at 130°F. (55°C.), but the heat of the reaction raised the temperature of the solution, which was not allowed to exceed 200°F. (95°C.). The reactions occurring in the digestion of the spent catalyst were the same, as regards the cobalt, as those given under the preparation of fresh cobalt solution. The solution of the magnesia and thoria were simple double decomposition reactions.

The digestion was carried to a point where less than 0.1% cobalt remained on the insoluble kieselguhr. The digestion required about 24 hours treatment per ton of cobalt in the spent catalyst. Ruhrchemie had 10 digesters for the treatment of spent catalysts, each with a capacity of 1100 cubic feet (32 cubic meters) and capable of digesting an amount of catalyst equivalent to one ton of cobalt.

Separation of Digested Materials

When the digestion was complete the mixture was filtered by means of a filter press, and thereby separated into a solution which contained the catalytic materials and a precipitate which consisted of the kieselguhr. The precipitate was washed with ordinary tap water, until the combined filtrate and wash water contained 50 to 60 grams of cobalt per liter of solution. The washing was continued until the kieselguhr was practically free from cobalt, the latter wash water being kept separate. The second wash water was treated with soda solution to precipitate the small amount of cobalt present and the precipitated cobalt carbonate was returned to the next digester charge. In this way 6% of the total cobalt requirement was circulated around the digesters.

The time required for the washing and filtration of one digester charge (one ton of cobalt) was about 4-1/2 hours, using two filter presses. The filter elements were cotton cloths on wooden spacers, the average life of a cloth being about 6 months.

The kieselguhr leaving the filter press contained 60 to 65% water and was a rather viscous fluid. The kieselguhr was partially dried in order to facilitate handling, and then thrown away. When completely dried and pulverized or briquetted the spent kieselguhr could be used as thermal insulator.

Iron Purification

The first purification step served to free the solution from the digestion from thorium, iron, aluminum, copper and nickel, together with a part of the magnesia. The filtrate from the digestion was heated to 140 to 160°F. (60 to 70°C.) and added continuously with the soda solution (containing 100 grams of soda per liter) to a 70 cubic foot (2 cubic meter) wooden mixing vessel. The mixing vessel was provided with a stirrer rotating at 150 R.P.M. The relative amounts of soda solution and impure cobalt nitrate solution were so adjusted that the pH of the solution after mixing was about 4. The soda solution had to be introduced in such a manner that local excesses of alkali did not precipitate the cobalt. The soda used in this step amounted to 15 to 20% of the total soda consumption.

Precipitation occurred immediately in the mixing vessel, but the precipitated mixture was run continuously to large tanks, and held there at about 130°F. (55°C.) and stirred at 26 R.P.M. for two to five hours. The purpose of the latter treatment was to permit growth of crystals. The ease of filtration depended upon the crystal size, which, in turn, depended primarily upon the rate of mixing, and secondarily upon the temperature and the rate of stirring in the large vessel. After about one hour's stirring in the large vessel, soda solution was added to bring the pH from 4.0 to 5.8-6.0.

The precipitated mixture was filtered on a filter press (although it was stated that a drum filter could readily be used) and washed with water which was alkali and iron-free. The wash water used here was so small that it was added directly to the filtrate. The cobalt concentration decreased in this step, on the average, from 55 to 48 grams per liter. The amounts of iron, copper, etc., allowable in the final catalyst could not be stated in weight per cent, but only in terms of catalytic activity. The presence of 2% or more of iron (based on cobalt) in the solution before precipitation reduced the activity of the catalyst slightly. 20% iron gave a completely inactive catalyst. It was thought that 1% iron was safe, but at Holten the iron content averaged 0.1 to 0.15% (on the cobalt). This rather complete removal of the iron was done for two reasons:

1. To prevent building up iron concentration in repeated regenerations of the spent catalyst
2. The iron precipitation step as carried out removed 90% of the undesirable organic matter in the spent catalyst

This organic matter may have arisen from:

(a) resins on the catalyst, or
(b) from the oxidation of the solid paraffins by the nitric acid used in the digestion of the spent catalyst

The presence of the organic matter was very harmful to the catalytic activity.

