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U. S. GROUP CONTROL COUNCIL, GERMANY
OFFICE OF THE DIRECTOR OF INTELLIGENCE

MANUFACTURE AND REGENERATION OF CATALYSTS

AT I. G. FARBENINDUSTRIE LUDWIGSHAFEN/OPPAU

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TABLE OF CONTENTS

	<u>Page</u>
I. Introduction.....	1
II. Catalyst 5058 (Figures I & II).....	1
III. Catalyst 6434 (Figure III).....	2
IV. Catalyst 8376 (Figure IV).....	2
V. Catalyst PH 86.....	3
VI. Catalyst for Methane Cracking.....	5
VII. Brown Oxide Catalyst.....	5
VIII. Catalysts 7935 & 7360.....	6

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MANUFACTURE AND REGENERATION OF CATALYSTS AT
I.G. FARBENINDUSTRIE, LUDWIGSHAFEN-OPPAU
(TARGET 30/4.03)

I. INTRODUCTION

The principal equipment in the catalyst plants at Ludwigshafen-Oppau was inspected and is presented in the form of flow sheets for the manufacture of four of the principal catalysts. The equipment is in many cases of special design rather than stock items that was built by the company and modified in the course of the growth of the high-pressure synthesis of hydrocarbons in Germany. It is believed that if the manufacture of catalysts were to be undertaken elsewhere, the selection of equipment for the operations involved could be made successfully from the guidance furnished by this rather general report. Five additional catalysts are described, also.

II. CATALYST 5058 FROM FRESH TUNGSTIC ACID

In a supply tank of about 2,000 liters capacity, 500 kg. of tungstic acid ($WO_3 \cdot H_2O$) that contains about 92-93 percent of WO_3 is dissolved at 60-70° C. in 1,500 liters of mother liquor. The solution is effected by stirring for about 1-1/2 hours. The mother liquor is obtained from a previous lot of catalyst and is first adjusted to a concentration of 13 percent NH_3 by passing in gaseous ammonia. The solution is allowed to stand without stirring for 1 hour, then is pumped into the saturating vessel through a cloth filter (three-quarters hr. to one hr.). The saturator is purged with H_2S and thereafter the solution, which has been cooled to about 55°C., is heated in an atmosphere of hydrogen sulfide with stirring to about 70°C. This charge is slowly cooled to 50°, and then more rapidly to about 20°C. (time of cooling 6-7 hours).

The precipitate of yellow salt ($(NH_4)_2WS$) is fed to the suction filter while stirred.

Nitrogen under pressure of 1/2 atm. is used in the filter. The mother liquor is collected in a stirred storage vessel and is used subsequently as mentioned above. The decomposition of the yellow salt is carried out in a screw-conveyor furnace in a stream of hydrogen at 400-430°C. The black powder (WS_2) is cooled at the end of the furnace by a stream of nitrogen. The capacity of the furnace is 1.2-1.5 tons per day. The black powder is then ground in a hammer-mill until 70-80 percent passes through a 100-mesh screen. (Important not to grind too fine.) 10 mm. pellets are then made in a Kilian press flushed with nitrogen. The sharp corners of the pellets are removed in a rotating screen drum, and the finished catalyst is packed in barrels that are flushed with nitrogen.

Catalyst 5058 from Regenerated Tungstic Acid.

The used catalyst is crushed to pieces of about 2-5 mm. and calcined in a revolving oven that is heated externally. The product is ground and dissolved in the supply vessel in mother liquor that is then discharged into a settling vessel. Further operations are the same as in the method of preparation from new tungstic acid. The crushing strength of the pellets is 250-300 kg. per sq. cm.

Regeneration of Catalyst 5058.

The pellets are ground, together with the dust that had been removed by screening, and are calcined at 600-800° in a stream of air in a gas-heated furnace. The calcined material is processed in the same way as yellow earth.

