T. O. M. Reel 14
PP. 602 - 611

U. S. Bureau of Mines

Hydro. Demon. Plant Div.

T-104
Trld-KCBraun
9/20/46

# Abstract of Report on the Processing of Hydrogenation Residue at Wesseling, based on a Visit to Scholven, 3 January 1939

Leuna Werke, 20 Feb. 1939

## I. The Development of Ball Kilns

### Dr. Urban

Square shaped milling elements weighing 25 Kg. were at first used in the ball kilns. These, however, were too heavy and were replaced by hollow square elements. Later, at the suggestion of Krupp's, who were of the opinion that in low temperature carbonization the product should be dispersed on as many grinding elements as possible, light hollow balls were used. But since these were not quite satisfactory either, double-edged pieces of pipes were used, which have more recently been replaced by cross-shaped cast steel elements weighing 1.5 Kg. with 100 mm edge length. Filling a kiln requires 9-10 tons of these, or about 5000 pieces. Unfortunately, the kiln wall wears relatively rapidly, about 7 mm in 100 days. Recently, however, 2 kilns with a cast steel, instead of a forged steel, liner have been put into operation, which promise a longer life because of the related materials. Chemical and technical data on residue processing at Scholven are summarized in Appendix 1. Appendix 2 attempts to compare the individual methods of residue processing.

### Dr. Junge

At first coking and dust clogging of the kilns occurred every 3 to 5 days, though a continuous running time of 120 days was once attained. The kiln wall thickness is 35 mm. In 120 days this wall was worn down to 27 mm.

From time to time the discharge becomes very oily. It appears as if a layer of coke on the kiln wall collapses, behind which the product shoots out.

Chemically, fairly heavy demands are made on the ball kiln. The bituminous coal hot-oil-let-down has a high asphaltic oil with little solids content. Also, compared to the spiral screw kiln, the ball kiln is much more filled with dust, which absorbs more oil.

In order to destroy coke layers on the kiln walls in their formative stage, the kilns are rotated alternately fast and slow in about 5 min. intervals.

**Dr. V. Blumencron**

The question arises, shall we use ball kilns or spiral screw kilns? The concentration of asphalts in the hydrogenation of rhenish brown coal is said to be considerably greater than at Leuna. According to Dr. Krönig, 13.6% asphalt in the centrifuge mixture oil must be expected, which would correspond approximately to 21.2% asphalt in the hot-oil-let-down. It is not expected that the asphalts can be eliminated at 700 atm. It is generally believed that the ball kiln is suited to larger quantities of asphalt than the spiral screw kiln.

**Dr. Bross**

Leuna has proved that brown coal hot-oil-let-down can be processed in screw kilns. Lu has developed the ball kiln for the bituminous coal hot-oil-let-down, but even there the balls got stuck in the product at first. Bituminous coal asphalt is constituted entirely different. As shown by Scholven, the ball kiln can process bituminous coal hot-oil-let-down, even though great mechanical difficulties must be overcome. In Dr. Engel's opinion the screw kiln is not suitable for processing bituminous coal hot-oil-let-down, because it will stall in a short time, whereas the ball kiln will at least run, even though it is still far from perfect. The ball kiln has proved that it is better suited to heavier products than the screw kiln, it will, therefore, run better.

## II. Other Methods of H.O.L.D. Processing.

**Dr. Urban**

The processing of hot-oil-let-down has not yet reached a satisfactory stage. The thermo-treatment is not the right method. Scholven is not satisfied with centrifuging, either, too much solids remains in the oil and the discharge is not sufficiently concentrated. Scholven is trying to get proper results by other means, such as:

a) Changes in Centrifuging,

b) Filtration.

### a) Centrifuging:

Lu has again taken up experiments with a Heine-Centrifuge, but which is supposed to have a continuous, solid discharge. Its designation is 1250. Dr. Junge has also conducted experiments with a small Rheinveld-Centrifuge of 10 Kg. capacity. The Laval-Centrifuge residue was diluted with thinning oil and centrifuged in this experimental centrifuge, thus combining the Laval and the Heine principle. The solids in the centrifuge or pasting oil does not disturb Scholven since this is low in ash content.

The following table summarizes the values of the first as well as the second centrifuging. The summary shows that in double centrifuging about 67% of the total solids is contained in the centrifuge oil, and that the residue going to the kilns is small in quantity and low in asphalt.

With this highly concentrated solid residue the conveying problem becomes difficult. How can one get a product containing over 60% solids into the kiln? A heat exchange is out of the question at the start. Dr. Junge proposes an extrusion press. A simplex pump has been able to convey a product containing 60% solids, although without asphalt. By concentrating the solids as much as possible, the quantity going to the kilns becomes small and low in asphalt, so that few kiln units are required and the demand on them becomes less severe. It has even been considered to waste the oil rather than try to extract it by low temperature carbonization (Schwelung), since it is less than 10% of the letdown oil.

## TABLE OF CENTRIFUGE DATA

| | I. Laval Thruput | Solids % | Solids Kg. | Oil Kg. | Dilution Kg. | Total Kg. | Asphalt % | Asphalt Kg. |
|---|---|---|---|---|---|---|---|---|
| Letdown | 1000 | 30 | 300 | 700 | -- | -- | 18 | 126 |
| Mixture | 1660 | 18 | 300 | 700 | 660 | 1360 | 9.3 | 126 |
| Residue I | 430 | 35 | 150 | 280 | -- | -- | 9.3 | 26 |
| Centrifuge Oil | 1230 | 12.2 | 150 | 420 | 660 | 1080 | 9.3 | 100 |
| | | | 570 | | | | | |

50% of the total solids are contained in the centrifuge oil.
26.3% insolubles are contained in the letdown centrifuge oil.

| | II. Heine Thruput | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| Residue I | 430 | 35 | 150 | 280 | -- | -- | 9.3 | 26 |
| Mixture | 250 | 20 | 150 | 280 | 320 | 600 | 4.4 | 26 |
| Residue II | 167 | 68 | 100 | 67 | -- | -- | 4.4 | 3 |
| Centrifuge Oil | 583 | 8.6 | 50 | 213 | 320 | 533 | 4.4 | 23 |
| | | | 263 | | | | | |

33.3% of the delivered solids are contained in the centrifuge oil
19.0% insolubles are contained in the letdown centrifuge oil.
In double centrifuging, 200 Kg. of the 300 Kg. solids have been proved to be in the centrifuge oil = 67%
The proportion of asphalt to solids changes as follows:

In the letdown, 1 Kg. asphalt to 2.3 Kg. solids = 43%
In residue I, 1 Kg. asphalt to 5.8 Kg. solids = 18%
In residue II, 1 Kg. asphalt to 33.3 Kg. solids = 3%

## b) Filtering at high temperature:

Scholven proposes to filter centrifuge residues at high temperatures. At temperatures of 200-300° C. twill filter cloths or ceramic substances can no longer be used, compressed braided metal fabrics must be used. We are getting samples of this metal cloth. At these high temperatures the evaporation of the oil must be taken into consideration. Because of this evaporation of the oils at these high temperatures, vacuum can no longer be used, but pressure must be used. When using a vacuum of 50 mm Hg the thruput is 300 $Kg/m^2/h$. The filtrate contains 10% insolubles, low in ash. At times, the production of the filters drops greatly, without any apparent reason. Middle oil, with an anilin point of 22°, is used as thinning oil. A revolving filter by Schüchtermann & Krämer, with 1 $m^2$ filter surface, is used as experimental filter. Our object is to obtain a highly concentrated filter cake containing over 60% solids for which low temperature carbonization would be unnecessary.

## III. Pressure Distillation

Pressure distillation was also discussed. Dr. Urban mentions experiments in which centrifuge residue, preheated to 18 mv before it reaches the screw kiln, is distilled together with superheated steam. With a super-heated steam addition of 100 Kg/ton of residue the concentration could be increased from 35 to 41%. The quantity of asphalt was increased thereby. It is probable that by the action of the $O_2$ content of the steam asphalt was formed from the remaining oil.

## IV. Filtration of Middle Oil

We were also shown the filtration of middle oil by means of columns (Kerzen). The columns consisted of a ceramic substance wound with felt. They are about 300 mm in dia. and 800 mm long. The load on them is 14 T/h and they must be replaced every 2 to 4 days, because their resistance is then increased by pollutions of tary residues and arsenic-sulfide. According to Dr. Urban, it is possible to keep the K-value of the heat exchangers at a uniform height.

## Appendix I

## Chemical and Technical Data of Residue Processing

1) **Stall letdown:** 30% solids (benzol insolubles)
30% ash in solids
70% oil
18% asphalt in oil

is diluted with about 60% catch pot heavy oil to about 18-20% solids.

2) **Centrifuges:** (Laval) at 2.3-2.4 T/h each hour and 160° C.

| | a) Centrifuge oil about 75% | b) Centrifuge residue oil about 25% of mixture |
|---|---|---|
| Solids | 12.5% | 35% |
| Ash in solids | 27.5% | 46% |
| Asphalt in oil | 11.0% | 11% |

3) **Kilns:**

Technical Data: 2.20 m dia. x 11 m long. Heating surface-abt. 75 m². Vol.-68 m³. Filling elements-abt. 5000 pieces - 9-10 tons filling with cross elements. R.P.M. = 9.5/19 temperature-abt. 28.5-30 mv.

Loading: 2.5 tons centrifuge residue/h, heated to 18 mv plus 30 Kg. steam, 0.2 tons additional rinsing steam.
Fuel gas for kiln drum-160 m³/h @ 5000 WE
" " " product heating-60 m³/h @ 5000 WE
(WE = heat unit). Drive motor abt. 100 KW.

Efficiency: Oil yield abt. 70-75% of asphalt containing oil.
Kiln residue abt. 28-33% ash.
3-4% asphalt

Coking: Seldom

Wear: At present 2 mm per month with the hard, sharp-edged elements.

## Appendix II

### Comparative Data on Kiln Drums

| | Screw Kiln<br>Lu | Ball Kiln<br>Lu | Ball Kiln<br>Scholven | Screw Kiln<br>Me |
|---|---|---|---|---|
| Diameter | 1m | 1.5 m | 2.20m | 0.9 |
| Length | 16m | 8m | 11m | 2 x 16m |
| Heating Surface | 50 $m^2$ | 38$m^2$ | 75$m^2$ | 90$m^2$ |
| Kiln volume | 12 $m^3$ | 14$m^3$ | 68$m^3$ | 20$m^3$ |
| RPM | 1 | 14/26 | 9.5/19 | 1 |
| Filling | Strip Screw with rods | 5 tons balls & edged elements | 9-10 tons cross element | Strip screw with heavy bars. |
| **Loadings:** | | | | |
| **Centrifuge residue, Kg/h** | 500-600 | 600-800 | 2500 | 2700 |
| Kg. solids | 200-240 (40%) | 240-320 (40%) | 870 (35%) | 1100 (40%) |
| Kg. oil | 300-360 | 360-480 | 1630 | 1600 |
| Kg. asphalt | 39-47 | 47-63 | 180 | 130 |
| **Steam, Kg/h/$m^2$ heatg. surface** | 300 | 350 | 230 | 1200 |
| Kg. solids | 4-5 Kg/h | 7-9 Kg/h | 11.5 Kg/h | 12.2 Kg/h |
| Kg. oil | 6-7 " | 9-12 Kg/h | 21.5 " | 17.8 " |
| Kg. asphalt | 0.8-0.9 Kg/h | 1.2-1.6 Kg/h | 2.4 " | 1.45 " |
| **Running times** | 3-4 weeks | Over 4 weeks without interruption | 2-4 months | 100 days |
| | Wear of screw | | Wear of wall | |
| Oil Yields | 83-87% | To 85% | 70-75% | 76-82% |

T.O.M. Reel 14
PP. 615-637

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T-105
Trld/KCBraun/jw
9/24/46

# Abstract of Reports on Operating Experiences with Ball Kilns Leuna Werke, 5 Nov. 1943

## Condensation Ball Kiln

Basis for design:

| | |
|---|---|
| Injection, 4.5 T/h with 60% oil | |
| Oil in injection, | 2.7 T/h |
| Oil yield - 80%, | 2.2 " |
| Precooler oil, | 2.0 " |
| Aftercooler oil, | 0.2 " |
| Oil inlet temp. | 370° C. |
| Oil outlet temp. | 130° C. |

## Experiences with Ball kilns

Drums:

Material in Gelsenberg TH 31 R (Strength 55-65 Kg/mm$^2$, C = 0.25, Mn = 0.6 - 0.7, Cu = 0.8, Mo = 0.2, Ni = 0.6) partly Izett 4 (standard boiler plate killed by aluminum, age-resistant) otherwise M4.

Lining of the drums is absolutely necessary. Lining consists of 2 layers of SH yellow or black, 2 layers Guronit (28% Cr) in beads 230 x 40 x 15 mm longitudinally staggered 35 mm apart. The lining extends 3 m from the separating wall. An additional lining on the drum inlet has been found necessary in certain cases. Gelsenberg also lines the separating wall with individual beads around the outlet openings. Scholven applies circumferential strips of 150 x 15 mm cross-section, adjoining each other, 1/2 m from the separating wall, in front of it the usual lining, recently with only one layer SH-black and one layer Guronit. The life of a lining is about 6000-7000 hours. After that a repair period of 6 weeks with shift operation is required.

The dividing wall is provided with outlet openings of various sizes. In Gelsenberg especially large, oblong outlet openings on the periphery have proved very satisfactory.

The filling of the drum is done at Wesseling and Scholven with filling elements proposed by Krupp, cast plates, Brinell hardness 420, 95 x 95 mm$^2$, with diagonal ribs on both sides running in opposite directions from each other. Gelsenberg uses milling elements consisting of triangular bars with spherical ends. Wesseling also uses 12-15 milling elements in the discharge chamber, consisting of 150 mm dia. boiler tubes pressed together at the ends at right angles to each other.

Drum Drive:

The pole reversal of the drive motors at Gelsenberg and Scholven has been put out of commission, because this running method, at 19 R.P.M., produced excessive dust and wear. Both works recommend a high speed squirrel cage motor drive for new installations. A Cyclo-Drive with flanged-on motor (3 RPM) is used as emergency drive. The Cyclo-Drive is also provided with a hand starter.

Discharge Device:

The discharge screw should be more rigid than those furnished by Krupp. The discharge chute should be vertical, where possible, and widened at the bottom. The chutes should be so designed that they could be poked in any direction. The scraper trough should contain more water.

Disposal of the Residue:

Wesseling supplies 8-10 $m^3/h$ water to each discharge tank. The scraper trough is provided with grating having 10 mm openings, through which all fine particles are carried away with the flushing water. Additional water flushes the scrapers and drop pipes. All the water is pumped to a gravel filter by a sludge pump, from which the clear water runs into the river. The sludge is loaded into cars by crab buckets.

In Gelsenberg the residue is conveyed by belts, which is an untenable condition in the long run, because the very fluid residue and the occasional large lumps do not stay on the belt. The tank is supplied with 2 $m^3/h$ water, and the overflow runs with a part of the dust into a scraper tank serving 3 kilns, where it runs over several weirs, is clarified and eventually discharged into the river.

Scholven conveys all of the residue by means of a cut-flight screw, 500 mm dia. The residue passes through a Rheinveld Centrifuge and a drier and dried to 8% water content. It is then burned in boiler house. Scholven also disposes of part of its residue, partly carbonized, as briquetting pitch.

Cranes:

All three plants agree that a crane is essential. The crane should be so arranged that the drums can be lifted at designated points by hand hoists. The trolleys should have a capacity of 6 tons.

Condensation:

The washer head at the gas outlet of the kiln is partly shut off at Wesseling, but is to be reopened. Scholven substitutes a diagonally downward leading tube for it. Apparently, however, this arrangement does not avoid clogging.

In all 3 plants, the precoolers and aftercoolers are directly cooled with precooler oil and phenol water. One aftercooler serves a group of kilns. Scholven has only one aftercooler. The precooler is cooled by a common circulating system. The circulating oil in Wesseling is cooled by a 60m³ unit cooler, in the other plants by simple coil coolers. The circulating water drawn from the sump of the aftercooler column is cooled by an Imperial Spiral Cooler. Only the excess oil-water mixture is run into the separating flask.

Drum Heating:

For heating the drums, Vistra-Burners have proved to be the best. In all 3 plants, 12 Vistra-Burners are used on each drum jacket. The gas supply is partly only under gasometer pressure. A combustion air blower is provided for each kiln.

Preheating:

In all 3 plants the kilns are provided with product preheaters consisting of horizontal finned hairpin tubes 60 mm dia. Wesseling has disconnected the product preheater because in sudden shut-downs the tubes were often clogged. Gelsenberg, as well as Scholven, also complains of the difficulty of heating the long preheater tubes with the 12 additional burners uniformly. Local overheating can hardly be avoided.

In Scholven the newest kilns are provided with product preheaters consisting of vertical finned hairpin tubes. The 12 individual burners have been replaced by a single, large Vistra-burner, which arrangement has proved very satisfactory.

Steam Superheater:

The Sicromal tubes of the steam superheater have in Wesseling been replaced by a coil of 50 mm dia. boiler tube, which has given no cause for complaint up to this time.

Temperatures:

The lowest possible drum wall temperature is recommended for the longest life of the kiln and particularly its lining. The drum and dividing-wall temperatures have been set at a maximum of 29-31 mv (544-576° C), using the lower limit wherever possible. The thermo-elements on the drums are housed in a high-pressure tube welded lengthwise to the drum. The current is taken off by 5 slip rings, with which 4 elements in succession may be tapped. For tapping the other 4 elements, a hand operated switch, revolving on the outer drum wall, is provided. No trouble has been reported with these switches.

Program: Kugelofen Me 884
Leuna Werke, 3 March 1943.

## Processing Filter Residue from Desanding

### Reason

Me 884 produces monthly about 2000 tons desanding residue with about 25-30% heavy oil. This heavy oil goes to the dump with the sand. About 80% of this heavy oil can be recovered by carbonization. For this purpose, a kiln with the necessary conveying equipment is necessary.