When working with catalysts with high thoria contents, the precipitate was dissolved as sodium thorium carbonate and precipitated as thorium hydrocarbonate. When only small amounts of thoria were present in the catalyst, the precipitate was sold to firms specializing in thoria refining.

Calcium Purification

This purification step removed practically all the calcium together with about one-half the magnesium. The source of the calcium, as well as the impurities removed in the first purification step, was in the kieselguhr. The pH of the solution from the previous purification step was lowered to 4.0 by the addition of nitric acid, and the temperature held around 85°F. (30°C.). The temperature control here was necessary in order to obtain a crystal size which could be filtered.

Sodium fluoride was very difficult to dissolve in water, but could be added as a slurry. The sodium fluoride slurry was added over a period of half an hour to the solution in a vessel provided with a stirrer rotating at 18 R.P.M. No premixing was necessary in this step and there was scarcely any change in the cobalt concentration since only a small amount of sodium fluoride slurry was used.

For the particular kieselguhr being used at Holten, 200 to

260 pounds (100 to 120 kilograms) of sodium fluoride was required per ton of cobalt. The solution after the first purification was carefully analyzed for calcium and magnesia, and the quantity of sodium fluoride necessary to precipitate the calcium completely and to precipitate 50% of the magnesia, was calculated. Such a procedure maintained the calcium concentration below 0.2% of the cobalt.

The raw German kieselguhrs contained about 20% organic matter which had to be burned out. It was thought possible that with the much purer sources of kieselguhr available in the United States the above calcium purification step might be eliminated or at least minimized. Only actual tests would determine the necessary treatment in the regeneration of a catalyst supported on American kieselguhr.

The mixture was stirred for about seven nours after the sodium fluoride addition, by which time the calcium had been completely precipitated. It was helpful to add magnesia at this point, since the magnesia aided in the precipitation of the calcium. The smaller the calcium concentration, the greater should be the quantity of magnesia added. When the magnesia contained large amounts of iron, it was preferable to add the magnesia before the first purification step. A small amount of fresh kieselguhr--never more than 0.25% of the solution--was added as a filter aid. At the end of seven hours, soda solution was added to bring the pH from 4.0 to about 5.8, and the stirring continued for about one hour.

The mixture was filtered on a filter press, the filter elements consisting of the usual cloths, together with a filter paper; the purpose of the paper being to retain the finely divided precipitate. Very little wash water was used; barely sufficient to remove the cobalt from the precipitate.

When magnesia was the only promoter used, the sodium fluoride slurry could be added to the first purification mixture before filtration, and the two precipitates filtered simultaneously. The two purification steps could not be combined when thoria was used as a promoter, since the latter was extremely difficult to recover from the fluoride precipitate.

Adjustment of Concentrations

The purified cobalt solution was taken to a large adjusting vessel--1400 cubic feet (40 cubic meters) capacity--where final concentrations of the catalytic materials were adjusted. The cobalt concentration was adjusted to 40 grams of cobalt per liter of solution by the addition of concentrated cobalt solution (from the solution of fresh cobalt) or by the addition of water, depending upon whether the cobalt concentration in the purified solution was greater or less than the desired 40 grams per liter. This fixed concentration of cobalt was maintained more in order to facilitate the subsequent soda and kieselguhr additions than for any effect it might have had upon the catalytic activity. For the catalyst being made at the time the Holten Plant was visited, the magnesia and thoria concentrations were 4 and 2 grams respectively, per liter of solution. About 20% of the magnesia was lost in the precipitation step (through the solubility of magnesium bicarbonate) so that the final catalyst was made up of $Co:0.08MgO;0.05ThO_2:2.0$ kieselguhr. The free acid in the adjusting vessel had to be 10 to 20 grams of free nitric acid per liter of solution when preparing the thoria catalysts, but the solution could be nearly neutral--pH6·1--when the magnesia catalyst was being prepared.