III. METHOD OF PREPARATION OF CATALYST 6434

300 kg. of Terrana A extra (Deggendorf) is etched with 344 kg. of 8 percent hydrofluoric acid in a stirred pan for about 15-20 minutes at ordinary temperature. 500 liters of a 10 percent solution of yellow salt (ammonium thiotungstate) is added slowly, and the pan is heated with steam. In 8-10 hours, the charge is dry. During a further two hours, it is cooled. The cooled product is broken up in a special hammer-mill fitted with a 5 mm. screen (Schlagkreuzmühle) and is then decomposed in a screw-conveyor furnace at 400-430°C. in the presence of hydrogen and hydrogen sulfide. The discharge end of the furnace is cooled with nitrogen. The capacity of the furnace is 1-1/2 tons/day. The cooled product is again ground in a hammer-mill, passing out through a 1 mm. screen. The ground product is wetted in an Eirich mixer, each 20 kg. of product receiving 6.2 to 7 liters of water. The mass is then pressed through a 3 mm. screen. This product is fed to the Kilian press, where it is made into 10 mm. pellets (capacity 700 kg. per day). The pellets are allowed to stand in the air for several hours, are tumbled in a screening apparatus and then dried in a drying oven or an electrically-heated vertical furnace (up to 200°C.). The final operation is calcining at 450°C. in a treating furnace in the presence of hydrogen and hydrogen sulfide. The finished catalyst is cooled with nitrogen and packed in drums under nitrogen.

Regeneration of Catalyst 6434.

The used catalyst has been regenerated only in a few instances by very careful roasting at 550-600°C., impregnating with a solution of yellow salt (1 percent WS_2) and sulfurizing at 450°C. The greater part of this used catalyst (several hundred tons) was worked up electrothermally into ferrotungsten at Bitterfeld. In this operation, the catalyst is roasted and then reduced electrothermally, alone or after admixture with ore.

IV. CATALYST 8376

Commercial aluminum sulfate ($Al_2(SO_4)_3 \cdot 18H_2O$) that contains about 18 percent Al_2O_3 is dissolved in water at 50-70°C. to an almost saturated solution (about 10 percent alumina in the solution). This solution is allowed to flow simultaneously with a 20 percent ammonia solution into a steam-jacketed stirred vessel to precipitate aluminum hydroxide. Solutions are so added to the vessel that there is always a small excess of ammonia in the mixture, which is controlled by an antimony electrode (pH between 8 and 10). 20 cc. of the filtrate requires about 10 cc. of N/10 H_2SO_4 . The precipitate is pumped from a storage vessel into the filter press and washed sulfate-free with weak ammonia solution (0.1 percent). The filter cake (about 19 percent solids) is dried in a drying oven or a rotating-tube dryer until the ignition loss of the product is 15-20 percent. The dried