### Description of Operation (See SK-1 for flow-sheet)

The sludge from the coal stalls contains about 2% sand. This sand must be separated, because it would clog the centrifuge nozzles and prematurely wear out the centrifuges. The sand is separated by thinning with converter letdown in letdown vessels (A), in which the sand is separated at the bottom, is taken away with an oil content of 30-35% by the screw (Aa), and freed of part of the oil by the revolving filter (Ab). The filter cake, containing about 25-30% oil, drops onto the horizontal screw (Ac) and is taken to the ball kiln (B) by the inclined conveyor (Ad). The ball kiln consists of an inclined revolving tube filled with impact elements of special form. The impact elements are intended to prevent the formation of a coking crust on the kiln walls and thus prevent clogging of the kiln. The product is advanced by the incline of the kiln and is then discharged over a screen retaining the impact elements.

The carbonization of the product is aided by superheated steam. The steam is superheated in the pipe coil (Ba), enters the kiln on the discharge end (Bb), passes over the feed in counter current, and leaves the kiln through the stub (Bc).

Heating the kiln and superheater is done by the pressure burners (Bd) supplied with fuel gas and compressed air by the blowers (Be) and (Bf) respectively.

The carbonized product drops through the water-trapped discharge chute (Bg) into the discharge tank (Bh) filled with water, from where it is removed by the scraper (Bi) onto the belt conveyor (Bk).

The kiln gases discharged with the steam at (Bc) first pass through the dust separator (Ca) in which a small amount of heavy oil is separated, as well as most of the dust. Dust and oil are collected in the trapped tank (Cb). The uncondensed gases and vapors leave the dust separator at (Cc) and enter the vertical precooler at (Ce). The precooler is filled with Raschig-rings and is cooled at the top by the spiral coils (Cf). The condensed heavy oil flows at (Cg) into the trap (Ch), in which the oil from the tank (Cb) is also collected.

The temperature of the gases and vapors leaving at the top of the precooler is so regulated that no water is condensed in the precooler, that is, about 130-140° C.

The gases and vapors leaving the precooler at (Ci) now pass through the aftercooler (Ck), a watercooled tube cooler, and the residual gas-pot (Cl), where the oil and water are separated from the uncondensed gases, which leave at the top and may be discharged into the atmosphere or burned under the kiln.

Oil and water are separated in the separating flask (Cm).

Program: Kugelofen Me 883.
Leuna Werke, 23 Feb. 1943

## Sludge Carbonization in Ball Kiln.

Description of Operation (See flow sheet Sk-2)

The ball kilns, as well as the screw kilns, are intended for the carbonization of the coal stall sludge and the residue from the carbonization centrifuges, produced in Me 884.

The plant consists essentially of 3 main parts:

A - the kiln.
B - the discharge equipment for the carbonized residue.
C - the condensation for the oil and water vapors produced.

The raw product, converter letdown and/or centrifuge residue, enters the kiln plant at (Aa) under a pressure of 6 atm. after passing through an Eckardt meter and a heat exchanger, then flows first through the preheater coil (Ab) and is then released into the kiln proper at (Ac) by dispersion with high-pressure steam at 15 atm. This kiln consists of an inclined revolving tube, filled with special shaped impact elements.

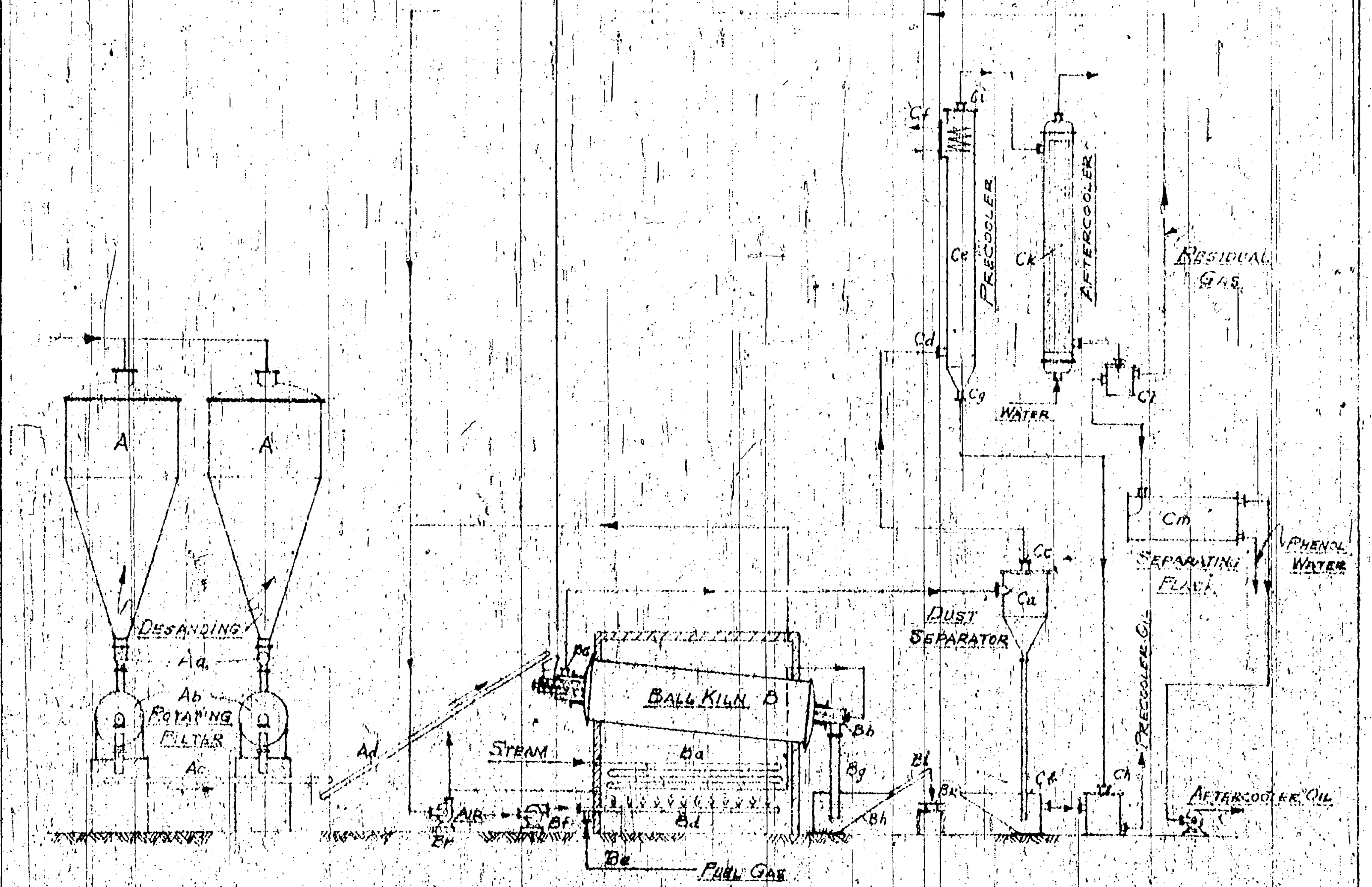
(The process to the dust separator (Ca) is identical with that described in the preceding chapter on Sludge Carbonization).

Steam and carbonization gases rise in the central tube (Cc) of the dust separator and the heat exchanger (Cd) surrounding it, until they can flow over the distributing cup (Ce) to the bottom, giving up their heat content to the raw product flowing in the pipe coil (Cf).

The condensed heavy oil flows off at (Cg) while the uncondensed vapors and gases leave the heat exchanger and enter the precooler at (Ck). The precooler is filled with Raschig-rings and is cooled at the top by helical coils. The condensed heavy oil flows off at (Cm) into the trap (Cn). The heavy oils collected in the dust separator tank, the heat exchanger, and the precooler head, run through a common pipe line (Co) to a storage vessel.

The temperature of the vapors and gases leaving the top of the precooler is held to 130-140° C., so that no water can condense there.

(The process to the aftercooler and separating flask is identical with that described in the preceding chapter on Sludge Carbonization).

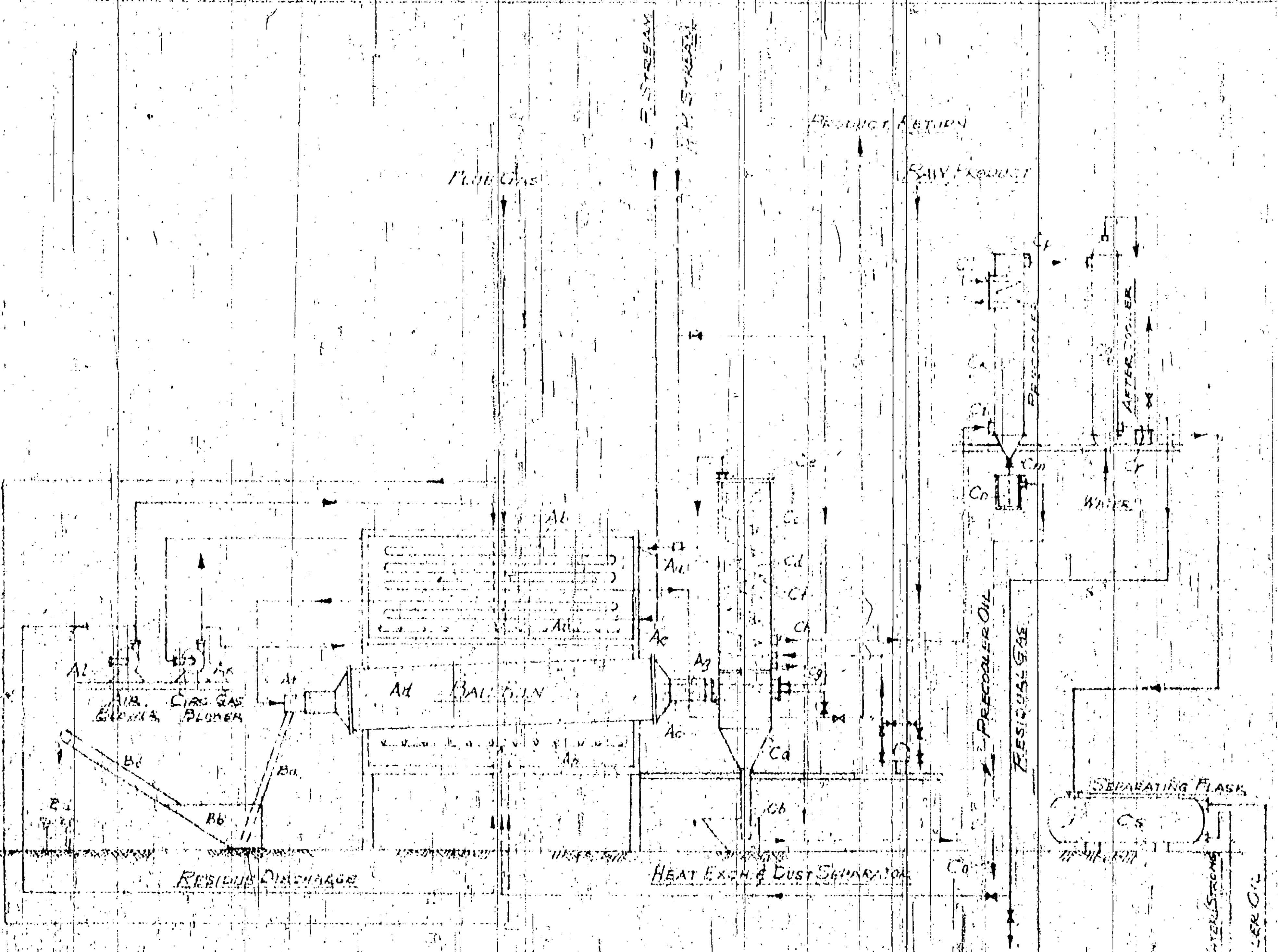


FLOW SHEET OF PROCESSING FILTER RESIDUE FROM DE-SANDING

Sk-1

T-105

T-105



FLOW SHEET OF SLUDGE CARBONIZATION IN BALL KILN

SK-2

T.O.M. Reel 163
Frames 264-265

U. S. Bureau of Mines
Hydro. Demon. Plant Div.

T-106

10-22-1942

# Phenols.

(A brief note by Hirschberger)

The demand for phenol has greatly increased since the development of synthethics. The only source for their production is coal. The amounts one may obtain depend greatly on the temperature at which the coal had been treated. The phenol content of low temperature carbonization tars is higher than from high temperature coke ovens and the temperatures used in hydrogenation have been found to be particularly advantageous. The yields, referred to coal, are about 40 times as high with pressure hydrogenation as from coke ovens.

Calculated to the coal used, 4 - 5% useful phenols is obtained during coal hydrogenation and they consist of about 20% phenol, 35% cresols and 45% xylenols. The proportion is similar with brown coal, but the recovery of the pure materials is made more difficult by the presence of other oxygenated substances.

The most common method of phenol production from oils and the off-waters is the extraction with sodium hydroxide, followed by setting the phenols free with carbon dioxide; further to mention is the phenosolvan process (extraction with water and distillation) the tricresyl phosphate process, the Fresol process (with methyl alcohol), and finally the method of extraction with superheated steam.

Leuna alone of the hydrogenation works recovers phenols on an industrial scale, using the last mentioned method. The other works merely de-phenolate water because of sanitary requirements.

There are no accurate results available on the effect of the removal of phenol on the quality of the gasoline obtained but in general only a slight reduction in the octane number (1/2 to 1 O.N.) may be counted upon.

| Material | Brown coal | Brown coal tar | Coal Gelsenk. | Coal | A-middle oil, Leuna |
|---|---|---|---|---|---|
| α phenols from gasol. + middle oil | 3.96 | 7.10 | 6.82 | 8.20 | 7.0, 4.25, 5.0 |
| Phenol | 1.31 | 0.77 | 1.37 | 2.60 | 1.-1.5, 4-4.5 |
| o-cresol | 0.70 | 0.80 | 1.05 | 0.78 | 3-4 |
| p & m-cresol | 1.50 | 2.06 | 2.43 | 2.67 | |
| xylenols | 0.45 | 3.47 | 1.97 | 3.15 | 1-0.5 |

Note: The above table was written in pencil and is very difficult to read. (Sternberg)

T.O.M. Reel 163
Frames 266-267

U. S. Bureau of Mines
Hydro. Demon. Plant Div.

T-107

## Production of Useful phenols During Hydrogenation of Various Materials

10-15-1942

| Material | Brown Coal Tar, Brüx | Hot soft coal low temperat. coking tar | Topped soft coal coking tar, Pölitz | Brown Coal Leinitz | Soft Coal Heinitz Colliery | | Gelsenberg |
|---|---|---|---|---|---|---|---|
| K or F numbers | 1397 | 1376 | | 148 | 1197 | | 1090 |
| Method | Gasol.+M.O. | S'oil +) | S'oil +) | Gas+M.O. | Gasol+M.O. | S'oil +) | Gas + M.O. |
| Pressure | 600 | 600 | 600 | 250 | 600 | 600 | 600 |
| %Phenols in total oil | 7.10 | 4.23 | 4.24 | 3.96 | 8.20 | 6.63 | 6.82 |
| Carbolic acid in Gasol. + M.O. | 0.77 | 2.19 | 1.74 | 1.31 | 2.60 | 3.64 | 1.37 |
| O-cresol in Gasol.+M.O. | 0.80 | 0.39 | 0.53 | 0.70 | 0.78 | 0.95 | 1.05 |
| P and M Cresol in Gasol. + M. O. | 2.06 | 2.83 | 1.34 | 1.50 | 2.67 | 3.83 | 2.43 |
| Xylenols in Gasol.+M.O. | 3.47 | 2.43 | 1.72 | 0.45? | 2.15 | 3.63 | 1.97 |
| Total, % | 7.10 | 7.84 | 6.33 | 3.96 | 8.20 | 12.05 | 6.82 |
| % Phenols from raw material | 5.95 | 3.43 | 3.18 | 2.62 | 4.92 | 4.44 | 4.43 |

X S'oil - Sump Phase Oil

The table was obtained by Podbielniak analysis and shows the amounts of useful phenols referred to the oil yield as well as to the gasoline and middle oil contents of the oil referred to the oil and the raw material. Computations were based on the very probable assumption that kiln oil contained no lower phenols. Around 1% phenols are dissolved in the off-water, which probably consist for the most part of carbolic acid.

The table shows, that soft coal yields much phenol. The largest concentration of phenol in low boiling oils is obtained in the process for excess of heavy oil, i.e. the conversion of the first obtained heavy oil into gasoline and middle oil produces lower-phenol oils - 325° 4 than the hydrogenation of coal. Gelsenberg coal produces somewhat less phenols, and apparently less carbolic acid than the oxygen-richer Silesian coal.

The low temperature coking tar produces somewhat more phenols than the coke oven tar, but the difference does not seem to be as great as one could expect from the oxygen content. The brown coal tar may be directly compared with it although it was obtained in the un-topped state and since the initial b.p. was at 250° C, its lower-phenol content could not be high. Brown coal produces most phenols, in particular of the higher homologues.

The values for brown coal were obtained from older experiments in 1935 and require verification. No figures are as yet available for the Rhine brown coal.

The Silesian process permits the recovery only of carbolic acid and the cresols.

Signed Hupfer.

Trld. - W. M. Sternberg

T.O.M. Reel 130
Ref. N.
PP 208-228

U. S. BUREAU OF MINES
HYDRO. DEMON. PLANT DIV.

T-109

# OVERCOMING DIFFICULTIES WITH CAVIAR FORMATION. DESANDING OF CONVERTER I. LEUNA, 1941

## Introduction

The life of a coal stall is in most cases limited by the grinding action of the solid components of the coal. The co-called caviar produced the greatest amount of difficulties for us. Its elimination was accomplished by the removal of the coarsest particle from the first converter, the so-called converter I desanding, which shall be discussed below.

To measure the progress brought about by this method, I shall present a few pictures taken before the introduction of this process.

Perforated thermocouple protecting tubes and catalyst tubes almost ground through have been seen in almost every dismantling of the stalls. Even the strong $V_2A$ could not lastingly withstand the caviar grains kept in motion by the stream of gas, and was perforated. When a stall was shut down, the same picture was always observed. Converter I was almost 2/3 full of caviar, which lay loose in part, and was in part embedded in coked layers. 10 te of residue recovered from converter I was no exception. It frequently had to be removed by mining methods, with pneumatic hammers, after days of hard work, before returning the converter to the shop for repairs. What still remained of the thermocouple tubes and cold gas pipes, mostly hung as a coil from the cover. How to eliminate caviar was unknown, and efforts were made chiefly to protect the equipment (pressure resistant thermocouple leads; their shortening; widening of the H.O.L.D. pipe line, more gradual curvatures, elimination of $V_2A$ jackets).