Measuring and Preheating Solutions

The adjusted solution was passed through a tubular preheater, wherein the temperature was raised to about 140°F. (60°C.) with indirect steam, to a storage vessel near the ceiling of the building in which the catalyst preparation was made. From this storage vessel the solution flowed to a measuring tank. 750 to 800 liters of the adjusted solution were measured at 140°F. (60°C.) and after measuring, heated with direct and indirect steam to 185°F. (85°C.). The adjusted solution then passed through preheating coils where its temperature was raised almost to the boiling point. Soda solution was made up which contained 103-104 grams of sodium carbonate per liter of solution, and this solution was stored in a large vessel near the ceiling. 750 liters of the soda solution were measured and run into the precipitation vessel where it was heated to boiling with direct steam. A pair of measuring tanks, one each for soda solution and cobalt solution, was provided for each precipitation vessel.

Precipitation

To the boiling soda solution in the precipitation vessel (750 liters) the measured, hot, cobalt solution (750 to 800 liters) was added over a one to two minute interval and the mixture stirred for 30 seconds after the addition had been completed. 62 kilograms of kieselguhr were then added over a 1-1/2 minute interval and the mixture thereafter stirred for 30 seconds. Thereupon the mixture was pumped (through open screw type pumps) to the filter press, 2-1/2 minutes being required for filtration. The precipitate was washed with condensate water at 185°F. (85°C.) until the concentration of sodium in the washed catalyst was as low as at least 0.015% on the cobalt, averaging 0.009%.

The precipitation vessel was provided with a large bladed stirrer rotating at 930 R.P.M. It was imperative that the mixing be done thoroughly and rapidly. It was also necessary that after all the materials had been mixed, all operations be done as quickly as possible, until the completely washed catalyst had been obtained.

The catalytic activity was not affected by adding the soda solution to the cobalt solution, nor by adding the two to the precipitation vessel simultaneously. Likewise the kieselguhr could be added at the same time as the solutions, provided there was no great excess of sodium carbonate present, but preferably it was added shortly after the mixing of the two solutions, with the object of minimizing the time in which the kieselguhr was in contact with the alkaline solution.

In each precipitation the following materials were used:

750 liters soda solution	103 to 104 grams sodium carbonate per liter
750-800 liters cobalt solution	39 to 40 grams cobalt per liter 4 grams magnesia per liter 2 grams thoria per liter 5 to 7 grams sodium nitrate per liter
62 kilograms kieselguhr	

The precipitate contained:

68.2 pounds (31 kilograms) cobalt
5.5 pounds (2.5 kilograms) magnesia
3.3 pounds (62 kilograms) thoria
136.5 pounds (62 kilograms) kieselguhr

The filtrate contained, per liter of solution:

2 grams sodium carbonate
6-7 grams sodium bicarbonate and magnesium bicarbonate
70 grams sodium nitrate

The sodium nitrate concentration might be as high as 80 grams per liter of filtrate without harmful effect upon the activity of the catalyst.

At Holten, two precipitation vessels were used with one filter press. The precipitations were so timed that just at the moment that one precipitation mixture had been pumped to the filter press, the precipitation mixture in the second precipitation vessel was ready to be pumped to the same filter press.

The capacity of the filter press was thus two precipitation charges, or a catalyst quantity equivalent to 62 kilograms of cobalt per press filling. This amounted to about 34 cubic feet (960 liters) of catalyst which required 250 to 300 cubic feet (7 to 9 cubic meters) of wash water.

Eighteen such charges were filtered per press per day. Four presses were in use at the time the plant was visited, and this corresponded to 72 charges per day, or a total catalyst output (dry and reduced) of 33,000 to 35,000 pounds (15-16 tons) per day. Five minutes were required for filtering one filter press charge (two precipitation charges), fifteen minutes required for the first wash and ten minutes required for the second wash.