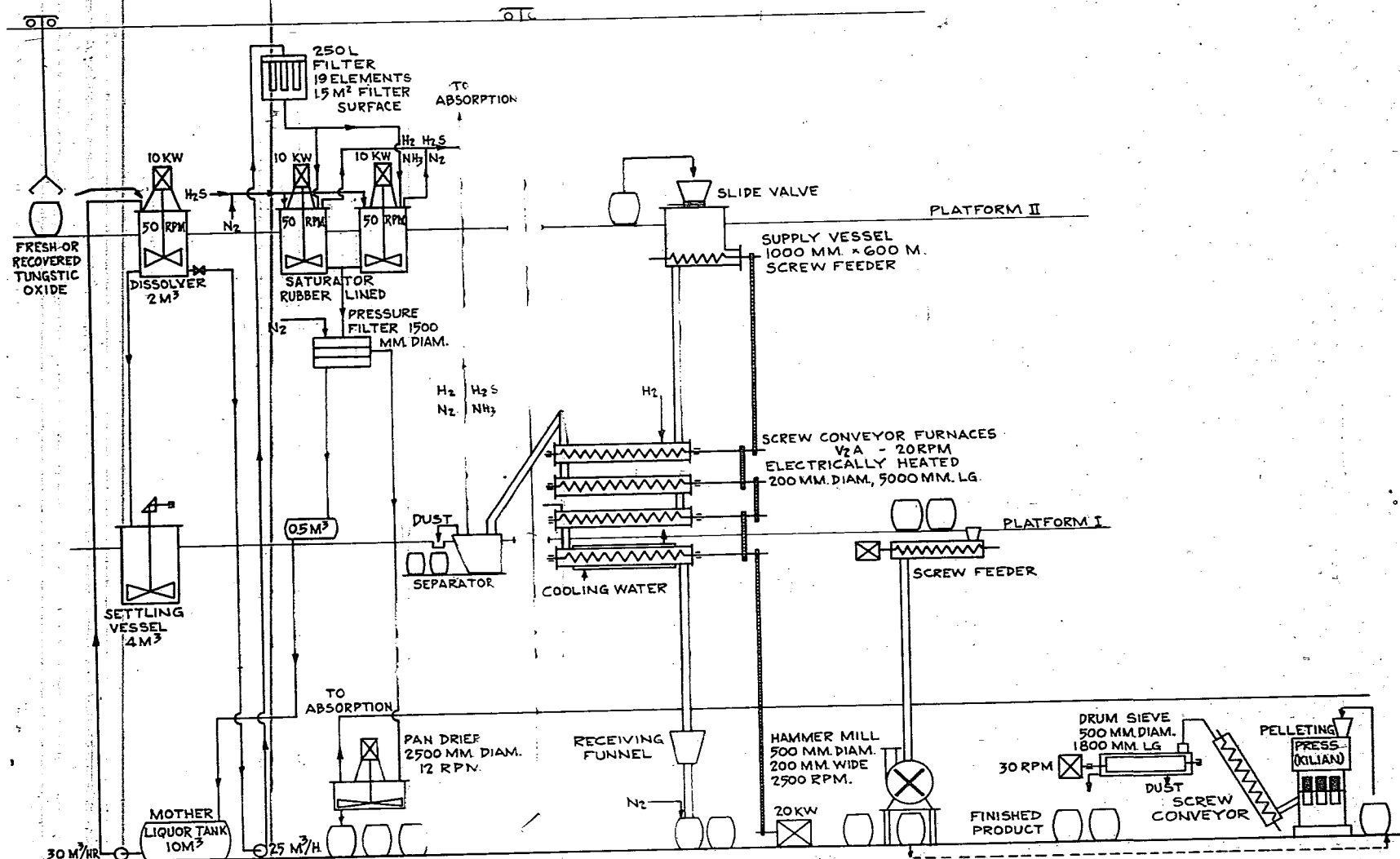


FIGURE I- DIAGRAM OF APPARATUS ARRANGEMENT FOR THE PREPARATION OF CATALYST 5058 (1 TON/DAY).