A. Dr. Krönig's observation on small scale equipment in Ludwigshafen has permitted the relatively simple method for overcoming caviar. Dr. Krönig hydrogenated mid-German brown coal in a 10 li. converter. Coarse particles of ash accumulated during operations and interfered with stirring by mechanical stirrers. Testing this accumulation of ash showed the presence of structures similar to the caviar in Leuna, only much smaller in size. After 10% converter sludge, referred to coal, has been withdrawn, the converter became free and stirring could be resumed.

B. 1). It was necessary to repeat this test on an industrial scale in Leuna. After some initial difficulties we succeeded in keeping up production in the converters I of two stalls during the whole operating period (315 and 304 days).

A 3 - converter stall has now an operating period of 253 days. The desanding of all the other coal stalls is at present on the order of the day, and it may be expected that in the future the shut-down for desanding of converter I will coincide with that of the stall. Dismantling of the two stalls showed that no caviar was formed in converter I. The thermocouple tubes and the cold gas tubes were in good shape.

2). One sketch, sheet 2, illustrates the arrangement for desanding in converter I, and a second sketch 1799, sheet 3 shows the pipe line of the HOLD from the converter to the pressure release.

The desanding of converter I amounts to about 300-600 li/h, while the usual HOLD is 6000-7000 li/h. After releasing the pressure from 200 to 0 atm. the two streams are combined in the same conical vessel (Spitzgefäss) and pumped for operations on residues. The amounts are regulated behind two temperature measuring posts in the desanding pipe line (10a and 10b). Because of the small amount, the pressure release is not continuous, and the pressure release valve is opened slightly every 2-5 minutes. This method of operations has resulted in Dr. Weiss's developing an automatic pressure release which operates on the above principle. The times of opening may be set on the unit, and a brief opening followed by immediate closing is produced. The pressure release valve is equipped with the usual nozzle and ball of walramite (tungsten carbide). The valve is opened and closed over a membrane, actuated with compressed air. The life of the nozzle is somewhat shorter than in ordinary use. (Desanding by hand 250-800 hrs, diam. about 400 mm. Automatic desanding, life 70-200 hrs d. abt. 130 mm, HOLD, 300-1100 hrs, d. about 2500 mm.

The HOLD valves have had a much shorter life in the past because of the action of the coarse sand, and we get here an added advantage. The grating noise plainly heard and caused by the crushing of the sand particles when the pressure is released is a good indication of the demands made now on the valve. 2 injection tubes with a throttling on the second one are arranged behind the pressure release valves, exactly as in normal operations. However, the automatic pressure release of the desanding in its present form still has some defects, and efforts are continued on its improvement.

Sketch 1799 shows an oil pressure valve placed behind the converter at the beginning of the desanding line of a length of about 80 m. The purpose of it was to permit a quick shutting down at the first indication of leaks (grinding thru, etc). It is operated from the service walk. Originally it was placed still closer to the stall, but had been moved because of the heat radiated from the converter, in spite of the asbestos shield. The hot glycol nevertheless made the hot leather sleeve completely soft and the pressure on glycol was released in a few seconds. The products of the desanding from converter I were originally sent to special pressure-relief vessels for purpose of measurement as well as for some other reasons, and from there one part of it was sent thru a special pipe line for the working of the residue, the rest with the normal HOLD. This introduced difficulties because of the absence of special pumps, except in a few experiments. The handling of the desanding had to be done by means of the normal equipment. Moreover, the wear of these pumps was extraordinarily high because of the high sand-contents. With the present arrangement of exhausting in a common container, all these difficulties are overcome, and a dependable method of operation has been worked out. Samples are taken every two weeks by connecting with the desludging pit. The changing over is done when, i.e., an elbow in the conical vessel becomes perforated, or when the reserve nozzle becomes defective. In case of necessity, the desanding can also be by-passed. It is merely necessary in this case to rinse the desanding with the so-called flushing oil (which usually is the pasting oil of the coal, or the injection feed of the tar phase stall). Starting with the exhaust end, i.e. at the outer end of the pipe line, flushing oil is added, to keep the desanding of converter I mobile. Difficulties were also originally experienced in changing over to hydrogenation gas and idling. It happened as follows: after changing over to pasting oil the temperatures dropped. As a result of cooling, tablets of lime were deposited in converter I and plugged up the desander outlet from the converter. At present the converter temperature is not permitted to drop so low. This was also desirable to hasten the return to normal operations. As soon as the order is received to resume operations, paste is injected into the stall. The desanding however is only resumed 4-6 hrs after full injection has been resumed, to flush out of the converter any shale and similar coarse material.

3. Screen analyses of the converter I desanding and of the normal HOLD were made to determine the proportion of corase and fine sludge. Curve A shows the percent distribution and B the actual amounts involved. The desanding from converter I is seen to carry more coarse material.

The desanding product can be readily kilned, because the proportion of asphalt to solids is very favorable. 14 kg asphalt are withdrawn in 100 kg desanding material from converter I, while the same amount of HOLD will contain 25 kg asphalt. The ash content of the solids of converter I-desanding is 88% on the average, against 96% in the HOLD residue, which proves that in addition to an accumulation of solids some rather fully broken down coal had deposited. The determination of ash furnishes the best proof of perfect operations of desanding. When converter I becomes filled with coke, sedimentation is no longer good, and the ash content of the sand becomes lower. In addition, a larger amount of gas is produced, which leads to a wear of the piping behind the desanding.

C. A comparison with laboratory tests has lead to the assumption, that the arrangement of the Leuna equipment is not as effective as in the small installation. Experiments have therefore been run for the development of better desanding.

Sketch 1734 shows the results of these experiments. A series of experiments from 1938 on have proven that the inclined plane produced better sedimentation. However, the dead corners of the inclined planes were feared as potential sources of trouble, and corresponding tests confirmed these suspicions. Inclined planes built into the converter disturbed the regular coarse of operations. Spots were formed where the stirring was insufficient, which caused coking. No further experiments have been run after these failures.

We may consider a flow thru the converter which is directed upward from the center, partially reversed on top and proceeds downward along the converter walls. Some of the sand formed by the reaction with coal settles and becomes collected in a funnel. The proportion of not reacted coal is rather small in the converter I desanding. Interference with this flow increases the amount of unreacted coal and ash determinations will directly prove the imperfect operations of the desanding, as mentioned above.

D. We do not consider any further improvements urgent for the following reasons:

1). The formation of caviar is avoided, as has been satisfactorily proven by results so far obtained. Converter I can be perfectly freed from sludge, with no residue (except lime). Destruction of the catalyst tube, funnel, cold gas and thermocouple tubes has been stopped.

2). The better sedimentation in a small scale unit may be explained by there being a single converter instead of the four on an industrial scale, so that the sediment formed in the converters II - IV becomes part of the desanded material.

On the other hand, the large particle which have reached the ascending piping in converter I of a large unit can no longer return to the desanding. They are carried thru converters II - IV because of the higher gas velocities and the introduction of cold make-up gas into the HOLD.

3). The small scale unit improvement of gasoline and middle oil and the lowering of the converter temperature (with a resulting lower gasification) is not observed on a large scale, because:

With the single converter in the small unit a larger accumulation of ash will mean a greater reduction in reaction space than in the large units, where according to experience caviar collected only in converter I. Some caviar does reach the other converters, but is carried over into the HOLD because of the higher gas velocities. The HOLD sludge always contains fragments of caviar which are crushed during exhausting. This knowledge could not be applied to converter I, since greater rates of flow would affect the operations of the preheater.

Conclusions:

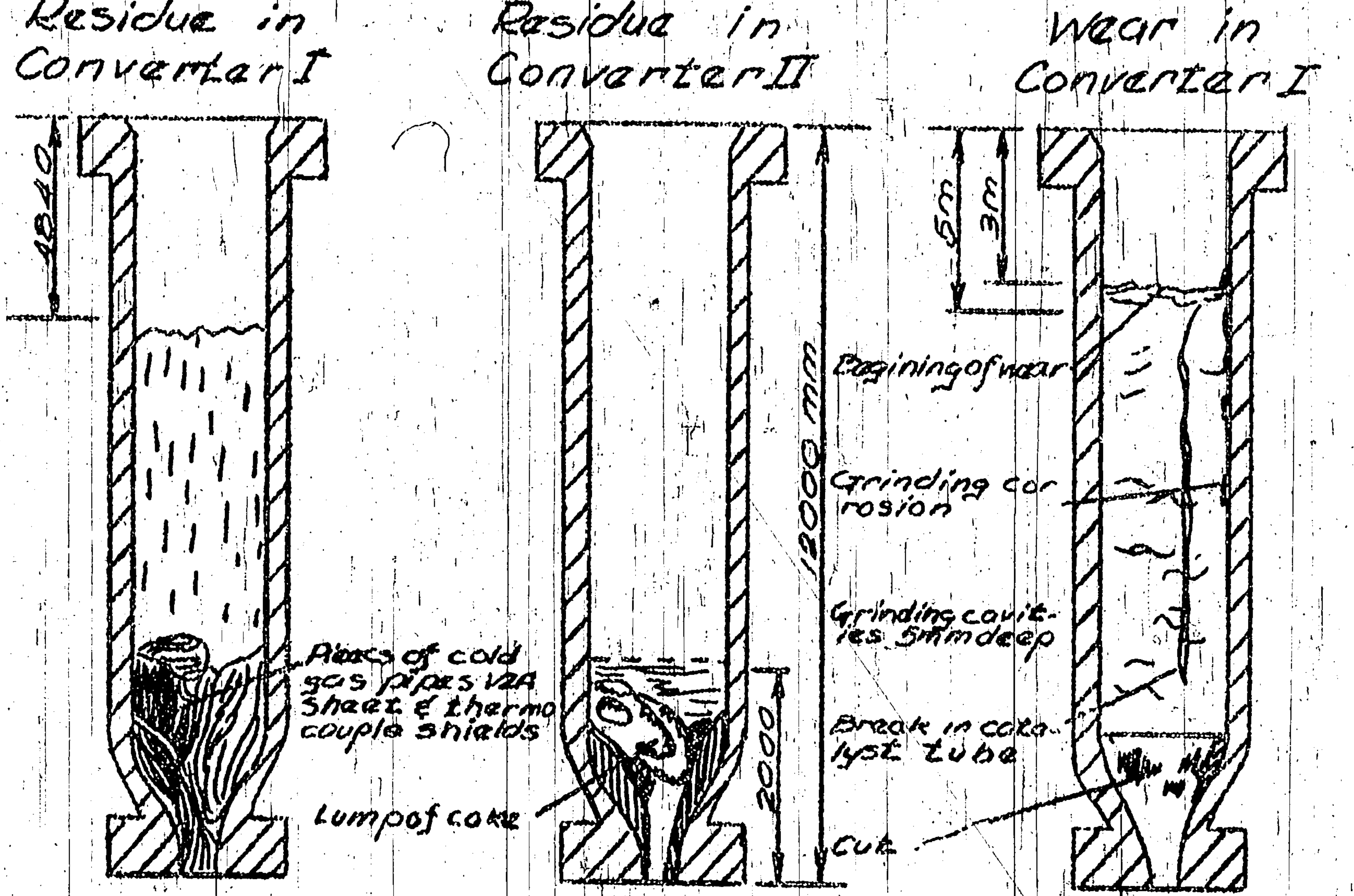
Desanding of converter I completely eliminated the formation and settling of caviar in the coal stall converters. No more difficulties are experienced in the shut down of injection, whether for operation with hydrogen off-gas or when "idling". Similarly, stopping injection for any other reason (i.e. change of blowers) can be undertaken without fear in resuming operations, unlike the previous experience. The regulation of the converter temperature became simplified, and the coke formation in converter I should become completely overcome. In case of shutdown for a general over-hauling of the stall, the converters can be completely emptied, while formerly converters I and II could not be let down. The laborious emptying, especially of converter I, required much time and labor.

Desanding of converter I represents a large forward step. The life of the liquid phase stall has not been greatly lengthened, but this is to be blamed on the grinding action of the solid constituents of the coal between the heat exchanger I and the intake of converter I, particularly in the gas preheater. Only after these difficulties are overcome will the full benefit be had from desanding of converter I.