The thickness of the filter-cake varied from 22-25 millimeters. When such a cake was washed under the above conditions with fresh water, 30 gallons of condensate water were required per pound of cobalt (250 cubic meters water per ton cobalt). When the washing was done in stages, the water requirement was about 17 gallons per pound of cobalt (140 cubic meters per ton cobalt).

Adjustment of Water Content for Extrusion

The washed but still moist catalyst was transferred to a mixing vessel and thoroughly mixed with a water slurry of the fines from the screening of the dried catalyst. The catalyst coming from the filter press contained 62% water and 38% solids. The water content was raised to 83% in the mixture of the fresh catalyst and the fines from the screening. This slurry was transferred continuously to a rotary vacuum filter where the water content was reduced to about 65%. A centrifugal filter was undesirable at this point for two reasons:

1. The abrasiveness of the kieselguhr would quickly wear out the filter
2. The filter cake from the centrifugal filter would not be homogeneous

The fines which had to be reincorporated with the wet filter cake amount to 30 to 45% of the total catalyst stream. At the time the plant was visited, this dust amounted to 38% of the total catalyst. The addition of the fines to the fresh catalyst served the purpose of hardening the final dried catalyst. Attempts were made to mix the dry fines with the filter cake, but it was found better to make a slurry of the fines and water, separately, and then to incorporate the slurry with the filter cake.

Extrusion

The catalyst fell from the rotary vacuum filter directly into the extruder. The extruder was located immediately above the centrifugal dryer and was so oriented with respect to the radius of the dryer that radial distribution of the extruded material was obtained directly from the extruder. The catalyst was extruded in the form of 6 millimeter rods from 1 to 4 inches in length, averaging about 2 inches. The rods were quite soft and pasty, having only sufficient body to support, on the average, a 2-inch length of rod. A more detailed description of the extruder will be found in the section dealing specifically with equipment.

The preceding description was of the method of extrusion in use commercially. On a smaller scale it had been found that the catalyst could be extruded in 2 millimeter rods from a piston type extruder. The extruded rods fell onto a conveyor belt, which was covered with a fine mesh screen (2 millimeters) and was surface dried on the belt--the water content reduced from 65 to 60%. In falling onto the screen, the rods were nicked, and after the preliminary drying the rods broke at the nicked point. From this point on the treatment of the catalyst was the same as that to be described for the commercial practice. The extruded material could not be roughly handled until completely dried.

Drying and <u>Forming</u>

The dryer was of a centrifugal type, the trays bearing the catalyst rotating against fixed brushes, which transferred the catalyst from higher to lower trays. The catalyst was fed into the top of the dryer by the extruder, and left the dryer at the bottom. The dryer was provided with high pressure steam coils on the outside shell and hot air was circulated over the trays, fresh air being introduced at the bottom of the dryer and discharged from the top. The temperatures were so adjusted that the catalyst in the top of the dryer was never hotter than 200 to 212°F. (95 to 100°C.), and the catalyst temperature leaving the bottom was not higher than 250°F. (120°C.). The passage of the catalyst through the dryer required about two hours. The catalyst entering the dryer contained about 65% water, and that leaving the dryer contained 10% water. The catalyst was not completely dried, since the presence of about 10% water facilitated temperature control in the reduction step.

The capacity of each dryer was about 1100 pounds (500 kilograms) of dried catalyst per hour. Three such dryers were in operation at Holten at the time the plant was visited, although these dryers were not operated at full capacity. It might be mentioned that the design of the dryers has to take care of the recirculated fines, that is, it must be 30 to 45% larger than calculated on the dry catalyst output. It was stated that any type of dryer might be used in which the temperature could be controlled, and in which the catalyst would not be subjected to too rough a treatment.

Sizing

The material from the dryer was separated into three particle sizes:

Fines	1 millimeter or less	35%
Useful	2 to 3 millimeters	20%
Larges	8 to 10 millimeters	45%

The fines were made into a slurry with water and mixed with the fresh, wet filter cake and again extruded, dried, etc. The larges were pressed through a screen and re-screened. The useful size catalyst was placed in paper bags for transfer to the reduction plant.