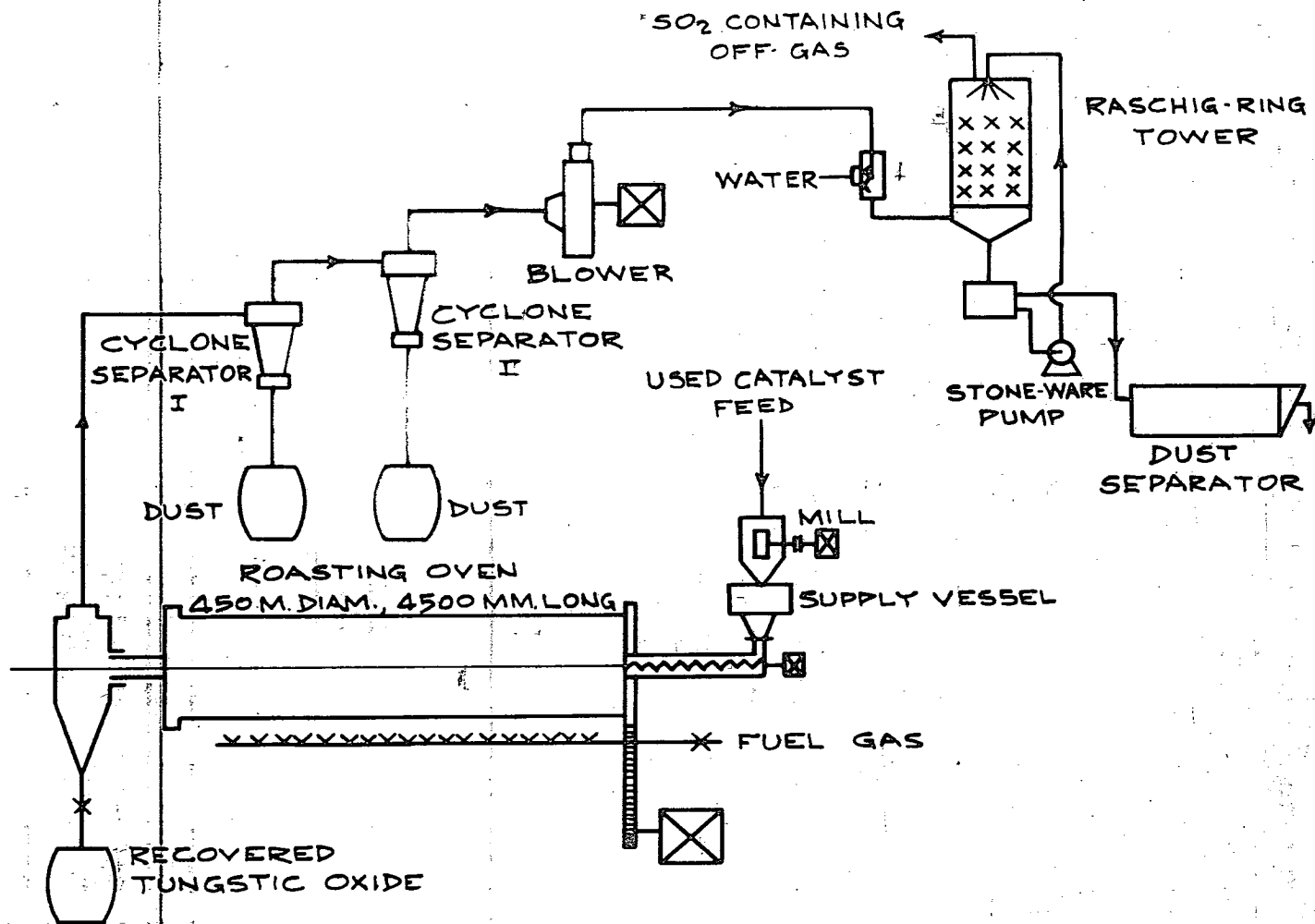


FIGURE II. DIAGRAM OF ROASTING APPARATUS FOR RECOVERY OF TUNGSTIC OXIDE FROM USED CATALYST 5058.