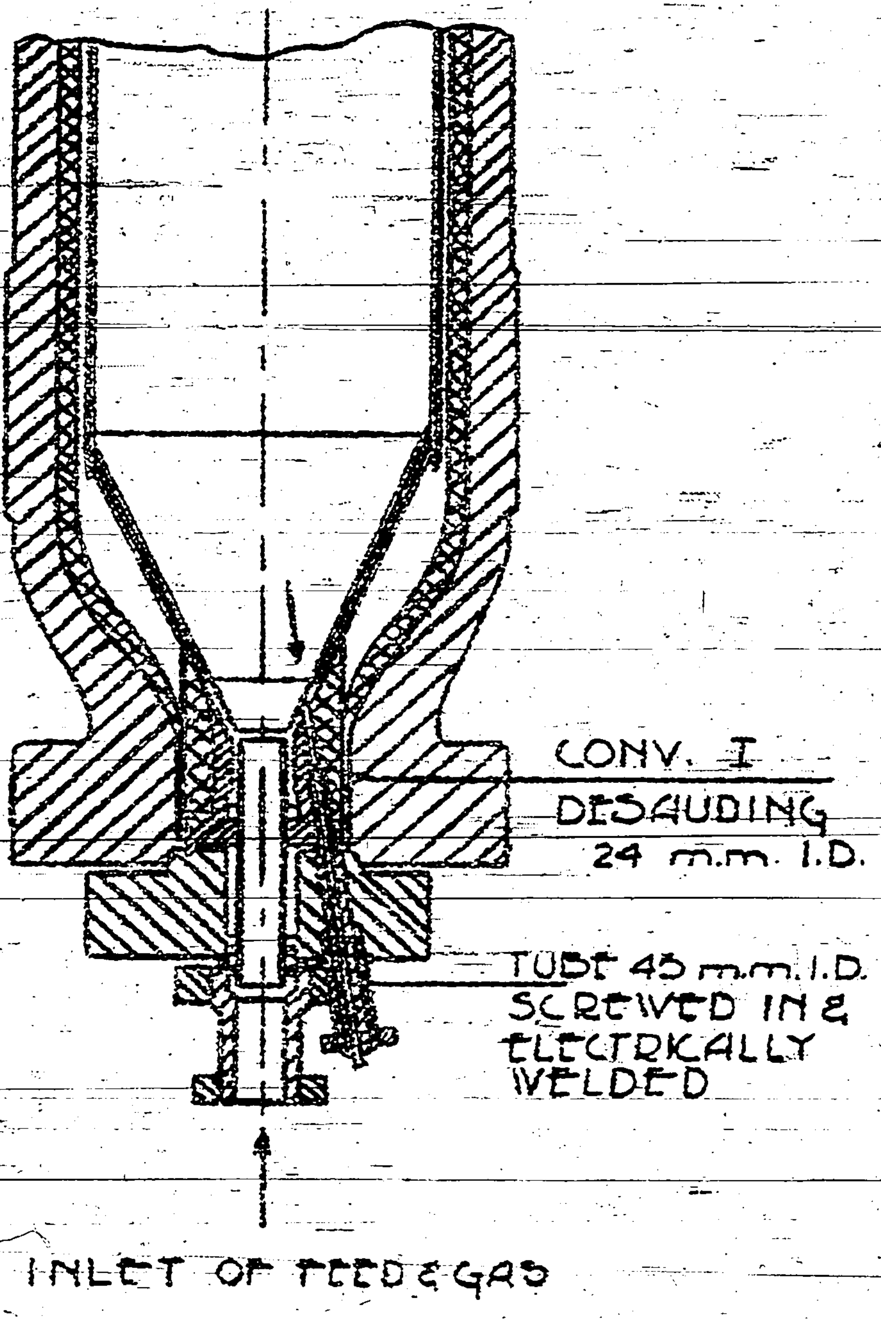
W.M. Sternberg
1/6/47

T-109

# Residue and Damage by Wear in Converters 1&2, Stall 8



Sheet 1



CONV. I
DIRECT DESAUDING

T-109

Sheet 3

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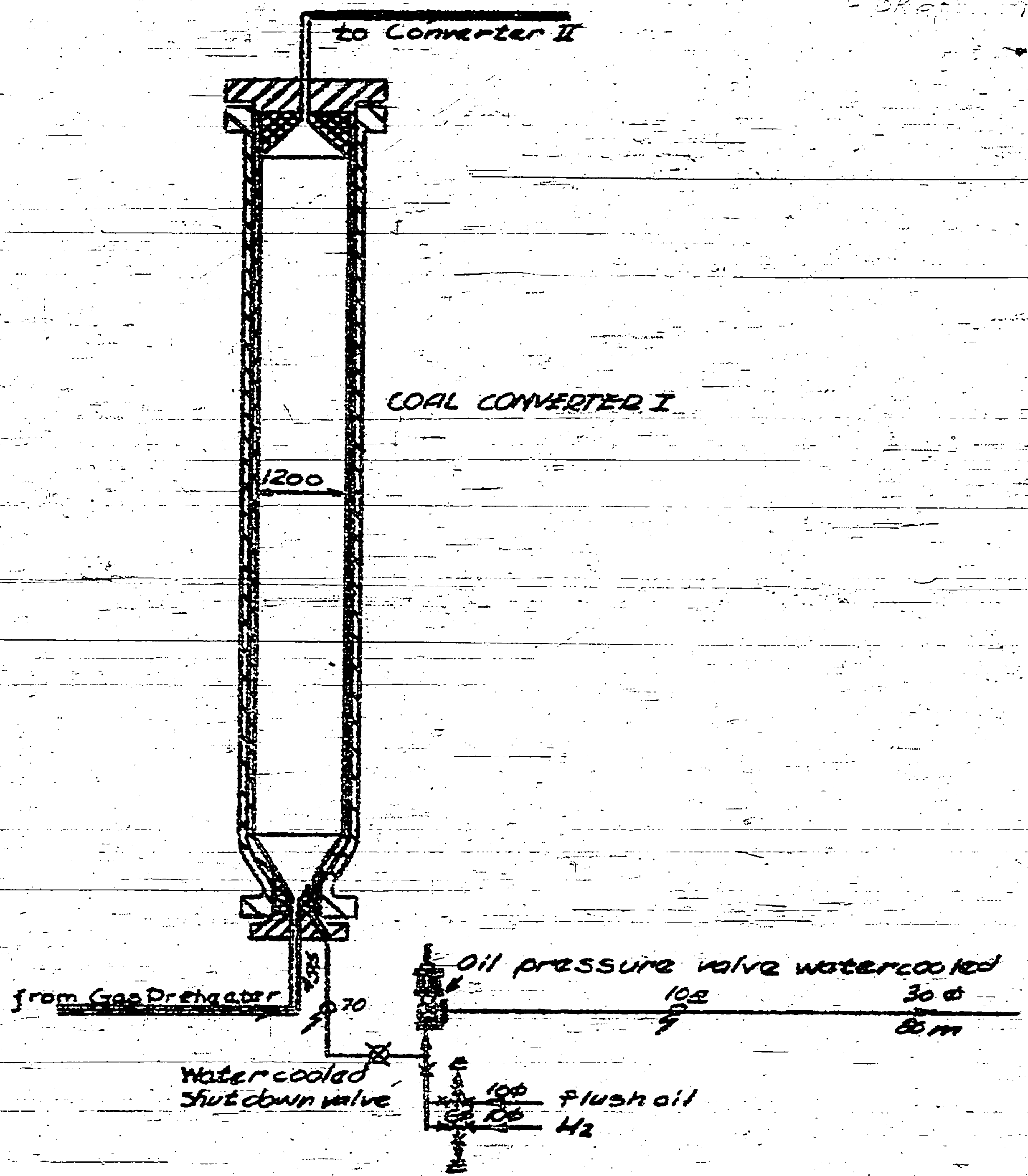
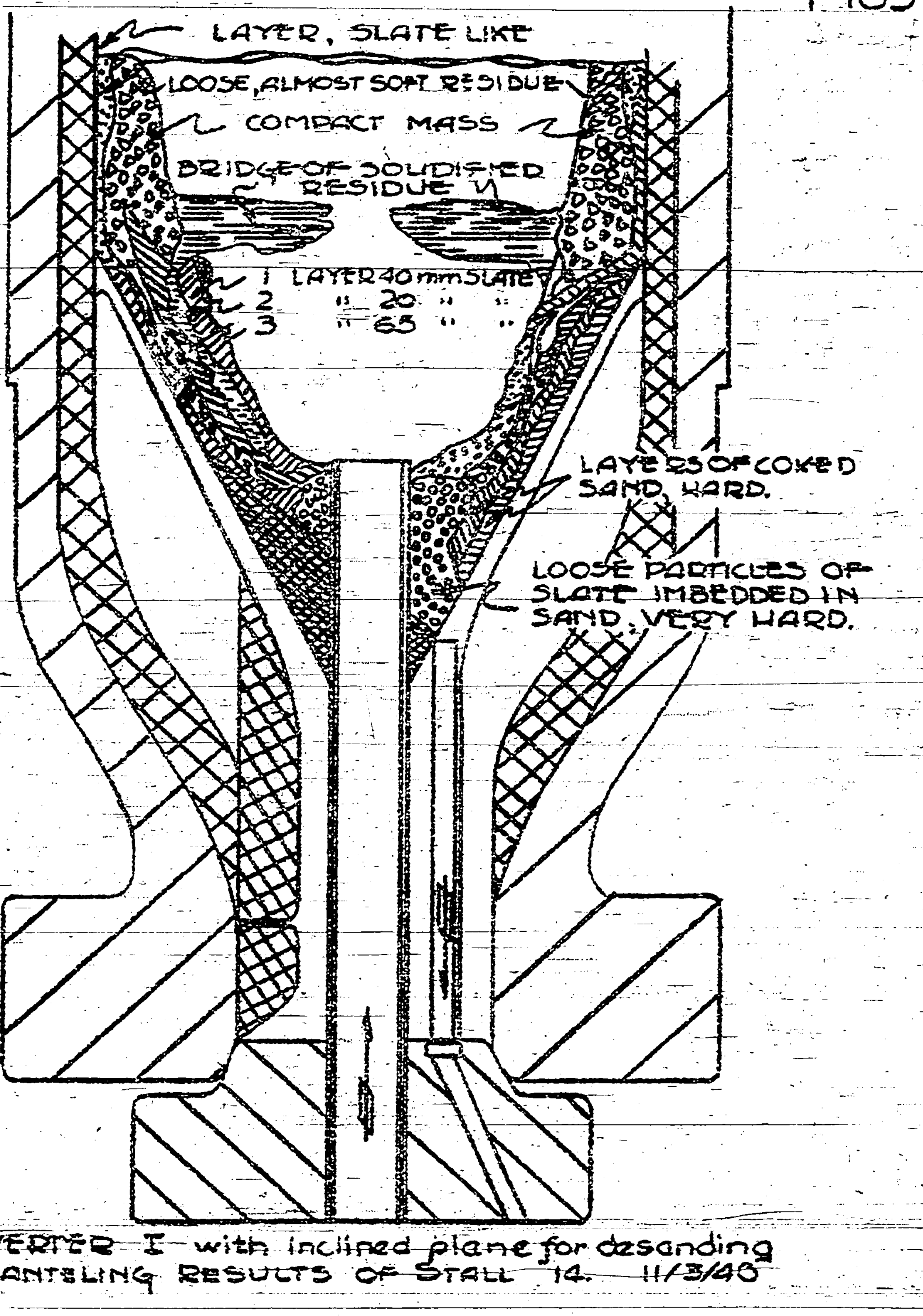
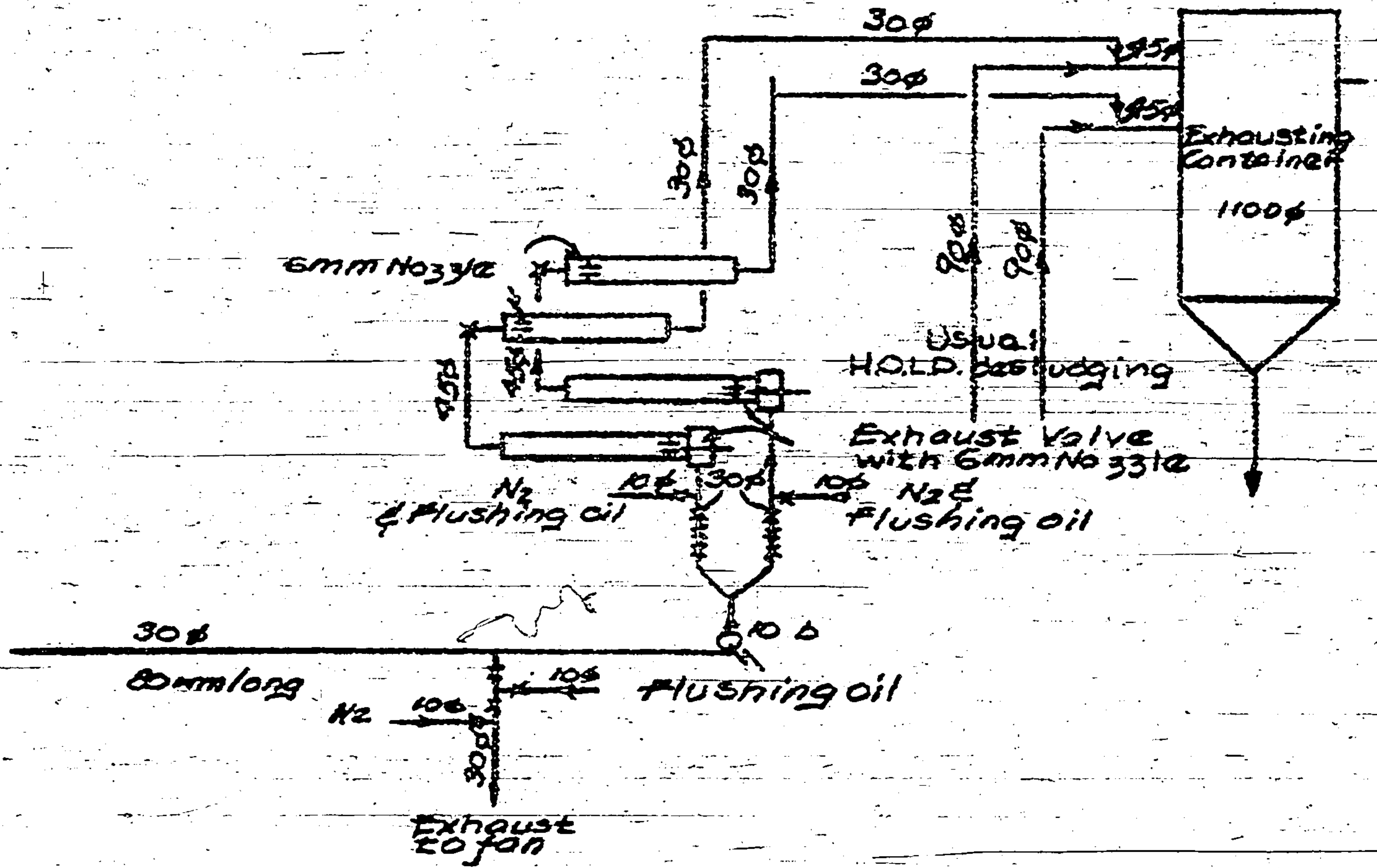

to Converter II
COAL CONVERTER I
1200
from Gas Preheater
Ø35
70
Oil pressure valve watercooled
10⌀
30 at
80 m
Watercooled
Shutdown valve
10⌀
10⌀
flush oil
H2

T-109

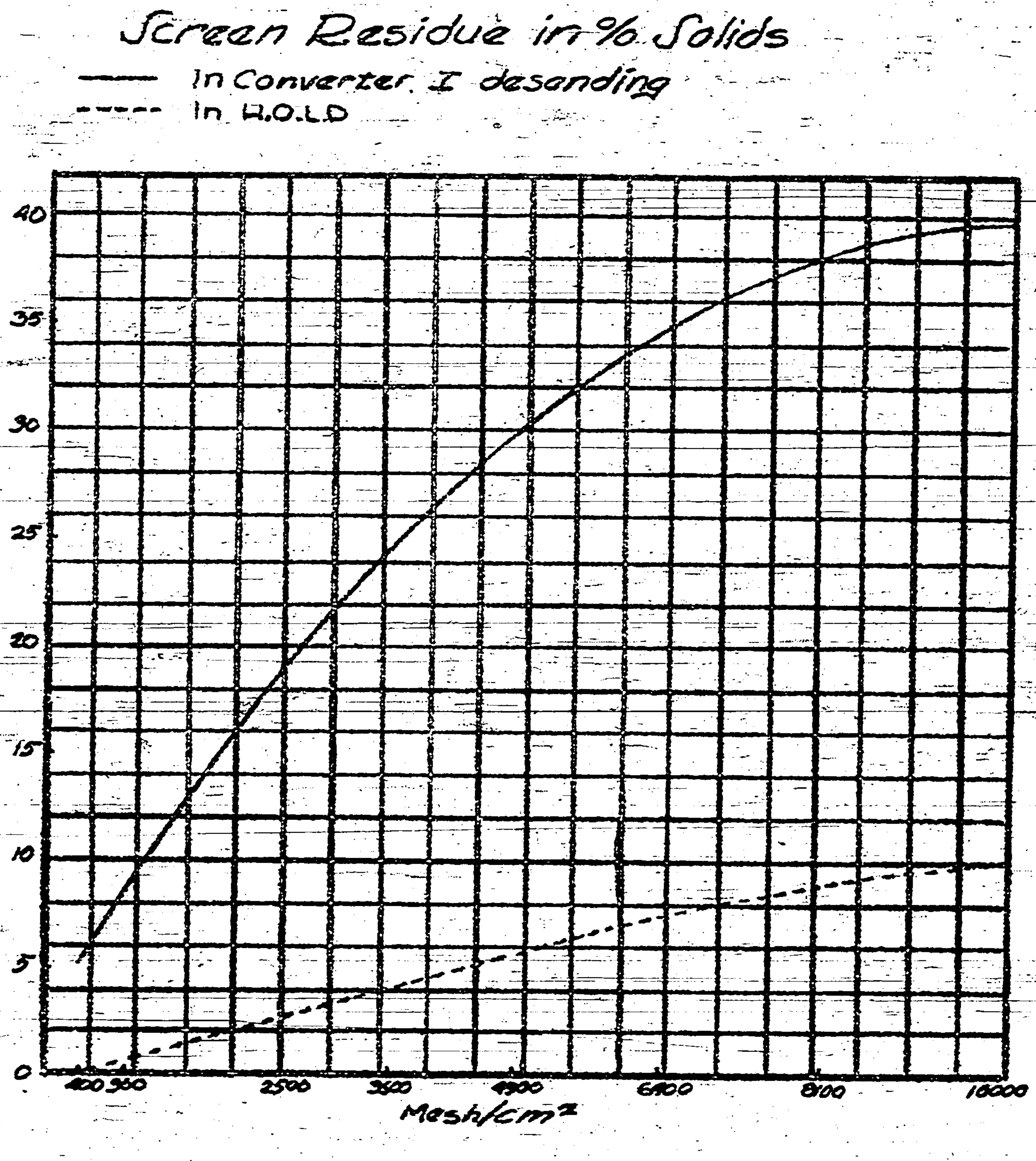


CONVERTER I with inclined plane for desanding
DISMANTELING RESULTS OF STALL 14. 11/3/40

T109

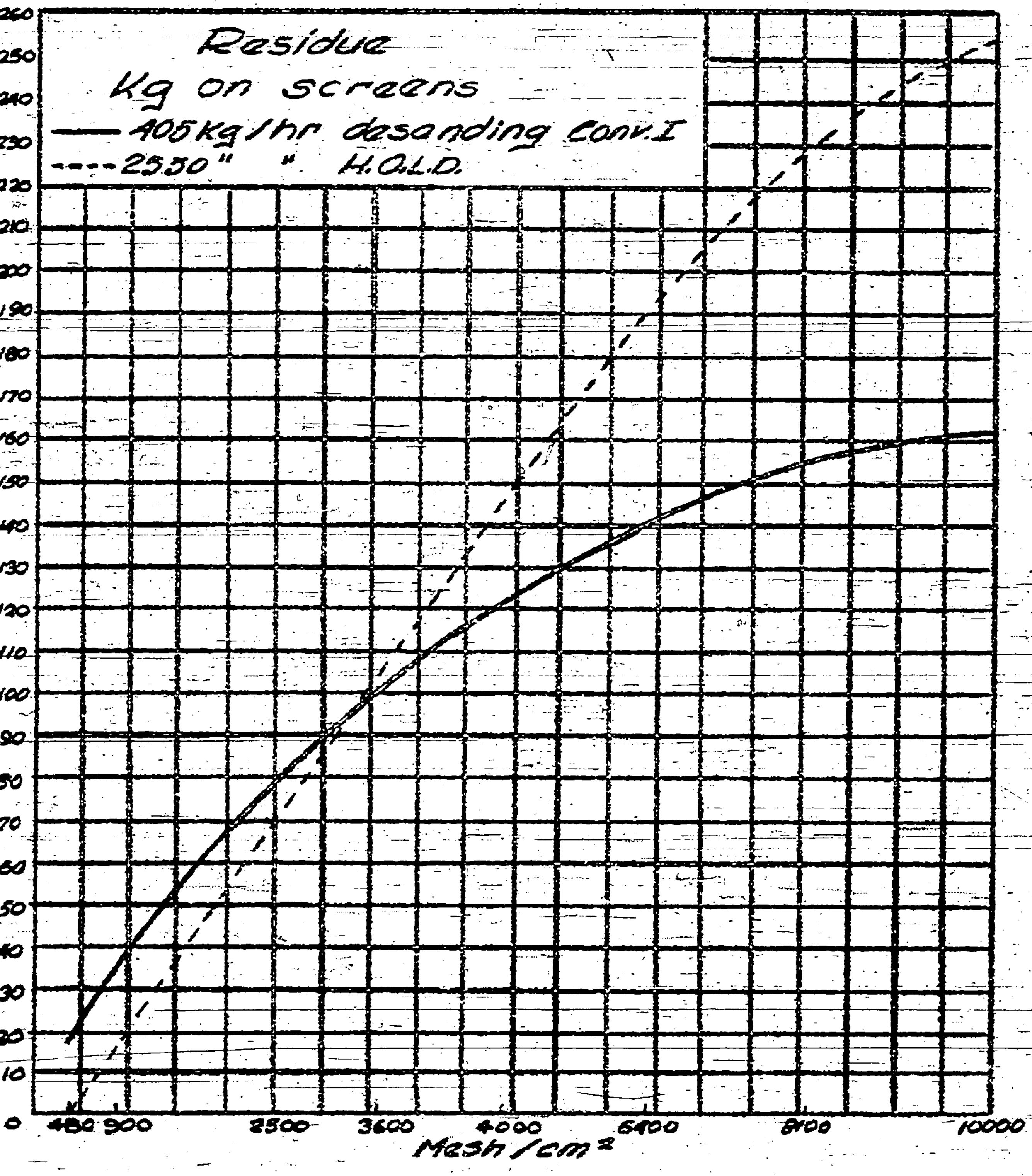

30ø
30ø
45ø
45ø
Exhausting Container
1100ø
30ø
30ø
90ø
90ø
6mm No 33/2
45ø
45ø
Usual
H.O.L.D. desludging
Exhaust Valve
with 6mm No 331a
N2
& Flushing oil
10ø
30ø
10ø
N2 &
Flushing oil
10ø
30ø
80mm long
10ø
Flushing oil
N2
10ø
30ø
Exhaust
to fan

T-109



Screen Residue in % Solids
In Converter I desanding
In H.O.L.D
40
35
30
25
20
15
10
5
0
400
900
2500
3600
4900
6400
8100
10000
Mesh/cm²

T-109


Residue
Kg on screens
—— 405 kg/hr desanding Conv. I
- - - - 2530 " " H.O.L.D.
0
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160
170
180
190
200
210
220
230
240
250
260
480
900
2500
3600
4000
6400
8100
10000
Mesh/cm²