Forming Method for Small Size Catalyst

The fines from the screening operation could be formed into a more desirable particle by a very interesting process. The dry catalyst fines were placed in an Eirischmischer, which consisted of an upright cylinder about 6 feet in diameter, provided with a rotating bottom and with two scrapers and two rakes, each rotating in a direction opposite to that of the bottom of the mixer. The rakes and scrapers were so adjusted as to have a minimum clearance between the sides of the cylinder and the bottom. The bottom of the mixer was rotated at a speed of 5 R.P.M., and the rakes and scrapers at a speed of 60 R.P.M. When the mixer had been started, a quantity of water equivalent to about half the weight of the catalyst fines was sprinkled over the top of the catalyst being stirred. After some time the speed of the revolutions of the bottom and of the rakes was doubled, exact time figures not being available, since the apparatus was still in an experimental stage. Apparently the quantity of sized material was a function of the time of mixing and of the clearance between the scrapers and the bottom of the cylinder. It was stated that up to 70% of the charged catalyst fines could be recovered as round balls with the diameter of about 1 millimeter.

The above apparatus was developed in an effort to decrease the particle size of the catalyst, since it was thought that a greater catalyst surface was beneficial to the activity. From the standpoint of activity, the smaller the particle size the better the catalyst, but physically there was a limit to the particle size, concomitant with the necessary mechanical strength. Two or three commercial chambers had been filled with the round balls of catalyst, about 1 millimeter in diameter, and were undergoing tests at the time the plant was visited. There was apparently no change in the products with change in the particle size, and no detrimental effect upon catalyst life was anticipated.

Reduction

The sized catalyst was transferred from bags to reduction chambers, which held about 21 cubic feet (600 liters) of catalyst. The reduced catalyst from seventeen reduction chambers was sufficient for filling one commercial synthesis chamber. Hydrogen at 840°F. (450°C.) was passed through the reduction chamber at the rate of 100,000 cubic feet (3,000 cubic meters) per hour.

It was calculated that the time required for the reduction at the above temperatures and rates, was 18 minutes, but actually 35 to 50 minutes were used for the preheating and reduction in the plant at Holten. The average time schedule for the various operations in the reduction step was given as:

Preheating and reduction	50 minutes
Changing connections	10 minutes
Emptying	5 minutes
Refilling	5 to 10 minutes
Making up joints	10 minutes

Purging time was included in the time given for making up connections. It was stated that the overall time required for reduction could be reduced 50% by the use of automatic equipment.

The time required for preheating was not known. The reduction vessel and the catalyst were cold at the start and were heated entirely by the hydrogen entering at 840°F. (450°C.). At the start, the temperature difference between the hydrogen just before entering and just after leaving the catalyst bed was 800°F. (425°C.), and at the end of the reduction the temperature difference was 175°F. (80°C.). The reduction temperature, therefore, varied from 700°F. (370°C.) for the bottom of the catalyst bed, to perhaps 840°F. (450°C.) for the top of the catalyst bed.

The catalyst which was reduced at 575°F. (300°C.) was more active, but the time of reduction was about four times that required at 840°F. (450°C.). The higher the reduction temperature, the less sensitive was the catalyst to the presence of water and carbon dioxide in the hydrogen used for the reduction. If a temperature much higher than 840°F. (450°C.) was used, the resulting catalyst was less active.

The gas used for the reduction at Holten consisted of about 75% hydrogen and 25% nitrogen, with less than 0.1 grams of water, and about 1 gram of carbon dioxide per cubic meter. It was desirable to use for the reduction, the purest hydrogen available.

Carbon
Dioxide
in Reducing
Gas

Any carbon dioxide present in the hydrogen was reduced to methane upon contact with the reduced catalyst in the presence of hydrogen. In this reduction of the carbon dioxide a large quantity of heat was developed which partially deactivated the catalyst. The gas throughput could be decreased by about 17% when carbon dioxide-free hydrogen was used. The carbon dioxide content of the gas was held at about one gram per cubic meter by passing the gases from the reduction over spent synthesis catalyst at 480-570°F. (250-300°C.), which served to convert most of the carbon dioxide and all the carbon monoxide to the harmless methane.