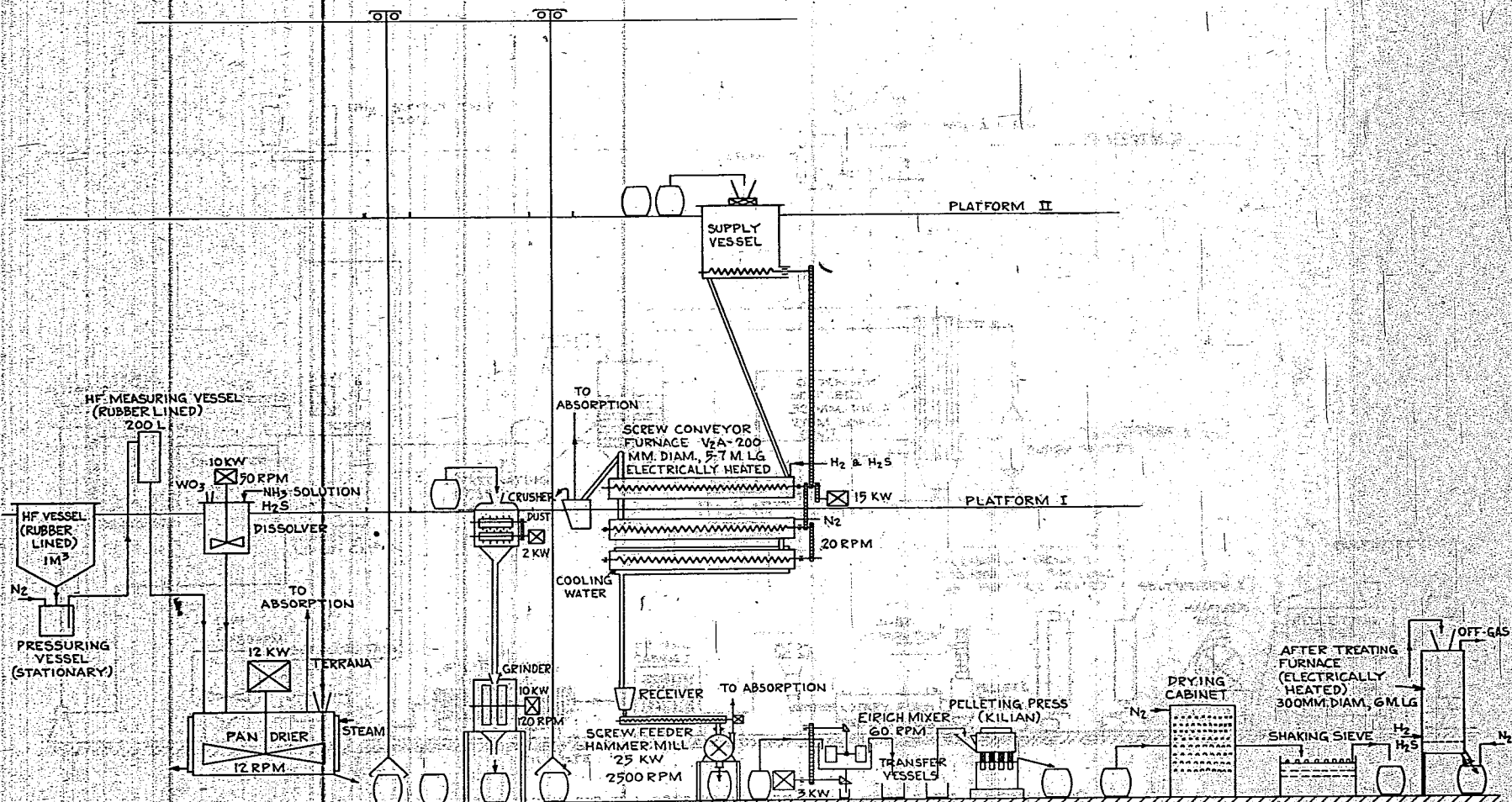


FIGURE III DIAGRAM OF APPARATUS ARRANGEMENT FOR THE PREPARATION OF CATALYST 6434 (1 TON/DAY).