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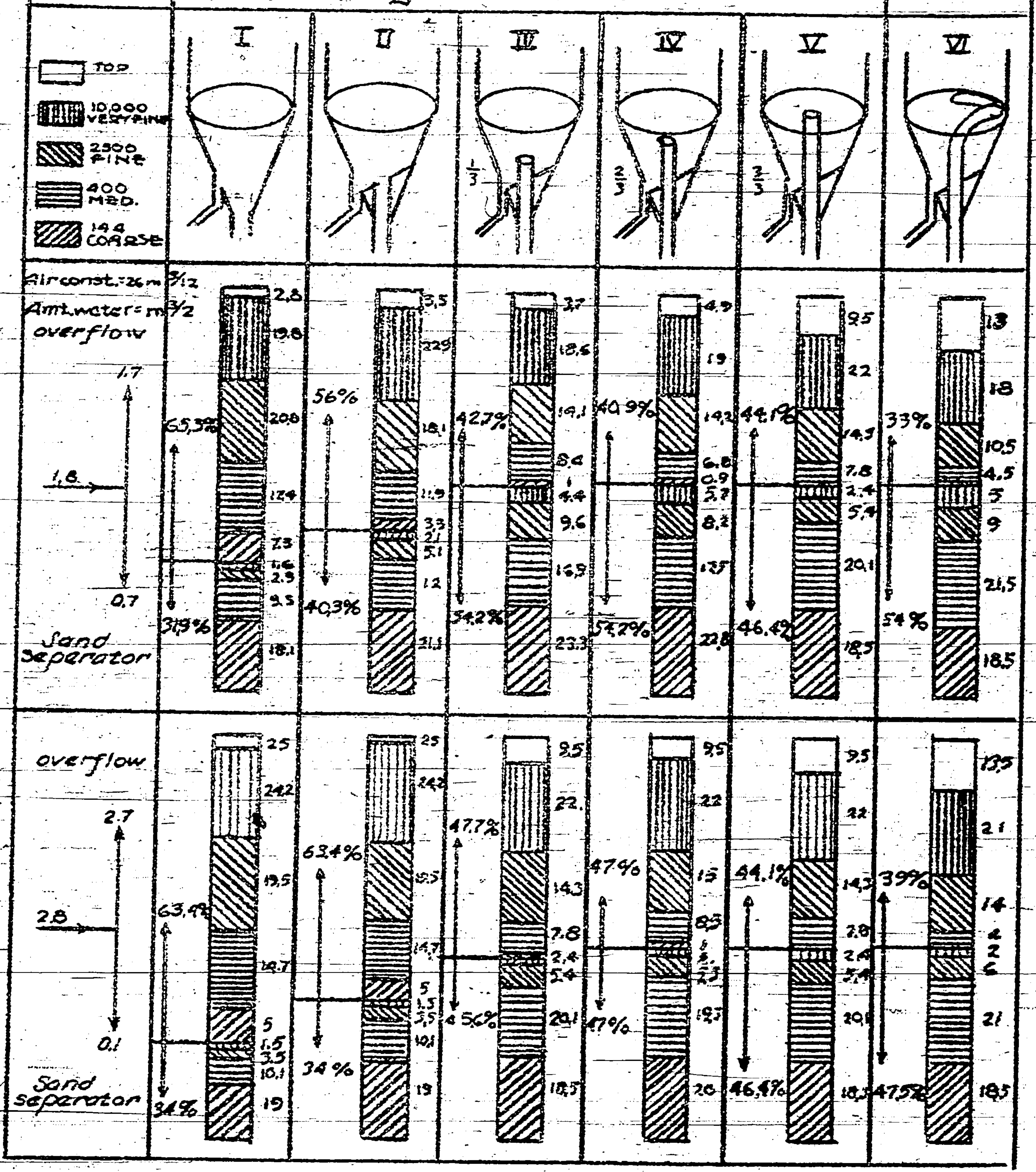
# Desanding Test - Converter I

T-109



T.O.M. Reel 162
pp. 1126-1133

U. S. Bureau of Mines
Hydro. Demon. Plant Div.

T-110
Trld-KCBraun
9/26

## Abstract of Report on Increasing the Oil Yield in Low Temperature Carbonization by the Addition of Catalyst and Superheated Steam.

Lu 558, 29 April, 1943

In a letter dated February 2, 1943, (T.O.M. Reel 162, pps. 646-659), Hydro-Works Politz states that in practical operation, as well as in the laboratory, an increased oil yield in low temperature carbonization had been obtained by the simultaneous addition of superheated steam and sulfur. Other experiments with the same objective have since been made by Gelsenberg, Scholven and Ludwigshafen. The reported results at hand give the following overall picture:

Laboratory Experiments:

I. a). Without simultaneous addition of steam, the addition of sulfur, to a max. of 1.2%, has no beneficial effect on the oil yield of centrifuge residues.

b). Without simultaneous addition of steam, the addition of a mixture of 0.3% sulfur, 0.3% sulfigran ($Na_2S$) and 0.3% soda, the increase in oil yield is negligible. (This combination added in thin paste form may be substituted for sulfur and has about the same effect).

c). Without simultaneous addition of steam, the addition of gaseous hydrogen-sulfide, in quantities of 0.15-1.4% by weight, the oil yield is increased slightly, by 0.8-1.0%. $H_2S$ seems to act slightly better than either a) or b).

II. The addition of superheated steam alone causes a sharp increase in the oil yield. For example, Scholven obtained an increase in oil yield from 72.2% to 82.8% by the addition of 70% steam. Gelsenberg reported an increase in yield from 78.5% to 95.1% by the addition of steam alone, and only a very slight further increase to 95.3% by adding 1% sulfur, when carbonizing Pölitz centrifuge residue.

III. a). While the addition of sulfur without simultaneous addition of steam has no effect on the oil yield, the simultaneous addition of sulfur and steam will increase the yield slightly above that for steam alone. Ludwigshafen obtained an increase in yield from 80.0% to 85.7% by adding 1.2% sulfur to 100% steam, compared to an increase from 80 to 83% by adding 100% steam alone. By doubling the amount of steam to the same amount of sulfur, the yield increased to 87.3%. Gelsenberg obtained no, or only a slight, increase in yield (0.2%) by the addition of sulfur, presumably because of high steam addition.

b). For the simultaneous addition of steam and a mixture of 0.3% sulfur, 0.3% sulfigran ($Na_2S$) and 0.3% soda, the results were similar to those in III. a) above.

c). The simultaneous addition of steam and gaseous hydrogen-sulfide also showed an additional yield, which is several times greater than the effect of $H_2S$ alone. The addition of 0.35% $H_2S$ alone increased the yield from 72.2% to 73%, whereas the simultaneous addition of 7% steam and the same $H_2S$ increased the yield to 79.8% and the addition of 37% steam alone increased the yield to 81%, while the simultaneous addition of 37% steam and 0.35% $H_2S$ gave a yield of 84%.

IV. The carbonization of oil from centrifuge residue free of insolubles, compared to oil containing insolubles, shows an even greater steam effect.

Operating Experiments

Politz could increase its yield from 71.5% to 79.3% by the addition of 1.2% sulfur and an increase in the steam from 150 Kg/h to 320 Kg/h, when carbonizing centrifuge residue from coal, and at the same time increase the thruput in the ball kiln from 3.5 to 3.8 T/h.

Pölitz mentions sulfigran ($Na_2S$) and soda, besides sulfur, because these alkaline additions have a beneficial effect on operations by preventing the kiln residue from becoming plastic. (Plastic residue is due to incomplete carbonization). On the other hand, according to Pölitz and Gelsenberg experiences, alkalies tend to decrease the yield. Politz has equalized this decrease by sulfur addition, and has shown that a suitable mixture of sulfur, sulfigran and soda has the same beneficial effect as sulfur alone. With a mixture of 0.3% sulfur, 0.3% sulfigran and 0.27% soda and an increase in the steam quantity an increase in yield from 76.5% to 86.5-87.9% could be obtained in large scale production.

Properties of the heavy Oil:

In production, as well as in the laboratory, Politz reports an increase in the quantity of gasoline and middle oil in the kiln oil by the addition of sulfur and superheated steam. This might be explained, on the one hand, by a change in the cracking process due to steam and catalyst addition, on the other hand, by polymerization or condensation of cracking gases, caused by catalyst addition.

Use in Mass Production:

The use of these results in mass production depends on 2 factors:

1). The extent to which the quantity of steam may be increased without too great an increase in the dust content of the precooler oil.

2). On the economy of increased steam consumption and the cost of catalysts.

Scholven points out that the same increase in yield as in simultaneous steam and catalyst addition may be obtained more cheaply and simply by increased steam additions alone. (Results of extensive experiments conducted by Scholven are contained in TOM Reel 164, pps. 1005-1009, dated 20, March 1943).

T.O.M. Reel 118
pp. 727-736

U. S. Bureau of Mines

Hydro. Demon. Plant Div.

T-111
Trsld KC Braun/jw
9/28/46

# Abstract of Report on Reducing Resistances in Gas-Fired Preheaters.

April 27, 1939

The demands of Hydro-works Scholven to increase the capacity of one of their preheaters, with consequent greater volume of circulating gases, caused us to examine the question of the resistance to the flow of gases in preheaters. The resistance varies as the square of the velocity, so that pressure differences beyond the capacity of the single-stage Schiele blowers (max. 300 mm W.G.) could easily develop. It was intended, therefore, to determine the exact course of the pressure loss in the preheaters in operation in Scholven. Since this met with many practical difficulties, it was supplemented by measurements on sheet steel models built to 1/10 actual size.

The measurements on the preheater in service already showed that the pressure loss in the heating chamber proper, that is, the pressure losses applicable to heat transmission, were small compared to the total pressure loss. The curve plotted to show the distribution of the pressure loss in the preheater gas circulating system indicates that only 13.5 mm of the total pressure loss of 355 mm occurred in the heating chamber, the greatest proportion of the loss occurring in the inlet and outlet ducts and passages. This curve is based on a gas volume of 126,000 $m^3/h$ @ 400° C., with the passages 34% open. With the passages fully open, the volume rose to 165,000 $m^3/h$ @ 400° C, the total pressure loss dropped to 290 mm and the useful pressure loss in the heating chamber rose to 30 mm.

The curves indicate that particular attention must be paid to the resistances in the ducts and the distributing points. The gas distribution should be so arranged that the energy-consuming dampers could be eliminated. Where bends can not be avoided, guide vanes will considerably reduce the pressure loss.

The duct system could also be greatly simplified by using an Escher-Wyss axial blower, in which the vanes of the wheel can be adjusted while operating, as in the Kaplan turbine, instead of the Schiele radial blower. It remains to be seen how well this much more sensitive wheel will operate at high temperatures. Such a blower, with a capacity of 165,000 $m^3/h$, static pressure of 450 mm W.G. @ 350°C and 2900 RPM, has been ordered for Völklingen.

Reducing the pressure losses saves power and size of blower and permits an increase in the useful pressure drop, that is, an increase in the velocity of the gases in the heating flues and therewith an increase in the heat transmission in the hairpin coils or a lowering of the gas inlet temperature.

T.O.M. Reel 9
Bag 2733
Target 30/4.11
Pps. 311-314

U. S. Bureau of Mines

Hydro. Demon. Plant Div.

T-112
Trsld KCBraun/jw
9/27/46

## Experiences with Hot Catch Pots

Ludwigshafen/Rh, 2.2,1945

Letter addressed to
Ruhröl G.M.B.H.

The question has been raised, if the hot circulating pump could be omitted when processing pitch at 700 atm.?

Pölitz agrees with our experiences that, if need be, the hot circulation could be omitted if the quantity of cold letdown (Kaltabschlamm) were correspondingly increased.

We should like to inform you of the latest experiences with the hot catch pot at Pölitz, as follows:

When running pitch, tar or petroleum in the liquid phase stalls, we had frequent troubles with the hot catch pot because of coking. This coking is caused by irregular letdown yield, which cannot be avoided because of small temperature fluctuations in the stall. This causes interruption of the uniform flow in the hot catch pot and the letdown (Abschlamm) deposits the solids contained in it, largely catalyst solids, due to its low asphalt content. Coking of the product is initiated by this concentration of catalyst solids.

At the suggestion of Brabag, a perforated double jacket was inserted in the conical part of the catch pot, thru which about 3000 $m^3/h$ of cold gas was blown in continuously. By this agitation and cooling in the lowest part of the catch pot, catalyst deposits are prevented and the product receives a continuous added supply of hydrogen.

An inspection of a hot catch pot of this kind built into a petroleum stall indicated no coking after 158 operating days. A hot catch pot of normal construction was coked up to such an extent that it could be operated only with a much reduced capacity after such an operating period.

Letter addressed to
I. G. Farbenindustrie A.G.
Ludwigshafen/Rhein.

Ruhröl G.M.B.H., Feb. 20, 1945

Based on many years experience, we are also of the opinion, that when processing pitch at 700 atm. the hot circulating pump at the hot catch pot may be omitted.

In 1943 we submitted a new design for hot catch pot 44e to you, which, with us, has proved to be best for processing pitch.

In our liquid phase stall for pitch hydrogenation at 700 atm. we have never used a hot circulating pump. Nor have we ever used the upper and lower cooling coils in the hot catch pot, as used in Leuna. Unforunately, we seldom have long operating periods with this method. Quite often catch pot interruptions occurred after only a few days of operation.

For this reason, experiments were already made in 1942 to prevent these interruptions. Based on these experiments, we developed a hot catch pot construction, in which 5000-6000 $m^3/h$ cold circulating gas was continuously charged into the lower part of the catch pot through a perforated distributing ring, while the letdown (Abschlamm) was withdrawn above the gas inlet. The charged gas is intended to prevent deposits and coking by intensive agitation and at the same time cool the sludge. In normal operations this method cools the catch pot sludge up to 150° C, which prevents an increase in temperature through reactions and consequent coke formation. This cooling has a particularly beneficial effect when the regular flow to the catch pot is interrupted, either through a rise in temperature in the converter or for some other reason. In this case, the catch pot sludge (Abscheidersumpf) temperature is very much lowered by the continued influx of the circulating gases. A further advantage lies in the fact that the catch pot can never be completely emptied when the influx from the converter is cut off, even with a leaky letdown valve. This is of importance, inasmuch as at the renewed influx to the catch pot, after the interruption, unusually heavy letdown, with a tendency to deposition, is normally produced, which in this case, is immediately diluted by the cold sludge.

Bending the inlet pipe in the lower part of the catch pot towards the center is intended to prevent the heavy letdown from flowing down along the catch pot walls.

The volume of the expansion gas (Entspannungsgas) of the letdown is no greater in this catch pot than in the type used before.

With this improvement we have increased the operating period of our catch pots to such an extent that the shut-down of a stall has never been due to hot catch pot interruptions. After every shut-down of a stall, operating up to 269 days, we have always found that no solid residues were formed in this type of catch pot, so that practically an unlimited operating period may be assumed.

Design dwg. 1577-1 (not available) shows this catch pot.

By removing the lower cover, the catch pot interior is readily accessible, which cannot be claimed for the former conical catch pots.

T.O.M. Reel 163 U. S. Bureau of Mines T-113
Frames 27-29 Hydro. Demon. Plant Div.

## Different Processes for the Production of Water Gas.

October 18, 1942.

1. Oxygen-water gas from coke in rotating producers.

   After treatment: Desulfurization, compression, conversion, $CO_2$ removal, compression to 325 atm, CO removal.

   In addition to 80-85% zero water gas there is also produced 15-20% nitrogen-containing water gas which can find use as fuel. For each cub.m. hydrogen, 1.55 cub.m. total water gas is required. Of this amount, 0.31 cub.m. contain nitrogen and is to be used as fuel.

   The method is adapted to largest installations and with low cost coke it produces cheap hydrogen. Used in: Leuna, Scholven (Demag and Pintsch), Pölitz, Blechhammer, Welheim.

2. Oxygen-water gas from brown coal coke (Grude), dry brown coal or coal, using Winkler producer with oxygen from Linde installation.

   After treatment: Desulfurizing, compression, conversion, $CO_2$ scrubbing, compression to 325 atm, CO scrubbing.

   1.36 cub.m. total water gas required for 1 cub.m. hydrogen. The process is adapted to largest scale manufacture.

   Advantages: The use of the finest-powdered fuels, which could find no other use.

   Requirements: The fuel must be cheap because of the Linde unit.
   The process is in use in Leuna and in the Brabag works with brown coal, in Japan? with soft coal.

3. The Pintsch-Hillebrand Process.

   Use of Briquettes. The process in use at Wesseling.

4. Water gas from coke, hydrogen from Messerschmidt hydrogen producer.

After treatment: Hydrogen: sulfur removal, $CO_2$ removal with chalk; hydrogen compression to 325 atm.

2.2 cub.m. total gas required for 1 cub.m. hydrogen.

The process may only be considered for small units of up to 2500 cub.m./h.

Used in Gendorf: 2600 cub.m./h. water gas

5. Splitting of hydrogen off-gas or coke oven gas, etc, in tubular furnaces.

After treatment: Final desulfurization, conversion, compression, $CO_2$ scrubbing, compression to 325 atm., CO scrubbing.

Preliminary requirement: Low butane content.

The process may be used in large units.

Used in Pölitz and Wesseling.

Disadvantage for use during wartime: Special material for tubes.

6. Splitting of coke oven gas in Sachse converters with the use of oxygen.

The gas desulfurized prior to splitting.

After Treatment: Compression, conversion, $CO_2$ scrubbing, compression to 325 atm., CO scrubbing.

Because of rusting, the process is only adapted to operation with low BTU gases, up to coke oven gases. Methane, possibly small amounts of ethane, are the limit.

When coke oven gas is used, some 4% $N_2$ remains with the hydrogen.

The furnaces are heated by direct combustion of part of the gas.

Advantage: Somewhat lower installation costs.

7. Linde process for the decomposition of gas.

Desulfurization and $CO_2$ removal must be done first.

Advantage: The separated gases are available for independent use.

8. Linde Double Shaft Converter Process.

Has as yet not been tested in larger units.

9. Lurgi pressure gasification of solid fuels with the use of oxygen.

After treatment: $CO_2$ scrubbing, conversion, $CO_2$ scrubbing, compression to 325 atm. CO scrubbing.

Disadvantage: High methane content.

The methane content increases rapidly with increasing pressure, while the $CO_2$, hydrogen and CO contents are reduced.

10. Didier process.

11. Koppers process.

12. Electrolytic hydrogen.

Byproduct: oxygen

Only for small units with low price power.

