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MANUFACTURE AND REGENERATION OF CATALYSTS AT I. G. FARBENINDUSTRIE A. G. PLANTS, LUDWIGSHAFEN/OPPAU, GERMANY

BY

W. F. FARAGHER AND W. A. HORNE

FOREWORD

In the early part of 1945 as the Allied armies advanced, German laboratories and plants became available for investigation. Since German development work had been hidden from the eyes of the world by the Reich's national policy of secrecy, and by $5\frac{1}{2}$ years of war, it was obvious that much might be learned from such investigation. In particular, this was true in the synthetic-fuel industries deriving oil, gasoline, and a wide variety of chemicals from coal, for owing to the scarcity of domestic petroleum, Germany had been forced into intense development of this field in contrast to the limited amount of similar development by the United States and Great Britain. Before the fighting ended in Europe, the United States and Great Britain organized teams comprised of experts in all fields to investigate the research and industrial operations in Germany. The teams investigating coal, oil, gasification, and allied chemical fields included more than 30 American investigators and about an equivalent number of British investigators during 1945, and functioned with a reduced staff into 1946. German work in the synthetic liquid-fuels industries and allied fields was on such a large scale that even such extensive investigation could not possibly cover the subject in all detail. However, a great deal of information possible of direct application, and much information of a fundamental nature to help guide research work in this country for many years, was uncovered. Studies of the German industry are continuing, and it is hoped that such gaps in the information as now exist will be filled by future work.

The primary fields covered in the oil and synthetic-fuels investigation were concerned with petroleum refining and the gas-synthesis and coal-hydrogenation processes for producing oil from coal. The related fields of coal gasification, oxygen production, alcohol manufacture, lubricating-oil production, and the production of waxes and edible fats, as well as a variety of synthetic chemicals, were an inherent part of the investigation.

This report is one of a series which resulted from the investigations in Germany and other parts of Europe by the Technical Oil Mission, operating under the auspices of the Ministry of Fuel and Power for Great Britain and the Petroleum Administration for War and the Bureau of Mines for the United States. It is being published in accordance with the policy of the United States Government to make available to the interested public the results of the investigations of enemy research and industrial development.

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MANUFACTURE AND REGENERATION OF CATALYSTS AT I. G. FARBENINDUSTRIE A. G. PLANTS, LUDWIGSHAFEN/OPPAU, GERMANY

By W. F. Faragher[1/] and W. A. Horne[1/]

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ILLUSTRATIONS

1/ United States members of team.

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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 ($WO_3.H_2O$) 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 remo... 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 ... low earth.

III. METHOD OF PREPARATION OF CATALYST 6434

300 kg. of Terrana A extra (Deggendorf) is etched with 344 kg. of ... percent hydrofluoric acid in a stirred pan for about 15-20 minutes at o... nary temperature. 500 liters of a 10 percent solution of yellow salt ... (ammonium thiotungstate) is added slowly, and the pan is heated with ste... In 8-10 hours, the charge is dry. During a further two hours, it is coo... The cooled product is broken up in a special hammer-mill fitted with a ... 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 ... 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 lite... of water. The mass is then pressed through a 3 mm. screen. This produc... is fed to the Kilian press, where it is made into 10 mm. pellets (capaci... 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 nitro... gen 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 ferro... tungsten 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 ($Al_2(SO_4)_3 18\ H_2O$) that contains about 18 ... percent Al_2O_3 is dissolved in water at 50-70°C. to an almost saturated solu... tion (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 pre... cipitate 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 ...