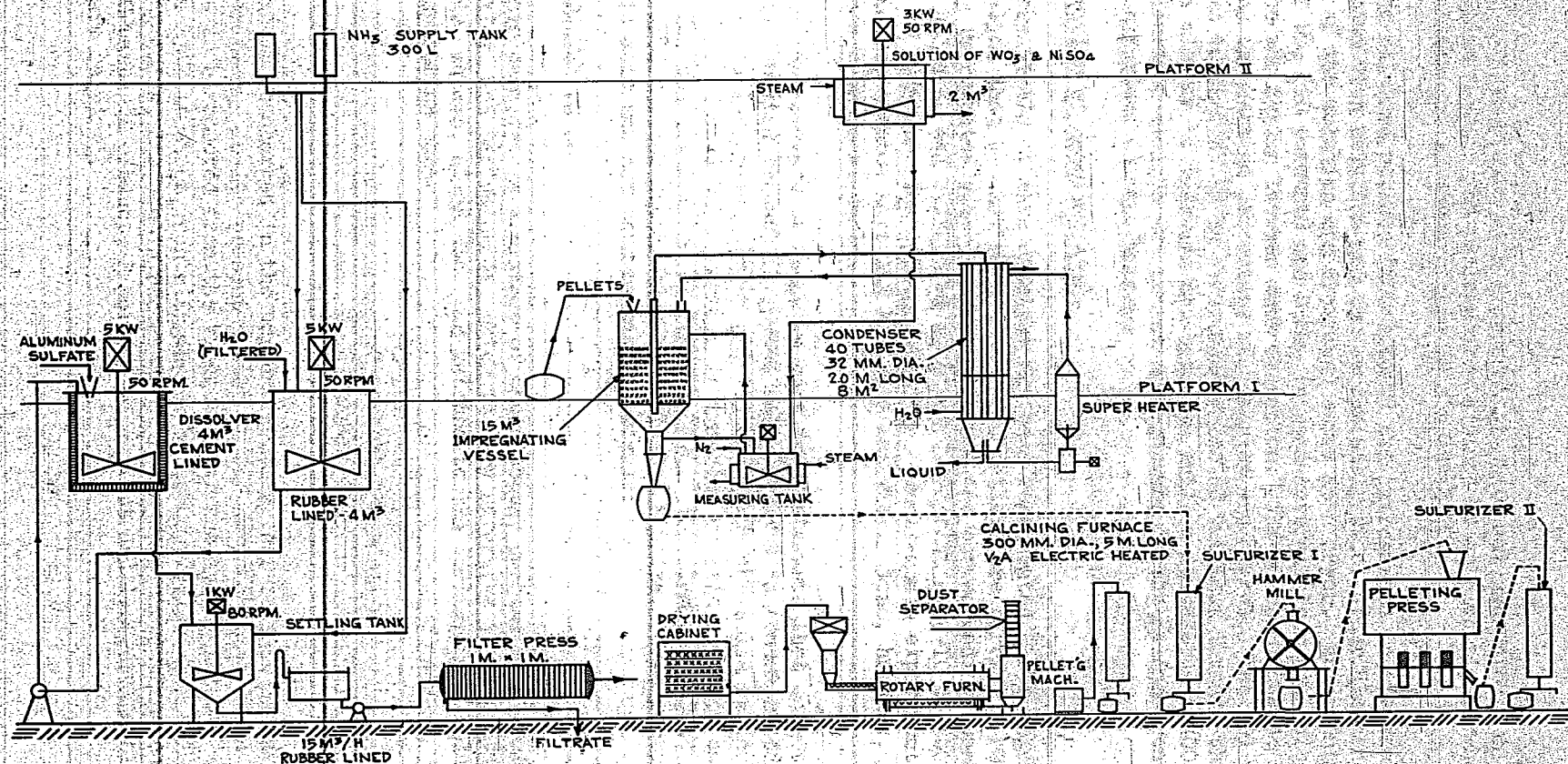


FIGURE IV. DIAGRAM OF APPARATUS ARRANGEMENT FOR THE PREPARATION OF CATALYST 83TG (1 TON/DAY).

product is then ground with 1 percent graphite and made into 10 mm. pellets in a Kilian press. The pellets are calcined in an electrically-heated vertical furnace in the presence of air at 450°C.

The calcined pellets (800 liters) are impregnated in a vessel that can be flooded with solution and can subsequently (i.e. after discharging the excess of the solution and draining) serve as a dryer. An ammoniacal solution of WO_3 (20 percent) and $NiSO_4$ is used several times with discharges of solution and drying between each operation. The number of stages is determined by the desired percentage of tungsten and nickel. The dry pellets are then sulfurized in an electrically-heated vertical furnace through which a mixture of hydrogen and hydrogen sulfide is passed at 400-450°C. The sulfurized pellets are ground and reformed in the Kilian press, and again sulfurized in the furnace.

Regeneration of Catalyst 8376.

Very little of this catalyst has been regenerated. For regeneration of catalyst that has had normal use, the pellets are carefully roasted at 600°C., impregnated with 1 percent WO_3 and the corresponding quantity of nickel sulfate, and sulfurized to a sulfur content of 9-10 percent in a stream of hydrogen plus hydrogen sulfide. Small-scale experiments showed that the regenerated material had good activity. None, however, has been used on a commercial scale.

For the recovery of tungstic acid from catalysts that cannot be regenerated, the roasted product is ground and dissolved in concentrated sulfuric acid. The solution is diluted and filtered from the solid residue. Tungstic acid is dissolved in ammonia or ammonium sulfide solution and is used either for the preparation of 5058 or 8376. The aluminum sulfate solution can be used for the preparation of activated alumina. This recovery of tungstic acid has not been made commercially.