## Operation and Installation Costs of the Different Processes

Cost are only calculated for the water gas installation, not for the after treatment. The amount of water gas produced at the water gas installation is sufficient for the production of 1000 cub.m. hydrogen and 100,000 cub.m./h hydrogen after compression.

| Process | Operating costs of the water gas plant per 1000 Nm$^3$ $H_2$, after compression RM. | Raw material costs | Installation costs of a water gas plant for 100,000 m$^3$/h of $H_2$, uncompressed after compression. RM. |
|---|---|---|---|
| Zero water gas from coke in rotating producers | 22.- | coke: 23m/te | 14,200,000.- |
| Zero water gas in Winkler producer | 29.- | coke: 23M/te<br>$O_2$ : 1.9 pfg/M$^3$ | 22,000,000.-<br>Included: Linde unit for 36,500 m$^3$/h of $O_2$; 16,000,000.- |
| Pintsch-Hillebrand: Water gas from brown coal briquettes | | | 22,700,000.- |
| Water gas from coke, hydrogen from Messerschmidt hydrogen producer. | 37.70 | coke: 23 M/te | |
| Splitting of hydrogen off-gas in tubular converters. | 22,80 | Hy. off-gas: 0,51 pfg/1000 H.U. correspond. to coke oven gas at 2.2 Pfg/m$^3$ | 16,500,000.-<br>Included fuel gas 118x10$^6$ H.Units (4,250,000.-) |
| Splitting of Coke oven gas in Sachse Converters. | 24.- | Coke oven gas 2.2 Pfg/m$^3$<br>Oxygen 1.9 pfg/m$^3$ | 14,000,000.-<br>Including Linde unit 4,500,000 |
| Electrolytic hydrogen | 93.-<br>After treat. & compression 109.80 | Power: 1.4fg/kwh | 65,000,000.- |

T. O. M. Reel 181 U. S. Bureau of Mines T-116
pp. 477-481 10/16/42
Hydro. Dem. Plant Div.

## Hydrogenation Properties of Various Coals

### 1. Hydrogenation ability in relation to the properties of coal.

Catalytic hydrogenation has now reached such high development, that practically any coal occurring in nature, from the older soft coals to young brown coals can be readily converted into oils. This does not mean that all coals are equally well adapted to large scale hydrogenation; and there is a multitude of factors in as complicated chemical substance which affect the case of hydrogenation. It appears possible and desirable to select, on the strength of the accumulated experience with the most varied coals, the grades best suited to hydrogenation.

Of the soft coals, the gas flame coal, as well as gas coals with a carbon content of 78 to 86% come first into consideration. There is a rough parallelism between the carbon content and ease of hydrogenation, but carbon content can not alone tell the hydrogenation behavior of the coal. Coals with the same C-content may react differently, depending on their origin. Thus, a coal with 83% C, from the Silesian coal basin behaves less favorably than a Ruhr coal with as much carbon. The reason for it is, that while the carbon contents are the same, the Selsian coal is higher in oxygen and lower in volatiles and sulfur, than the corresponding Ruhr coal. There are in addition differences in the composition of the ash, in that the ash of the Silesian coal frequently has an alkaline reaction because of the higher CaO content.

It is generally true that the younger (lower C) coals are more readily hydrogenated than the older coals; the results of their hydrogenation are always better. The utilization of the pure coal is higher, the production of gasoline and middle oil better, the quality of the heavy oil is higher, because of its lower asphalt, and the gasification is lower than with C-richer coals (v. curves). One can establish some relationship between ease of hydrogenation and the volatile matters, which are roughly inversely proportional to the carbon content. The oxygen content is very important because of the hydrogen consumption and affects hydrogenation because of the formation of asphalt-richer products. The chlorine and sulfur content are important and they both facilitate hydrogenation. The inorganic components of coal, as well as the organic, affect hydrogenation, depending on their amount and composition. Higher ash content reduces the coal utilization, but has also some favorable effect on the utilization of asphalt through its distributing action. The ash content may be kept low by proper selection of coal or by mechanical ash elimination, and in large-scale hydrogenation, coal with an ash content of 4 - 6% is usually used. Deashing coal saves reaction space and reduces the residues which require special operations. Coals with strongly basic, high - CaO ash, can not be successfully used with acid catalysts, because of the neutralization of some of the active catalysts and the harm to metals of the 6th group frequently present in the catalysts. For this reason with such high-ash coals, neutralization with an acid is frequently beneficial for hydrogenation.

A certain role is also played by the petrographic composition of the coal. The individual constituents of coal, the lustrous, dull, fibrous coals and bituminous shale all behave differently in hydrogenation. The first can be readily hydrogenated, the fibrous coal and the shale are difficult to hydrogenate. The fibrous coal usually has a considerably higher C-content, higher ash and much more CaO in the ash than the lustrous and dull coals. The latter contains much tar-formers (plant spores and algae) which yield much oil even in low temperature coking.

In conclusion we shall give the properties of different coals well suited to hydrogenation and obtained from different coal fields:

| | Ruhr Coal | Saar Coal | Silesian Coal |
|---|---|---|---|
| % C in pure coal | +84 | +84 | +825 |
| % Vol. Mat. pure coal | -38 | -37 | -37 |
| % Ash in dry coal | Below 4 and not over 6.5 | | |
| % CaO in ash | | low | |
| Fibrous coal and slate | | low | |

All brown coals can be readily hydrogenated because of their low C-content, and while they still show a relationship between hydrogenation and C-content, it is less pronounced than in soft coal. The ease of hydrogenation is affected by the ash content, the composition of the ash, the S, and most of all by the oxygen content. Low sulfur, high oxygen brown coals give upon hydrogenation high-asphalt and frequently unstable and high-phenolic reaction products. Higher sulfur content reduces asphalt and favors splitting. The higher oxygen content is also undesirable because of the higher hydrogen consumption. The action of the higher ash content is the same as in soft coal. The ash in brown coal forms skeleton-line infiltration deposits or else is in combination with humic acid (Ca), and no mechanical deashing is possible, as is done with soft coal. Naturally, neutralization of the basicity with acid is more beneficial in case of brown coal than with the usually lower ash soft coals. No improvement in hydrogenation is obtained by neutralization when the, at present much in use, alkaline iron catalysts are used, and is therefore not done in such cases.

The following are therefore the properties of the easy to hydrogenate brown coal:

| | |
|---|---|
| Ash content | below 13% |
| Oxygen content | below 25% |
| Sulfur content | high |

The pitch luster coals are, according to their composition, older brown coals, and the same applies to them as to brown coal.

## 2. Effect of Pressure on Hydrogenation of Coal.

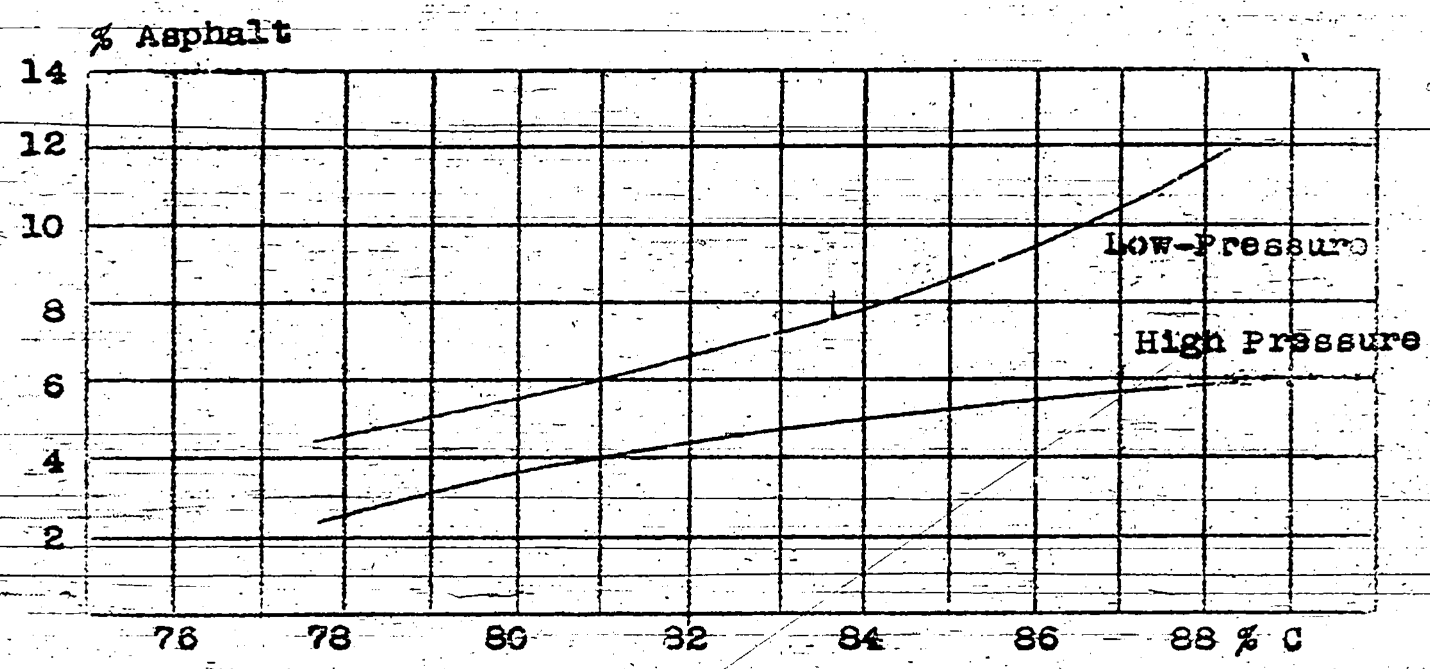
Increasing the pressure of hydrogen in general results in stronger hydrogenation and interfers therefore with the deposition of lower-hydrogen products, by offering the chance of working at higher temperatures, than can be done with lower pressures. Higher pressures increase the reaction velocities, permitting an increased thru put. Higher pressures favor particularly the hydrogenation of the older coals, because the effect of increased pressure is very much greater in their case than with younger coals, especially in the utilization of coal and in the reduction of asphalt production. Increasing the pressure permits in this case increasing the thruput, which affects favorably the yield and the reduction in gasification.

Moreover, increasing the pressure permits the use of cheaper non-corroding catalysts (iron), because the effects of increased pressure are more arked with the less active than the more active catalysts. It is now possible to obtain better results with an iron catalyst at 700 atm pressure than with tin + chlorine at 250 atm. The output is simultaneously increased by about 50% thru the use of higher reaction temperatures.

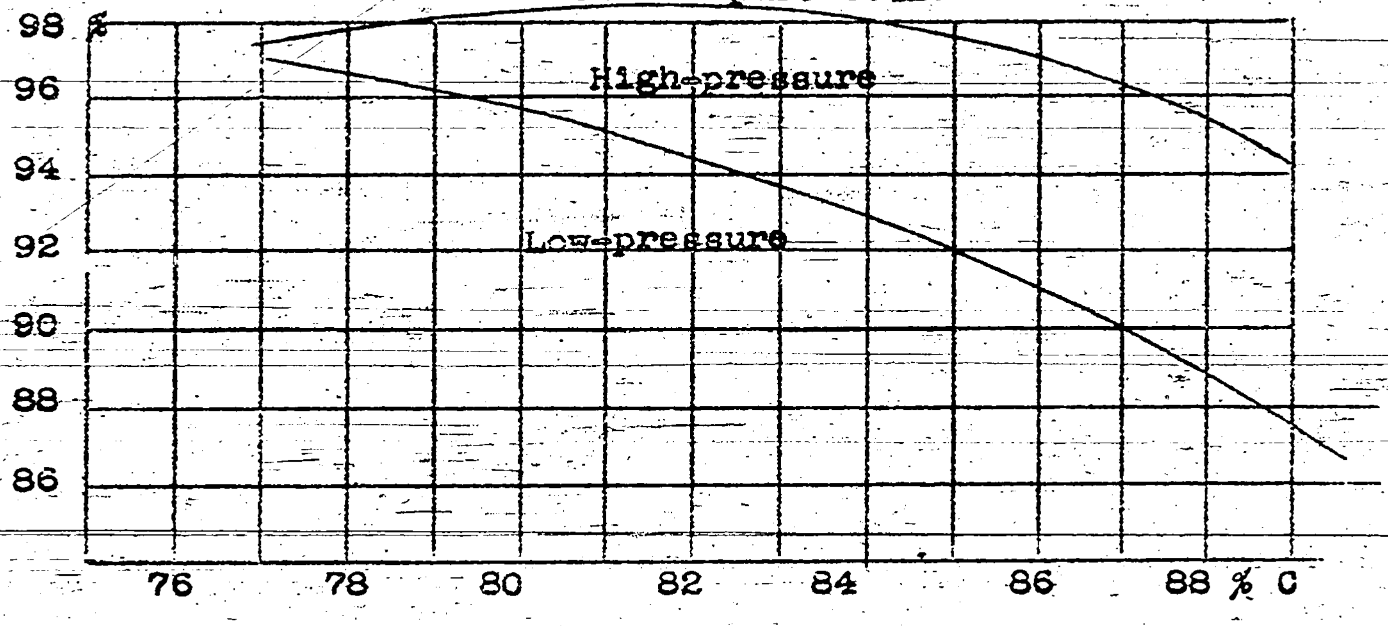
/s/ Grasse

Trld. - W.M. Sternberg

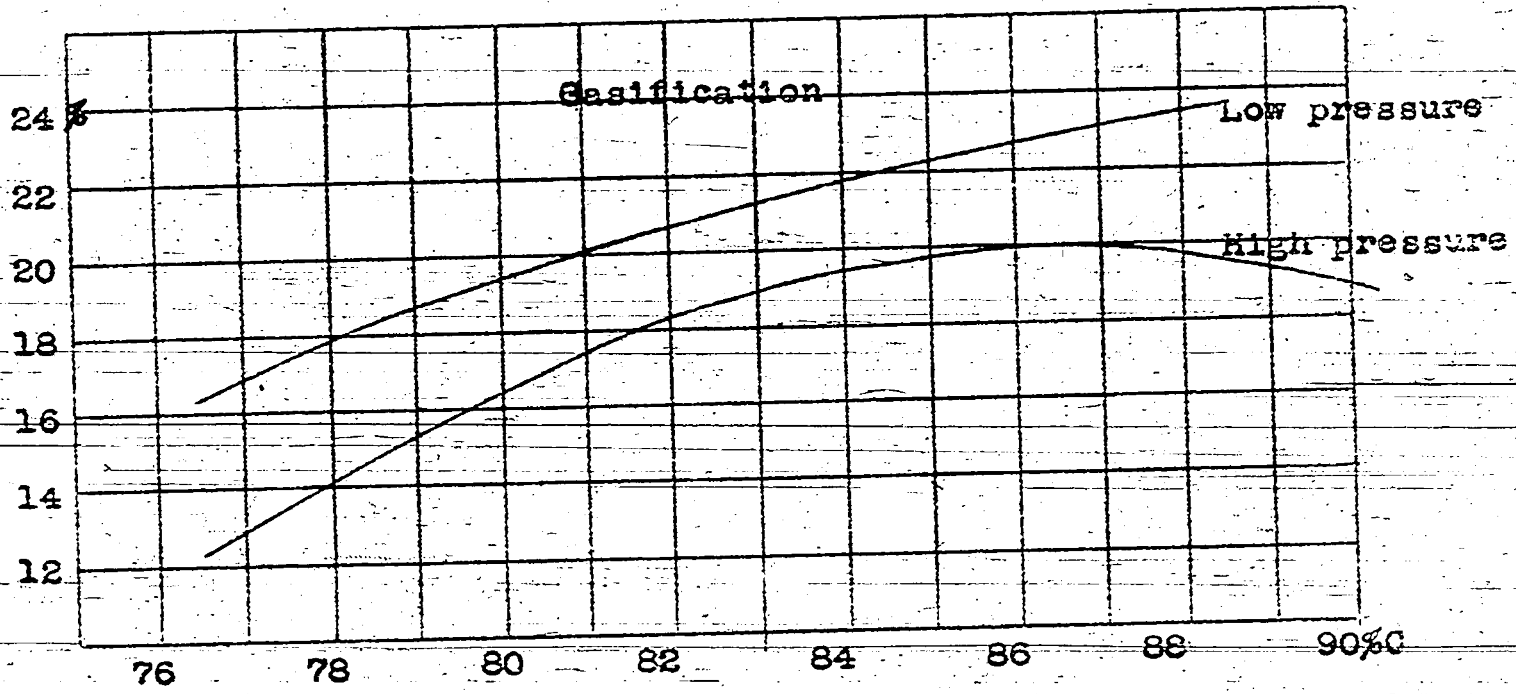
Asphalt in Heavy Oil

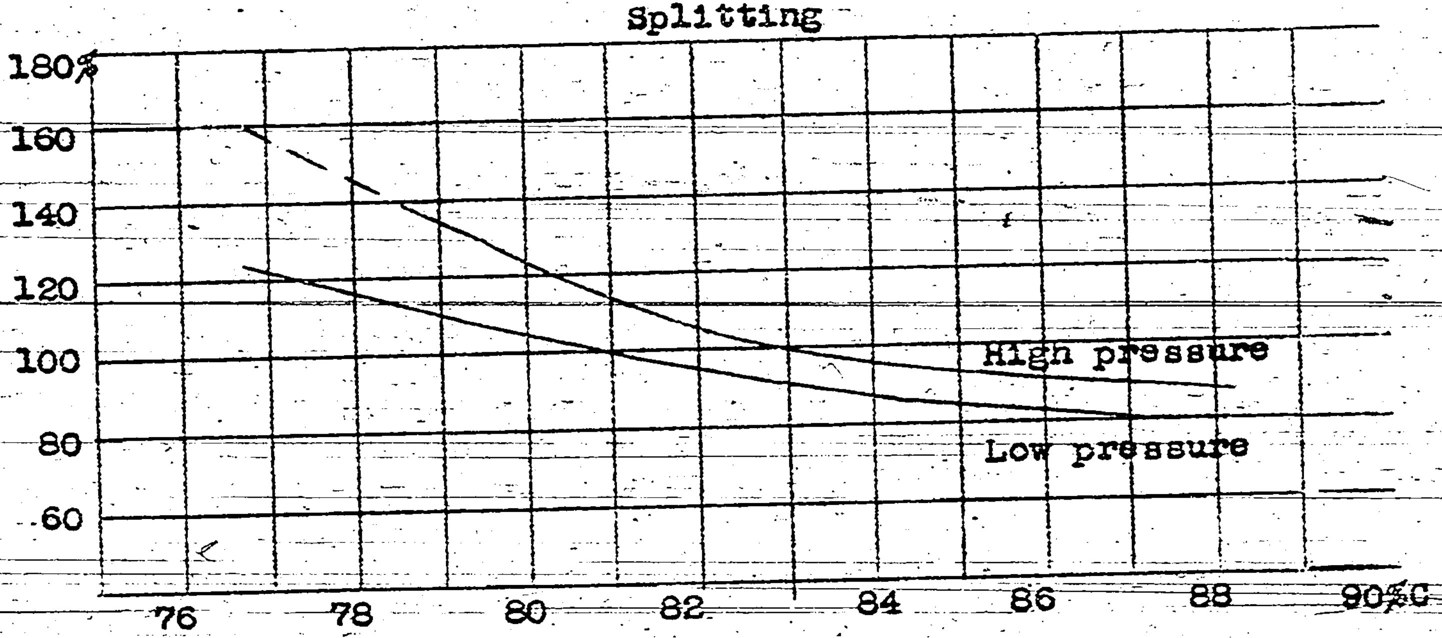


Utilization of pure coal



# Hydrogenation of coal under high and low Hydrogen Pressure.





T.O.M. Reel 163
pp. 201-211

U. S. Bureau of Mines
Hydro. Demon. Plant Div.

T-117

K. C. Braun
9/30/46

## Abstract of Lecture on Machines for Hydrogenation

(See also T-122 & T-125)
October 19, 1942

1). To meet the demands of the high pressures and considerable volumes used in hydrogenation requires a large assortment of heavy high-pressure machines, largely developed especially for this purpose.