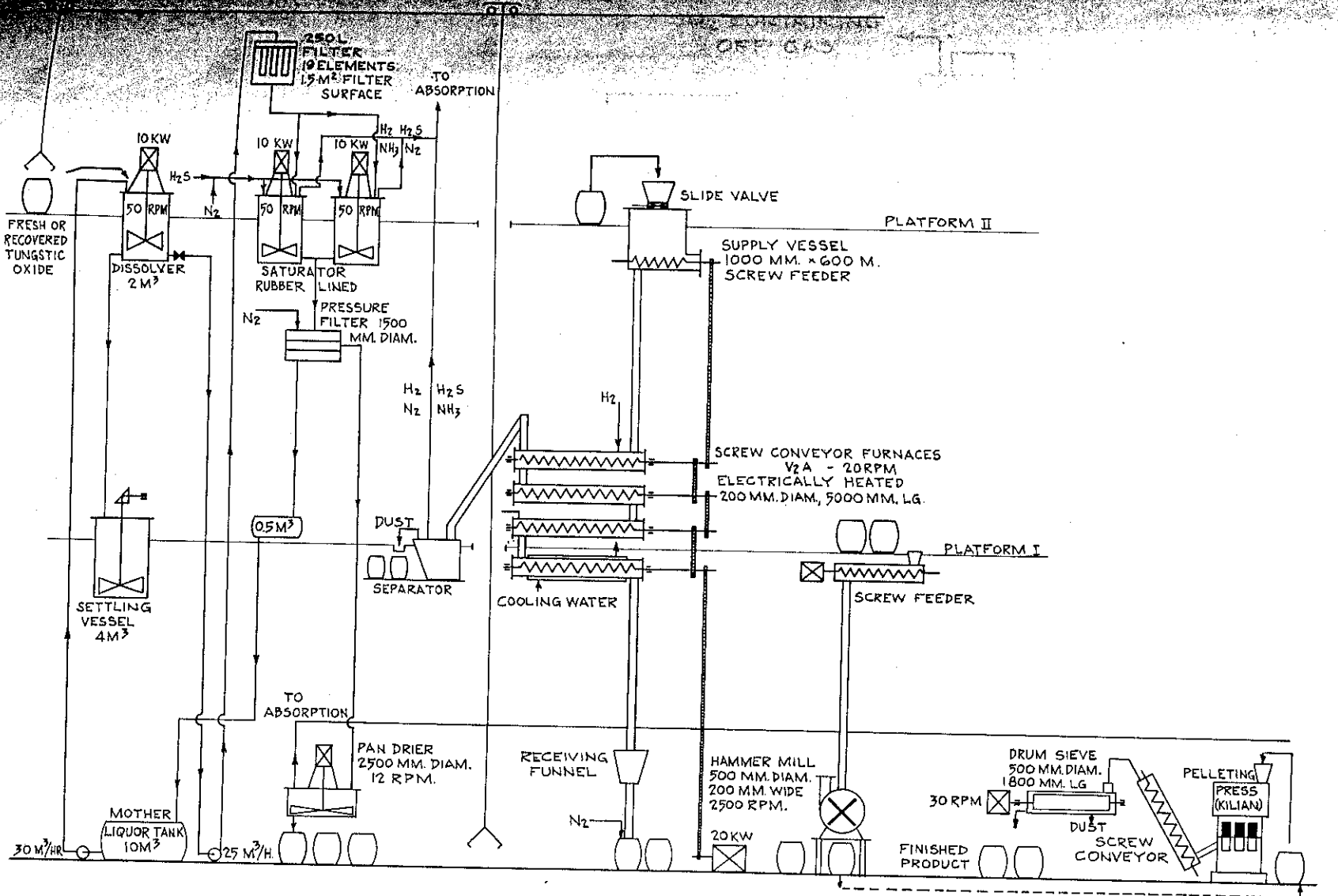

FIGURE I.- DIAGRAM OF APPARATUS ARRANGEMENT FOR THE PREPARATION OF CATALYST 5058 (1 TON/DAY).