V. CATALYST PH 36

This catalyst is a mixture of basic copper carbonate, chromium oxide, zinc oxide, and barium oxide, which is very effective for the hydrogenation of acids, esters, aldehydes, and ketones to the corresponding alcohols. Its composition is:-

45 percent copper
2 percent chromium
2 percent zinc
2 percent barium.

The contact is charged in the unreduced state, but is reduced during the hydrogenation. In its present state, it can be used only in the sump over and has to be removed from the product after the hydrogenation. This can be done by filtration, centrifuging or by decomposition with acid. When reducing acids, its use is recommended in conjunction with magnesium oxide. For 100 parts of product, 2 percent of contact and 1.8 percent of magnesium oxide are required.

The hydrogenation with this catalyst is carried out at temperatures between 230 and 270°C. and at a pressure of 230 atm. of hydrogen.

The catalyst has the great advantage of not forming any paraffin, even at higher temperatures.

Method of Preparation of Catalyst PH 86.

Materials for 100 kg. of catalyst:

105-108 kg. of sodium carbonate

56-59 kg. of copper, equivalent to 497 kg. of copper nitrate solution containing 11.8 percent of copper.

4.17 kg. of barium nitrate

3.53 kg. of zinc nitrate (6 mols of water of crystallization)

5.93 kg. of chromium nitrate

15.5 kg. of sodium bicarbonate.

Procedure for 632 kg. of catalyst:

7000 l. of sodium carbonate solution (12.5° Be') is diluted with water in a stirred container to a specific gravity of 8.5° Be' (final volume is about 10,800 l.). Into this solution is introduced (at room temperature) 3,150 kg. of copper nitrate solution (content of copper is 11.8 percent). The temperature should not be higher than 30°C., and the Ph between 6.5 and 7.5. The mixture is stirred for about 30-40 hours (sic), until the blue color changes to green. The precipitate is then washed by decantation (12 times with 10 m³ of condensate) until diphenylamine shows the absence of nitrates. After settling, about 5,700 l. of the clear solution is discharged.

The barium nitrate (4.17 kg.) is dissolved in a pressure vessel (100 l.) provided with a stirrer, in 850 l. of water. The zinc nitrate (3.53 kg.) is added to this solution and after it has dissolved, the chromium nitrate (5.93 kg.) is added. The chromium nitrate used is the anhydrous trihydrate.

The suspension of copper solution to (5,700 l.)

In the meantime, a solution of 10 kg. of sodium bicarbonate in 100 l. of water is put into a stirred vessel. This solution is added to the named mixture of copper carbonate and metal nitrates until no further precipitate forms. The filtrate from the finished mixture is weakly alkaline. Washing by decantation is carried out until diphenylamine shows the absence of nitrates (about eleven washings). The filtrate must be neutral towards litmus and phenolphthalein. Only when a sample is boiled should the filtrate turn litmus blue and phenolphthalein red.

After washing has been finished, the precipitate is allowed to settle and the clear liquid above the precipitate is discharged. The remainder is centrifuged, and the solid dried at 120°. The product is ground in a hammer mill (Schlagkreuzmühle).

VI. PREPARATION OF METHANE-SPLITTING CATALYST

The catalyst splits methane in the presence of steam at about 700-750°C. into CO₂, CO and H₂. Its composition is approximately:-

SiO ₂	20-21 percent
Al ₂ O ₃	17-18 percent
Fe ₂ O ₃	5.0-5.5 percent
NiO	19-20 percent
CaO	10-11 percent
MgO	8.5-10 percent

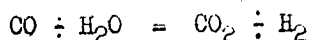
The specific gravity is about 1.0.

For the preparation of the catalyst, 184 kg. of nickel powder as a 14.5 percent nickel-nitrate solution is diluted with 1,000 liters of water, and is precipitated at 65-70°C. with 340 kg. of sodium carbonate (as a 10.5 percent solution). A slight excess of sodium carbonate should be present. The total contents of the precipitation vessel is separated in a filter press and the cake washed free from carbonate and nitrate at about 40°C. The filter cake is blown dry with compressed air for about 15 minutes.