Water in Reducing Gas

Any water which was present in the hydrogen tended to re-oxidize the reduced cobalt to the inactive cobalt oxide. Apparently the more reactive points on the cobalt were oxidized first, and the harmful effects of small amounts of water were out of all proportion to the actual quantity of water present. The catalyst could not be reduced with hydrogen which contained as much as 4 grams of water per cubic meter of hydrogen. Water was removed from the reducing gas by a combination of low temperature cooling and silica gel drying.

Nitrogen in Reducing Gas

Nitrogen in the hydrogen was not nearly so injurious to the catalyst as carbon dioxide or water. A change from 0.1 to 0.2 grams of water per cubic meter of hydrogen had more effect upon the catalytic activity than dilution with 10% nitrogen. The gas throughput could not be reduced proportionately when a nitrogen-free hydrogen was used, since a sweeping action was required to remove the water and carbon dioxide as products of the reduction.

Gas Rates

The gas rate (75% hydrogen and 25% nitrogen) over the catalyst bed was about 3900 cubic feet per hour per square foot of catalyst surface (1200 cubic meters per hour per square meter) or 100,000 cubic feet (3,000 cubic meters) per hour per reduction chamber. This gas rate was about the limit with the particular distribution system, since higher rates caused a turbulence which floated the catalyst to the outer edges of the reduction chamber. When pure hydrogen was used, either the temperature or the time of the reduction could be reduced, both of which changes were beneficial to the activity of the catalyst.

Depth of Reduction Bed

The activity of the catalyst was affected by the depth of the reducing bed. When the catalyst was completely reduced in a deep bed, the top layer was partially inactivated due to too long a time at the high temperature. When the catalyst was reduced only to the point where further treatment would have partially inactivated the top layer, the bottom of the catalyst be still would have been unreduced. Furthermore, reduction in a large bed was probably different from reduction in a small diameter tube.

On a laboratory scale, in a tube, a depth of 6 feet (2 meters) of catalyst could be successfully reduced, but this had never been duplicated commercially in large beds. Likewise, on a laboratory scale, the carbonates could be decomposed with hot nitrogen and this followed by reduction with hydrogen, but again the results could not be duplicated commercially in the large beds.

Holten Plant Capacities

At Holten, 12 reduction chambers were available, but at the time the plant was visited only six were in use. Each chamber had a daily capacity of about one synthesis chamber charge--1900 pounds (850 kilograms) cobalt. The gas used for the reduction was recycled, about 10,000 to 18,000 cubic feet (300 to 500 cubic meters) of fresh gas being added per hour, and a somewhat smaller quantity being withdrawn. Before repassage of the exit reduction gases over the catalyst, the water and carbon dioxide concentrations were reduced to 0.1 and 0.2 grams per cubic meter respectively. The methane content of the reduction gases was maintained at 1 to 3% by bleeding off a part of the recycle gas. Each ton of cobalt should have required about 18,000 cubic feet (500 cubic meters) of the reduction gas (hydrogen plus nitrogen) for reduction, but due to losses the figure was near 50,000 cubic feet (1500 cubic meters) per ton of cobalt. The depth of the reduction bed was 8 to 10 inches (200 to 250 millimeters) although the reduction chambers were designed for a 14 inch (350 millimeter) depth.

Control Tests

Control tests on the reduction of the catalyst were not of great utility, actual testing with synthesis gas being the only reliable guide to the catalytic activity. At the end of the reduction, a sample of the catalyst was taken to the laboratory and analyzed for cobalt metal. This was done by solution of the cobalt in sulfuric acid and measurement of the hydrogen evolved. When 70% of the total cobalt content had been reduced to the metal, the catalyst was regarded as being very well reduced.