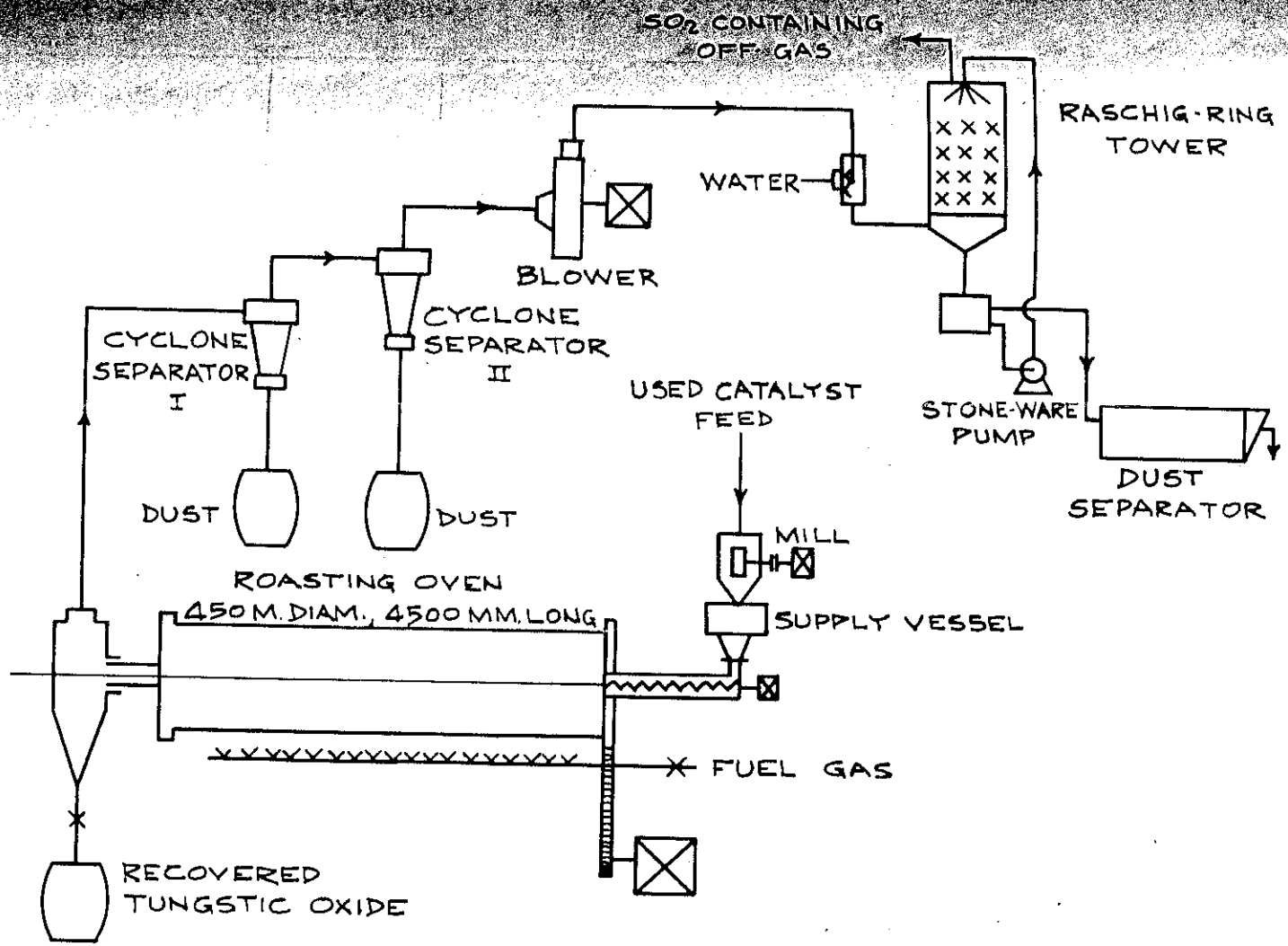

FIGURE II. DIAGRAM OF ROASTING APPARATUS FOR RECOVERY OF TUNGSTIC OXIDE FROM USED CATALYST 5058.