The change to 700 atm. meant something new for the machinery industry in the large units required. Even though smaller units of such machines for 700 and 1000 atm. were already in use at Ludwigshafen and Welheim, considerable development work had to be done on the large units. This great task, which could never have been done by a single firm, was accomplished by the newly formed Mineralolbaugesellschaft Berlin, combining the six (6) largest builders of compressors in Germany, Borsig, Demag, Ehrhardt and Sehmer, Schwartzkopff and Holberg, and Maschinenfabrik Esslingen. Their leading designers, together with I. G. engineers with practical experience in this line, undertook to develop the new equipment, particularly gas compressors and circulating pumps.

Three compressors, built by Borsig for 325 atm. hydrogen compression, whose precision construction and design based on many years operating experience offered a thermal efficiency never reached before, served as models for the new units.

The 6-stage unit-compressors had a capacity of 18,000 $m^3/h$ in low pressure and 13,500 $m^3/h$ in high pressure, with a synchronous motor drive of 4,000 kw. Depending on the $CO_2$ content of the gases, the gas capacities in the low and high pressure sections can be proportioned within very close limits. Each hydro-works has some compressors with stageless volume regulation as well, in order to proportion the gas delivery of the compressor installations to each other and to production. The regulation is usually done by keeping the suction valve open proportional to the speed of the machine (Borsig or Demag regulation, back-pressure regulation) or, on some machines, by proportioning the discharge openings to the working piston (opening regulation). In recent years, the automatic regulation (back-pressure or opening) is coming into general use because of its simplicity and operating reliability.

The unit compressors have proved generally satisfactory. They are of double cylinder construction. The first three stages have free-floating disc pistons, which keep the heating of the gases in suction to a minimum because of their small surface. The last three stages have a differential piston. The generous proportion of the cooler and shock absorbers assure low power requirements and large water and oil separators minimize the wear on piston rods, stuffing boxes and piston rings. Breaks in the valve plates have also been minimized by the good water separation. With a thermal efficiency of 69%, the unit compressor is unexcelled today.

2). The booster compressor (Nachschaltverdichter), whose purpose is to compress the 300 atm. hydrogen for the coal phase after it has been cleaned of $CO_2$ and CO, to 700 atm. in one stage, is similar in construction to the Demag Hypercompressor for the 900 atm. Claude process, except that it is much larger because of its capacity of 12,000 $m^3$ /h. Its drive is a 600 KW, 144 R.P.M. motor. The reciprocal operating pistons have no rings to seal the gas pressure, but run in a displacement chamber only a few millimeters larger in diameter than the piston. Suction and pressure valves are located in the head cover of the displacement chamber. The efficiency of 80.7% of these booster compressors is very good, considering the low compression ratio of 700:300 and its simple construction. The 700 atm. stuffing boxes are oil cooled and have given no trouble.

3). The 700 atm. unit gas circulating pump is similar to the booster compressors. It also has 2 reciprocating plungers, 770 mm dia., and a capacity of 55,000 $m^3$ /h. Difficulties with the 700 atm. stuffing boxes were expected, and the speed was, therefore, set at 106 R.P.M. Certain difficulties did develop in practice, so that we considered using the same piston construction used in the 300 atm. circulating gas pumps, inasmuch as a smaller pump of this type had been operating satisfactorily at 700 atm. in Welheim. This construction has the advantage of a large piston diameter compared to a relatively small piston rod and stuffing box. This piston pump was built for a capacity of 70,000 $m^3$ /h, and has proved very satisfactory. Its advantages over the unit circulating pump are the short compact body, small stuffing box and more accessible valves.

4). The following high pressure liquid pumps are essential for hydrogenation works operation:

- Middle oil injection pumps for 325 atm. vapor phase.
- Tar injection pumps for 325 atm. liquid phase.
- Coal paste pumps for 700 atm. coal phase.
- Hot tar circulating pumps for 300 atm. liquid stall and 700 atm. coal stall.
- Flushing oil and water pumps.
- Wash oil pumps for circulating gas washing.
- Copper liquor pumps for CO cleaning and
- Supply pumps for the expansion machines (Entspannungsmaschinen) in the circulating gas wash and CO cleaning processes.

The injection pumps for middle oil, tar, wash oil, copper liquor and water, that is, for all thin flowing, homogeneous products are horizontal or vertical triplex plunger pumps, motor and gear or belt driven, with capacities up to 30 $m^3$ /h @ 325 atm. and 12 $m^3$ /h @ 700 atm.

The injection pumps for coal paste, as well as the circulating pumps for hot let-down, that is, for pasty products containing solid particles of coal and ash, are horizontal hydraulic simplex pumps with large plunger diameters and slow speed stageless regulation from zero to maximum speed. The coal paste pumps are generally water driven, water supplied by large centrifugal pumps @ 60 atm. pressure. These hydraulic driven pumps have the advantage of being reliable and insensitive in operation. They slowly suck the viscous paste into the large plunger chamber and convey any desired quantity uniformly, which is of deciding importance in holding a uniform reaction temperature in the stall. They are designed for the following capacities:

15 and 25 $m^3$/h @ 350 atm. max. pressure, and

4, 10 and 20 $m^3$/h @ 750 atm. max. pressure,

and are built by Maschinenfabrik Esslingen.

The 350 atm. paste presses have the drive cylinder on one end and the rear plunger is connected to the driving piston by tension rods. On the 750 atm. presses the drive cylinder is in the middle and the 2 pump bodies are reinforced on both sides by strong lantern flanges, which form a rigid guide for the plungers. The stuffing boxes of these pumps have lasted as long as 15,000 hours in operation and the valves (ball valves) over 6,000 hours with ~~goal~~ GOOD COAL grinding and screening of the coal paste. Their maximum production could in some cases be increased as much as 50% by a slight change in the controls.

Difficulties with the injection pumps have so far been due to breaking of the pump bodies caused by the pulsating inner pressure and the high alternate impact loads. With the 750 atm. paste presses, also, breakages of pump bodies and stuffing box housings occurred. In each instance it could be shown that failure was due to defective material, which had not been forged and heat treated with the necessary care. The test on materials for material segregation and flaking has been made much more severe, because these small flaws in the material form the starting point of breaks at high alternate stresses, while the strength and elongation limit of the sound material may fully satisfy requirements.

The expansion machines (Entspannungsmaschinen) developed and built at Leuna, which had been successfully operating for years on the copper liquor washing of the ammonia synthesis at 220 atm., were adapted for operation at 300 and 700 atm. The capacity of a 700 atm. expansion machine with a cylinder dia. of 500 mm is about 65 $m^3/h$ of fluid conveyed by water pressure. The required energy is largely furnished by the fluid discharged from the washer. Except for some erosion of the control gates, due to the big pressure differential from 700 to 50 atm., these expansion machines have given very good service.

Besides these high pressure machines, many other machines, pumps, blowers, centrifuges, mills, agitators, screens, conveyors, etc., are, of course, required to give impulse to a hydrogentation works.

T.O.M. Reel 180
pp. 836-846

U. S. BUREAU OF MINES
HYDRO. DEMON. PLANT DIV.

T-118
KCBraun/jw
10/1/46

# Experiments with Baffles in High-Pressure Vapor-Phase Hydrogenation Converters
Leuna Werke, 21 Dec. 1942

## INTRODUCTION:

Slotted baffles are built into vapor phase hydrogenation converters to obtain a uniform temperature distribution over the entire converter. Based on experiments by Cron in 1934 and by Schwab in 1938, further experiments were made in 1942 with nitrogen in models at atmospheric pressure, in order to clarify the following:

1.) Permissible widening of the slots without jeopardizing the uniform temperature distribution in the converter. The baffle spacing had to be kept close to avoid loss of catalyst volume.

2.) Pressure loss in the baffles.

## ARRANGEMENT OF EXPERIMENT:

A model was made of our 800 mm baffle converters. (See Appendix 1). The baffle spacing and width of slot could be varied to suit the experiment. The diameter of the thermo-element protecting housing being constant (50 mm in the converter), there will be a free space around the housing in the center of the baffle, if the slot width is greater than the housing diameter, through which the gas can flow unhindered. In order to avoid this, vanes were provided in the center of the baffle around the thermo-element housing, although experiments were also made without these vanes.

The model was filled with 5058 catalyst and cold nitrogen admitted at the bottom, corresponding to the circulating gas of the converter, while just below the baffle hot nitrogen @ 170°C corresponding to the cold gas of the converter, was admitted. The mixture of hot and cold nitrogen emerges freely at the top, and the temperature is measured by 32 thermometers extending into the catalyst. The general arrangement provides a flow condition similar to that in an 800 mm converter with downward flow. Appendix 4 shows the arrangement of the experimental equipment.

The pressure loss in the baffle could be determined between measuring points 1 and 2 or 2 and 3. The catalyst resistance was determined by the pressure measurement at 2, Appendix 1.

Of interest to the converter stall operation was, above all, the behavior of baffles with slot widths b = 25 mm (former construction), 50 mm (present construction), 75 mm (newly introduced construction) and 100 mm. Baffle spacings a = b, a = 0.75 b and a = 1.5 b were to be investigated. Because of the reduced model dimensions, I.D. = 448 mm, compared with the 800 mm converter and an inside catalyst tube diameter of 655 mm, the model baffles were made to the following dimensions:

| | Slot Width | Baffle Spacing | Slot Width | Baffle Spacing | Slot Width | Baffle Spacing | Slot Width | Baffle Spacing |
|---|---|---|---|---|---|---|---|---|
| | | 19 | | 38 | | 56 | | 75 |
| Converter | 25 | 25 | 50 | 50 | 75 | 75 | 100 | 100 |
| | | 34 | | 75 | | 112 | | 150 |
| | | -- | | 25 | | 38 | | 51 |
| Model | 17 | -- | 34 | 34 | 51 | 51 | 68 | 68 |
| | | 25 | | 51 | | 76 | | -- |

Because of the great difference in density between the circulating gas and the atmospheric nitrogen, the same Reynolds number as in the converter could not be obtained, in spite of high gas velocities ($^R$Model = 12.9 x $10^4$, $^R$Converter = 20.2 x $10^4$).

TEMPERATURE DISTRIBUTION ABOVE THE BAFFLES:

The temperature above the baffles, that is, after mixture of the cold with the hot nitrogen, was measured at 32 points. (Temperature distribution charts not reproduced).

EXPERIMENT #28: Was run only with cold nitrogen. The temperatures should be all alike. The discrepancies due to inaccuracies in reading, incorrect thermometer indication and the various gas velocities, are clearly discernible.

EXPERIMENT #17. Baffle dimensions, slot width b = 34 mm, baffle spacing a = 51 mm, correspond to the present dimensions used in converters with b = 50 mm and a = 75 mm.

EXPERIMENT #13: Baffle dimensions, slot width b = 51 mm, baffle spacing a = 51 mm, correspond to the baffles to be installed in the future, with b = 75 mm and a = 75 mm.

EXPERIMENT #25: Shows the temperature distribution after removal of the baffles.

In order to find a criterion for the excellence of the temperature distribution, the mean value of the 32 individual temperatures in all experiments was determined and the deviation Δt from this mean was calculated for each measuring point. The expression

$\Sigma \Delta t^2$, calculated from 32 readings, is the criterion of excellence of the temperature distribution. Appendix 7 shows these results. They indicate that the baffle with a slot 17 mm wide, corresponding to 25 mm in the converter, represents the ideal condition. Baffles with a slot width of 68 mm, corresponding to 100 mm in the converter, as well as baffles without vanes proved to be impractical.

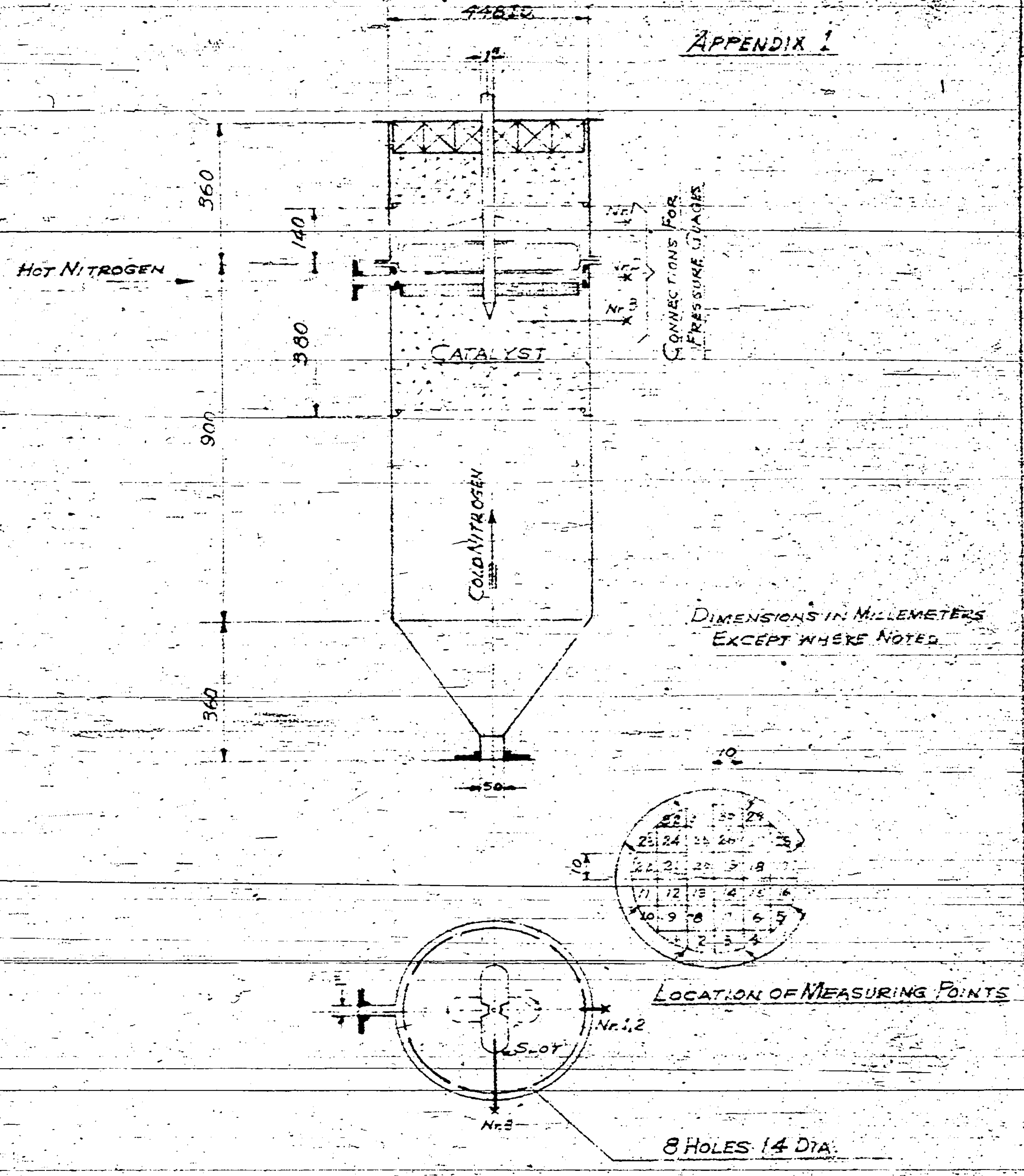
PRESSURE LOSS IN THE BAFFLES:

The pressure loss in the baffles was measured by a U-tube between measuring points 2 and 3, appendix 1. It was shown that this resistance is proportional to $MV^2/2g$. Appendix 5 shows the relation of the baffle resistance $\Delta p$ to the product $MV^2$. The advantage of greater slot width is best recognized in Appendix 6, according to which our widening of the slots in the converter should result in a lowering of the pressure loss of about 50% in the baffles.

RESULTS:

Based on these experiments, the slots in the baffles of the vapor phase converters at Leuna were widened from 50 to 75 mm, with the constriction at the thermo-element housing (vane, Appendix 2).