Cooling And Transference Of Reduced Catalyst

The catalyst was removed from the reduction chambers while still hot and transferred to the transport vessel. A large transport vessel--capacity of seventeen reduction chamber charges--required five to eight hours cooling time. The small transport vessel--capacity of four to five reduction chamber charges--required about two hours cooling time. The catalyst was cooled by the recirculation of nitrogen. When the catalyst temperature had fallen to 110°F. (45°C.), carbon dioxide was passed over the catalyst for ten minutes to prevent oxidation of the cobalt upon exposure to the air.

The catalyst was transferred to the synthesis chambers directly from the transport vessel and was ready for immediate use.

Semi-Plant Scale Catalyst Preparation

The preparation of catalyst on a semi-plant scale, that is, in batches of from one to ten kilograms of cobalt, was made in equipment that was almost identical with that used in the large catalyst plant, except as regards size. The solutions were made up in 200 liter vessels made of V-2a steel. The precipitation was made in an alloy steel barrel which was so mounted that it could be turned rapidly end over end. The filtration was done in a standard filter press, which contained only a few filter plates, or in some instances, was carried out in an alloy steel lined box filled with filter stones which, in turn, were covered with paper. This filter box was provided with a means for obtaining suction, in order to filter the precipitated mixture rapidly. The precipitated catalyst was transferred in thin plates (about 1 to 2 inches thick) to a drying rack which was pushed into an oven heated to 212 to 250°F. (100 to 120°C.) through which warm air was circulated. The dried catalyst was screened to give about 50% sized particles and about 50% fines. The fines could be returned to a fresh wet batch of washed catalyst precipitate, mixed, dried and resized, but this method of operation resulted in a catalyst with very inferior mechanical strength. When the dust was returned to the wet catalyst, it was found preferable to extrude the catalyst through a meat chopper, turned on its side, and then to dry the worms. The mechanical strength of the catalyst made by the latter method was equivalent to that of the catalyst to which no fines had been added.

Preparation Of Catalyst From Chlorides

Catalyst made from the chlorides in a manner identical to the manufacture from the nitrates had fully as high an activity as the best catalysts from the nitrates. No difficulties were encountered at any stage of the preparation. The use of chlorides has certain advantages over the use of nitrates:

1. The catalyst regeneration was much simpler
2. The solutions were much more easily made

About the only disadvantage of the use of chloride was the corrosiveness of all the acidic solutions.

Ruhrchemie would use chlorides if:

1. They manufactured hydrochloric acid
2. The present catalyst manufacturing equipment were sufficiently resistant to corrosion.

Preparation Of Catalyst From Sulfates

The catalysts prepared from sulfates were being tested for activity and life at the time the plant was visited, and it was too early at that time to state definitely if sulfates could be used in place of nitrates. So far as the experimental work had gone, no difficulties were encountered.

Cobalt-magnesia catalyst could be prepared from the sulfates in the same manner as from the nitrates. In preparing a cobalt-thoria catalyst, the thorium had to be separately precipitated from a nitrate solution, and this washed precipitate added to the wet, washed precipitate of cobalt (or cobalt-magnesia) from the sulfate solution. The precipitate from sulfate solution required a much more thorough washing than that from the chloride or nitrate solution. The exact washing requirements had not been determined accurately, but experiments to that end were in progress. The completeness of the washing could be decided without carrying out the synthesis reaction by:

1. Testing the exit gas from the reduction for hydrogen sulfide

2. Testing the reduced catalysts for sulfides

If hydrogen sulfide was found in (1), the catalyst definitely had not been sufficiently washed. If upon treating the reduced catalyst with the mineral acid, appreciable hydrogen sulfide was evolved, the catalyst probably had not been sufficiently washed, but if only traces of hydrogen sulfide was evolved, it was necessary to test the activity of the catalyst towards the synthesis reaction in order to ascertain if the washing had been sufficient. At the time, it was not certain just what hydrogen sulfide evolution indicated insufficient washing.