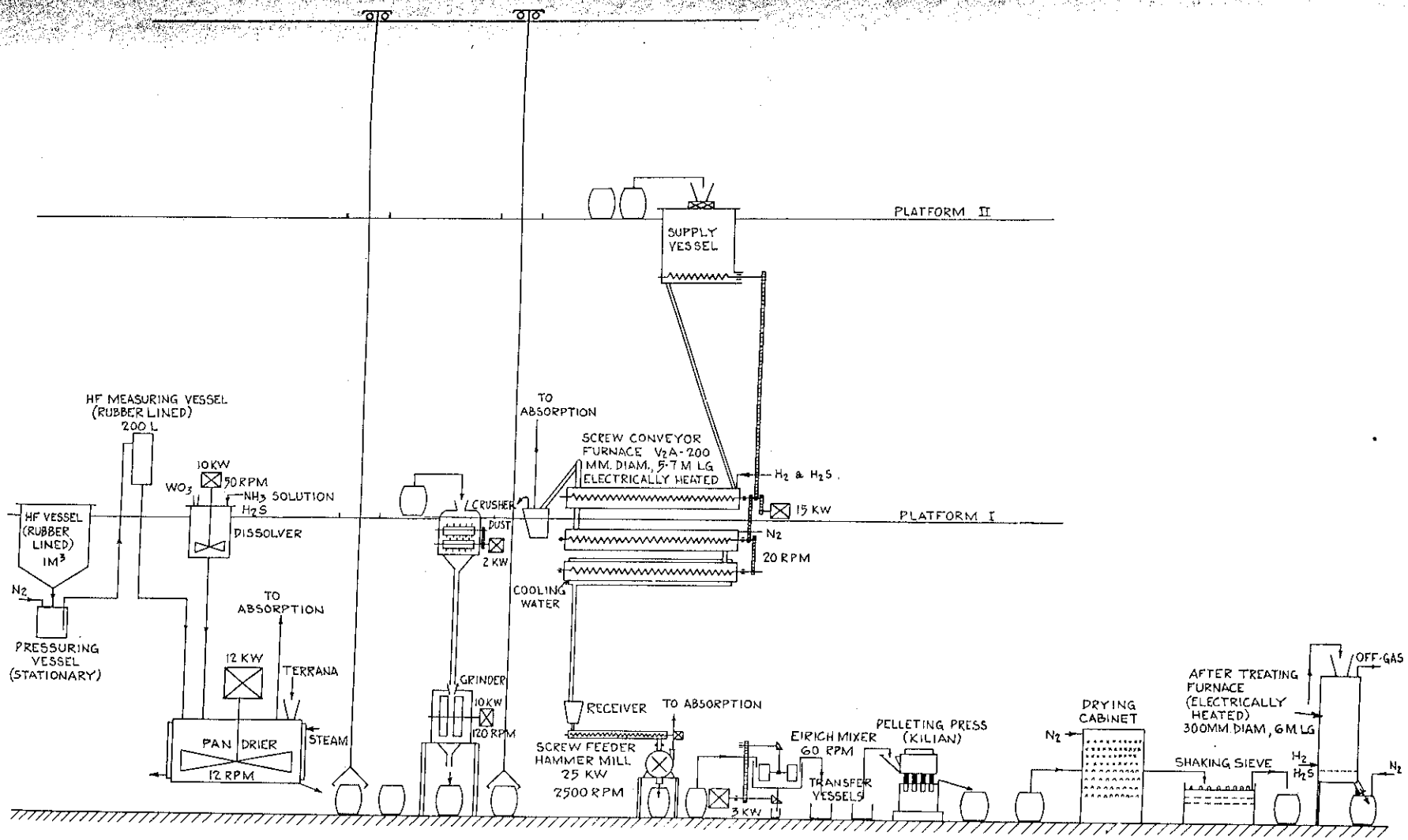

FIGURE III DIAGRAM OF APPARATUS ARRANGEMENT FOR THE PREPARATION OF CATALYST 6434 (1 TON/DAY).