To about one-third of this filter cake (about 360 kg.), in a kneading machine, is added 178 kg. of kaolin, 76 kg. of magnesium oxide and 36 kg. of nickel powder (as about a 15 percent solution). After kneading, the mass is spread about 20 mm. thick on plates and ignited for about 7 hours at 500°C. The ignited material is ground to powder. Fifty kg. of this powder is mixed with 23 kg. of alumina cement in a mixer, with the addition of 12 liters of water, screened through a 2 mm. mesh sieve and pressed in a tableting machine to Raschig-ring shapes (16-18 mm. diameter and 12-14 mm. long). These rings are piled up and sprayed with water twice a day for three days to set the cement. They are then packed.

VII. PREPARATION OF BROWN OXIDE CATALYST

Brown oxide is a CO-conversion catalyst and works according to the following equation:-



It contains approximately:-

Fe ₂ O ₃	86-87 percent
Cr ₂ O ₃	7-7.5 percent
Sodium and Iron Sulfate - Balance	
(approximately 1 percent SO ₄)	
Specific gravity is about 1.17.	

The preparation of this catalyst is divided into three operations:-

- Preparation of the iron oxide
- Preparation of the chromium nitrate solution
- The further working up of both products.

For the iron oxide preparation, iron sulfate ($\text{FeSO}_4 \cdot 7 \text{H}_2\text{O}$) is dissolved in water to give a 20-percent solution and the solution is pumped into a storage vessel. Sodium carbonate (10-12 percent solution) is put into the precipitation vessel, and the iron sulfate is added with stirring at about 30-35°C. Quantities are adjusted to give a slight excess alkalinity at the end of the precipitation. The iron carbonate precipitate is allowed to settle and is then well washed on a rotary filter with warm water (60-70 percent). It is then dried in a rotary kiln and decomposed in an annealing furnace. The iron oxide formed (about 95 percent Fe_2O_3) should have a weak red glow on leaving the furnace. It is then cooled in a screw-propeller cooler and stored in bunkers.

The chromium nitrate solution is prepared by dissolving a 34-40 percent wet slime of chromium oxide in nitric acid at about 70-90°C., with stirring. The nitrate solution should contain a minimum of 15 percent Cr_2O_3 .

The further working up of the catalyst consists in filling a kneading machine with the previously prepared iron oxide and adding, with kneading, enough chromium nitrate solution to give the desired composition of the finished catalyst (86-87 percent Fe_2O_3 , 7-7.5 percent Cr_2O_3). The product from the kneader is pressed into cakes (10-12 mm. thick) and is roasted on plates in a tunnel kiln at 500-550°C. The dried cakes are broken in a cylindrical crusher. The fines (under 5 mm.) are screened out and the material above 5 mm. size is again calcined in a furnace at 550°C. It is then screened into small-kernal size (5-10 mm.) and large kernel-size (over 10 mm.) and packed in barrels.

The fines mentioned above (under 5 mm.) after a fine-grinding can be used when kneading up a new batch.

VIII. CATALYSTS 7935 AND 7360

7935

The activated alumina is prepared as described for catalyst 8376. The calcined pellets are treated in the combination impregnating and drying apparatus in batches of 800 liters with an ammoniacal solution of MoO_3 (about 5 percent of ammonia and 12-15 percent MoO_3) until the finished catalyst contains 15 percent MoO_3 . After drying in the apparatus at 190°, the catalyst is calcined in an electrically-heated vertical furnace in a stream of air heated to 400°C.

7360

Activated alumina is prepared in the form of cubes by the aluminate process, and the cubes treated in the same way as for catalyst 7935, until the finished catalyst contains 10-12 percent MoO_3 .

Regeneration of catalysts 7360 and 7935.

The used catalyst is roasted and ground. The powder is then moistened and dissolved in concentrated sulfuric acid; the solution is diluted and saturated with hydrogen sulfide. The impure precipitate of molybdenum sulfide is filtered, roasted and dissolved in ammonium hydroxide.