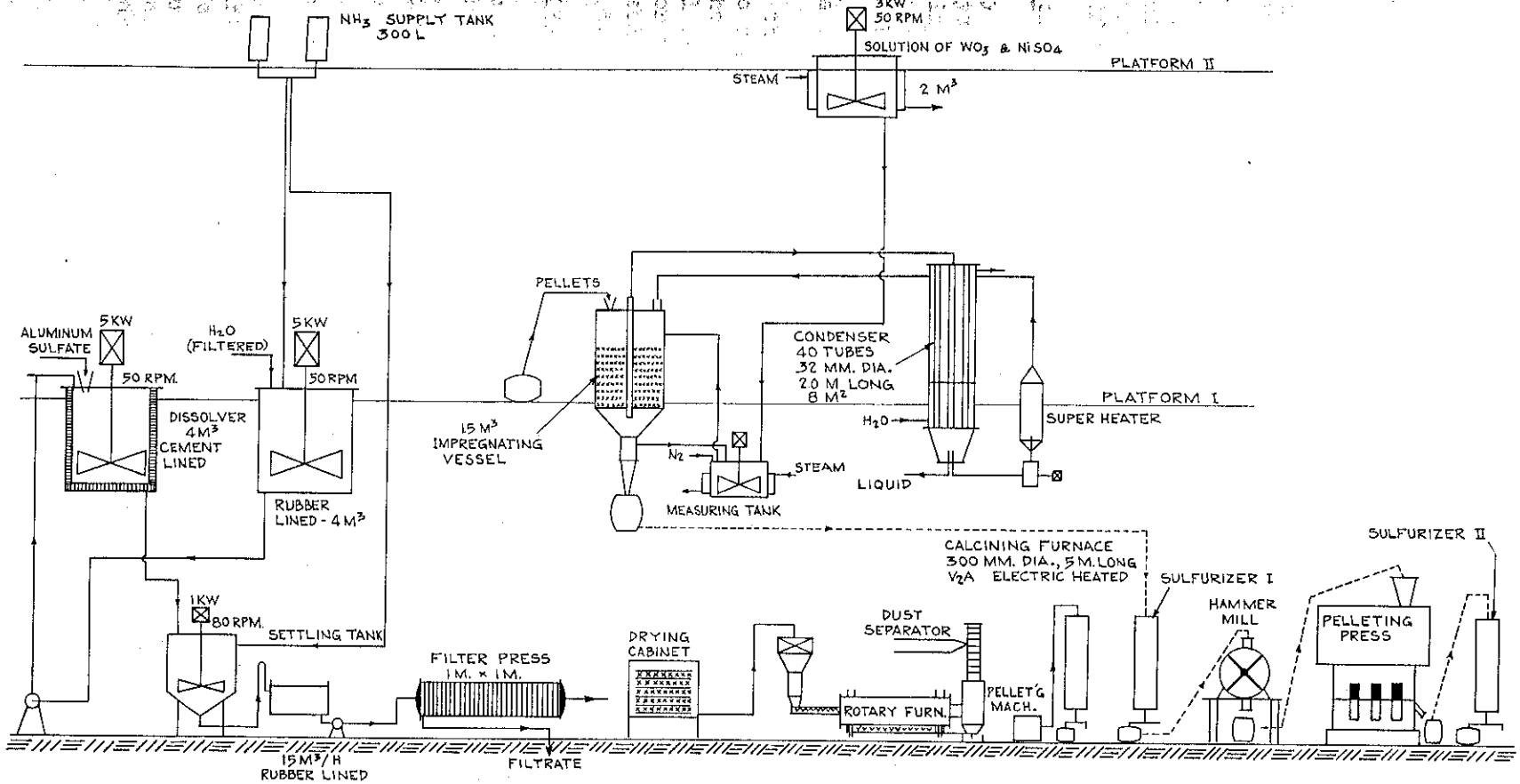

FIGURE IV. DIAGRAM OF APPARATUS ARRANGEMENT FOR THE PREPARATION OF CATALYST 837G (1 TON/DAY).

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 alumium sulfate solution can be used for the preparation of activated alumine. This recovery of tungstic acid has not been made commercially.

V. CATALYST PH 86

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 oven 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 temperatur 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, equivalant 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 wa in a stirred container to a specific gravity of 8.5° Be' (final volume 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 bl color changes to green. The precipitate is then washed by decantation (22 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 (26.3 kg.) is dissolved in a pressure vessel (1.5 cu.m.) provided with a stirrer, in 854.1. of water. The zinc nitrate (22 kg.) is added to this solution and after it has dissolved, the chromium nitrate (37.4 kg.) is added. The chromium nitrate used is the anhydrous, trice-purified grade.

The solution of mixed nitrates is added through a filter cloth to the stirred suspension of copper carbonate (5,700 L.).

In the meantime, a solution of 100 kg. of sodium bicarbonate in 1,000 l. of water is put into a stirred vessel. This solution is added to the above-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 (Schlagkreuzmuhle).

VI. PREPARATION OF METHANE-SPLITTING CATALYST

The catalyst splits methane in the presence of steam at about 700-750°C. into CO_2, CO and H_2. Its composition is approximately:-

SiO_2	20-21 percent
Al_2O_3	17-18 percent
Fe_2O_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 tabletting 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:-

$$CO + H_2O = CO_2 + H_2$$

It contains approximately:-

Fe_2O_3	86-87 percent
Cr_2O_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:-

a) Preparation of the iron oxide
b) Preparation of the chromium nitrate solution
c) The further working up of both products.

125

For the iron oxide preparation, iron sulfate ($FeSO_4$ 7 H_2O) is dis... in water to give a 20-percent solution and the solution is pumped into ... storage vessel. Sodium carbonate (10-12 percent solution) is put into ... precipitation vessel, and the iron sulfate is added with stirring at ab... 30-35°C. Quantities are adjusted to give a slight excess alkalinity at ... end of the precipitation. The iron carbonate precipitate is allowed to ... tle and is then well washed on a rotary filter with warm water (60-70 pe... cent). 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 ... red glow on leaving the furnace. It is then cooled in a screw-propelle... cooler and stored in bunkers.

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

The further working up of the catalyst consists in filling a kneadi... 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 produc... from the kneader is pressed into cakes (10-12 mm. thick) and is roasted ... plates in a tunnel kiln at 500-550°C. The dried cakes are broken in a cy... lindrical crusher. The fines (under 5 mm.) are screened out and the mate... ial 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 sul... fide is filtered, roasted and dissolved in ammonium hydroxide.