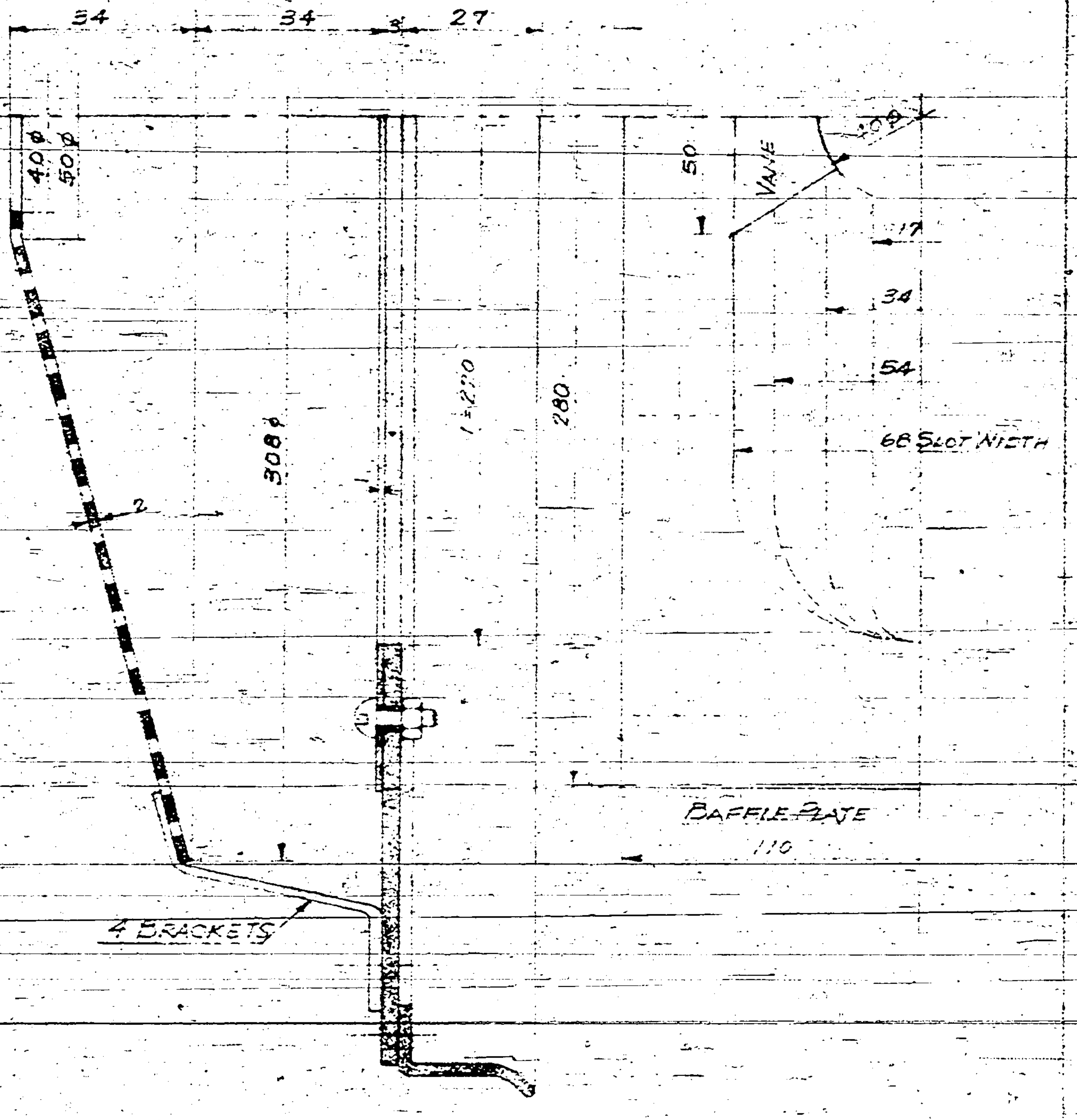
## APPENDIX 1



DIMENSIONS IN MILLEMETERS
EXCEPT WHERE NOTED

MODEL FOR BAFFLE EXPERIMENTS

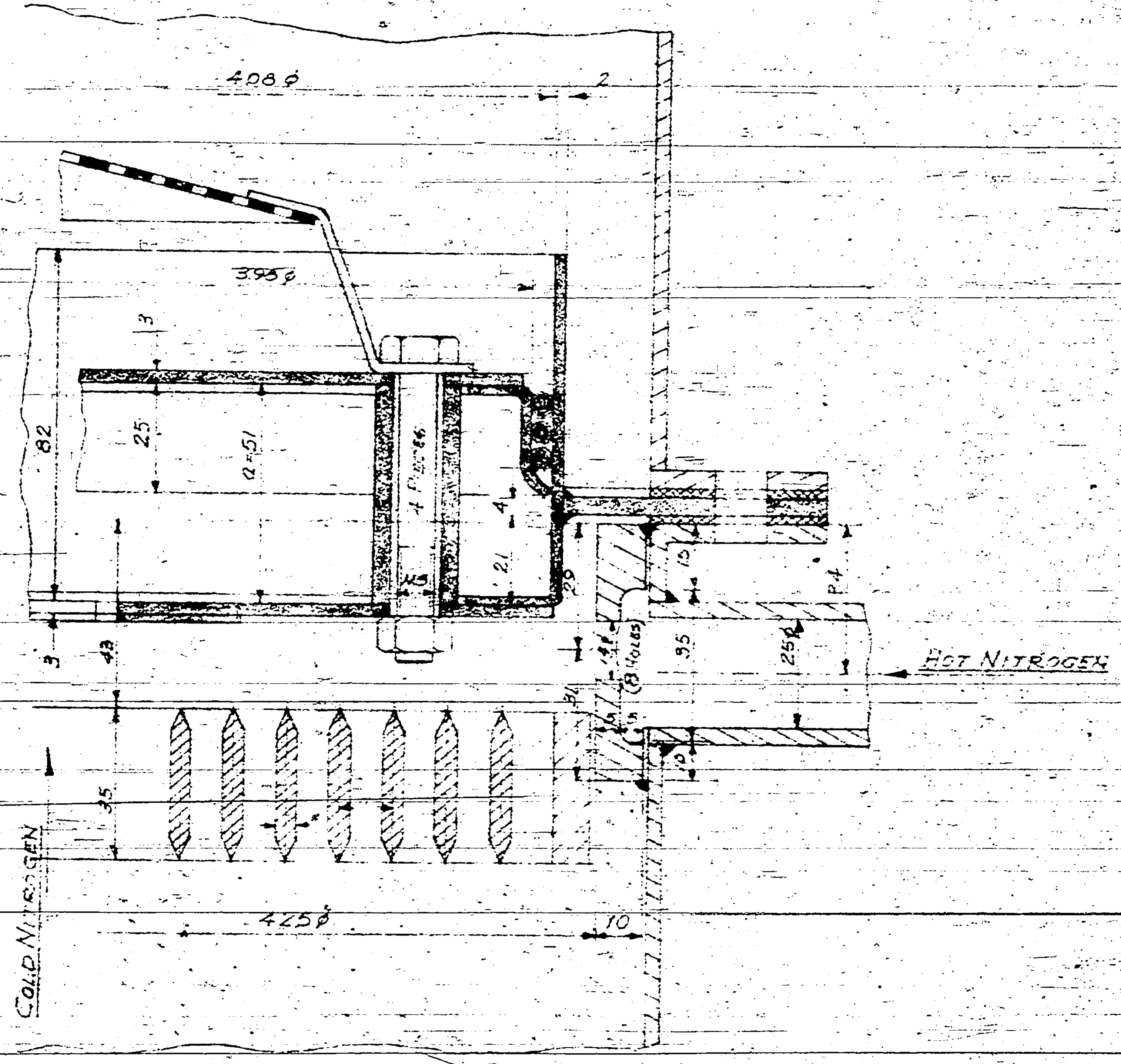
## APPENDIX 2



ALL DIMENSIONS IN MILLEMETERS

BAFFLE

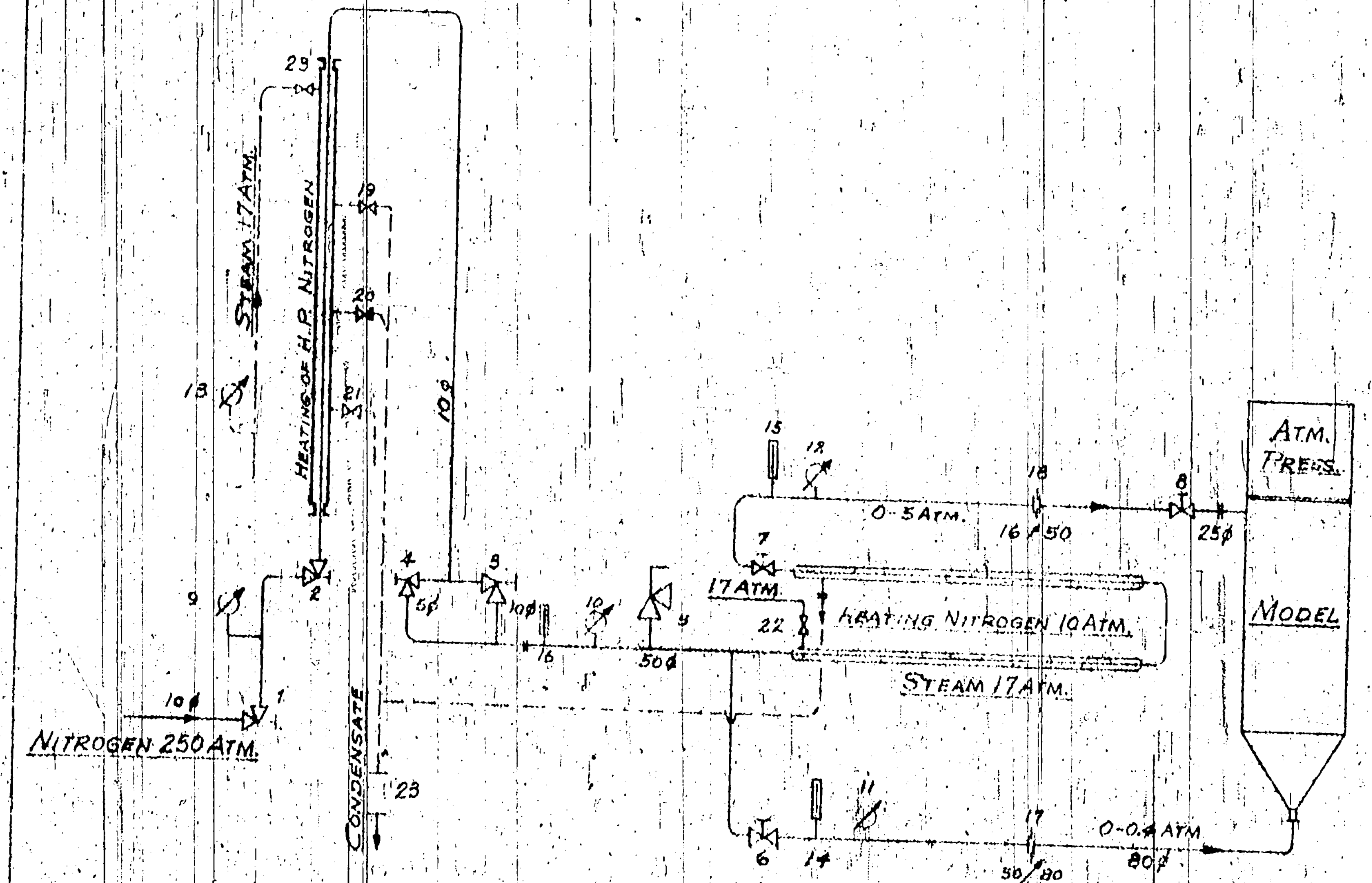
# APPENDIX-3



ALL DIMENSIONS IN MILLEMETERS

BAFFLE INSTALLATION

## APPENDIX 4

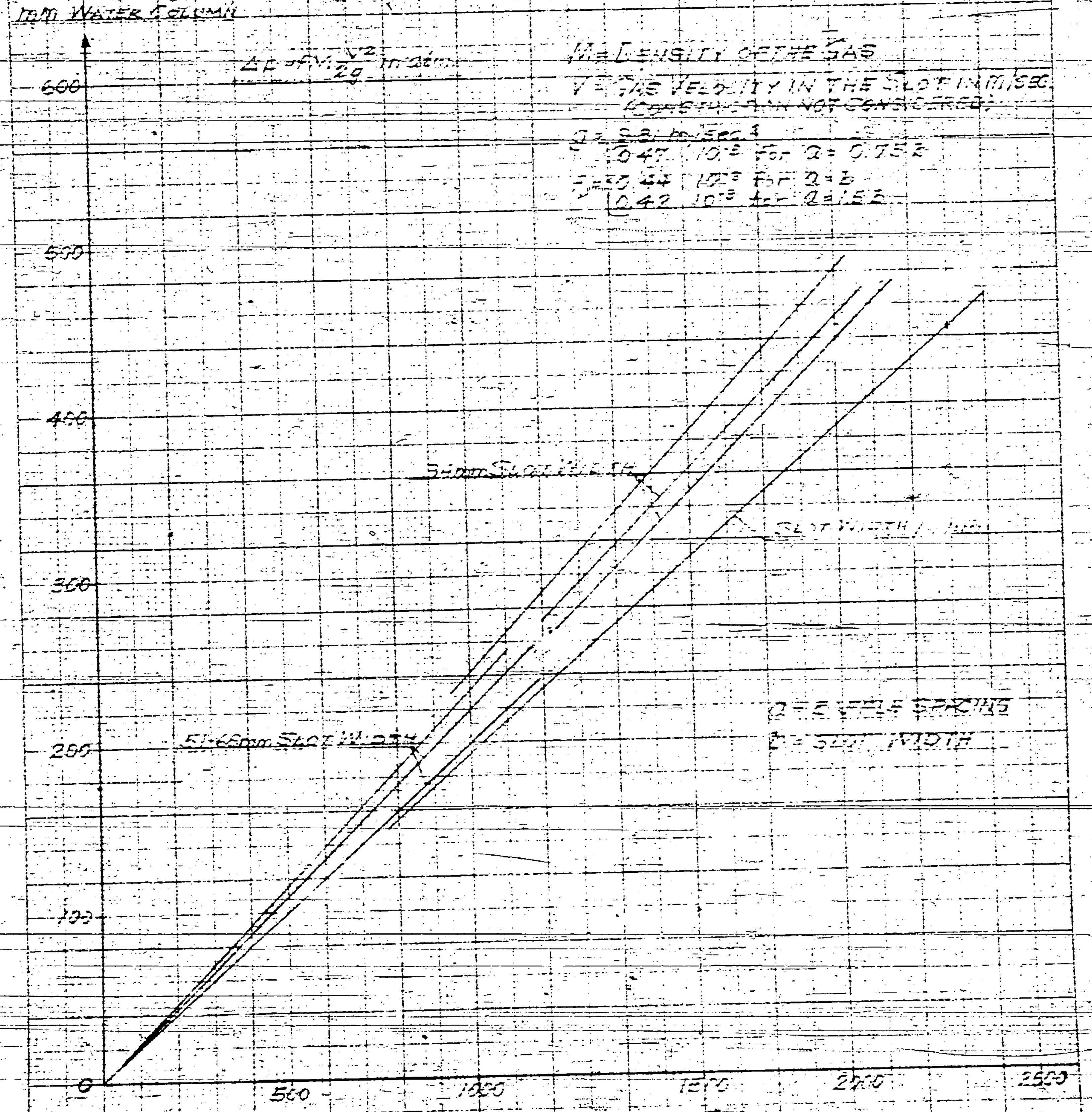


PIPE DIAGRAM.

ALL DEMENSIONS IN MILLEMETERS

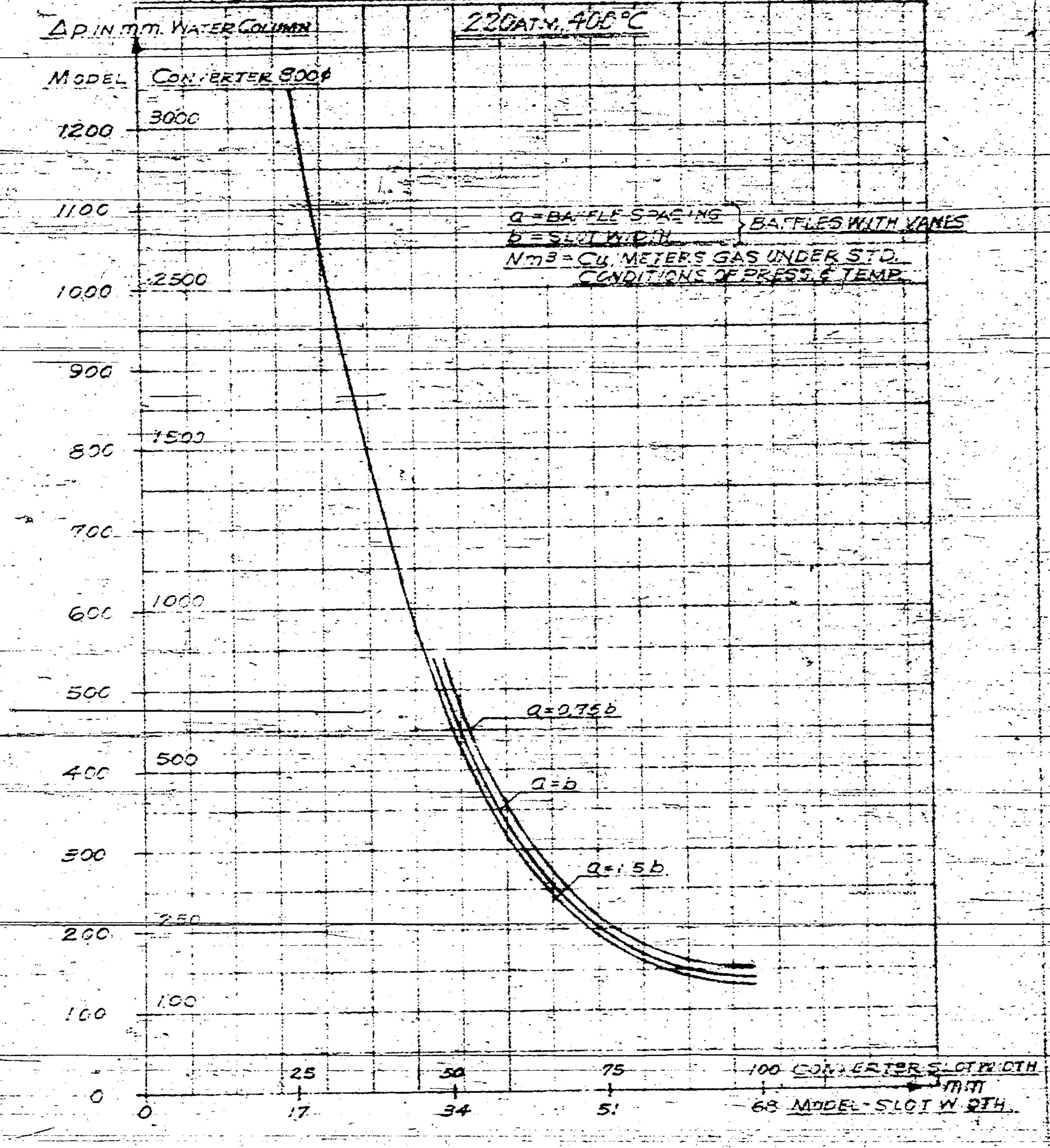
APPENDIX 5

## RELATION OF THE BAFFLE RESISTANCE ΔP TO THE PRODUCT MV²



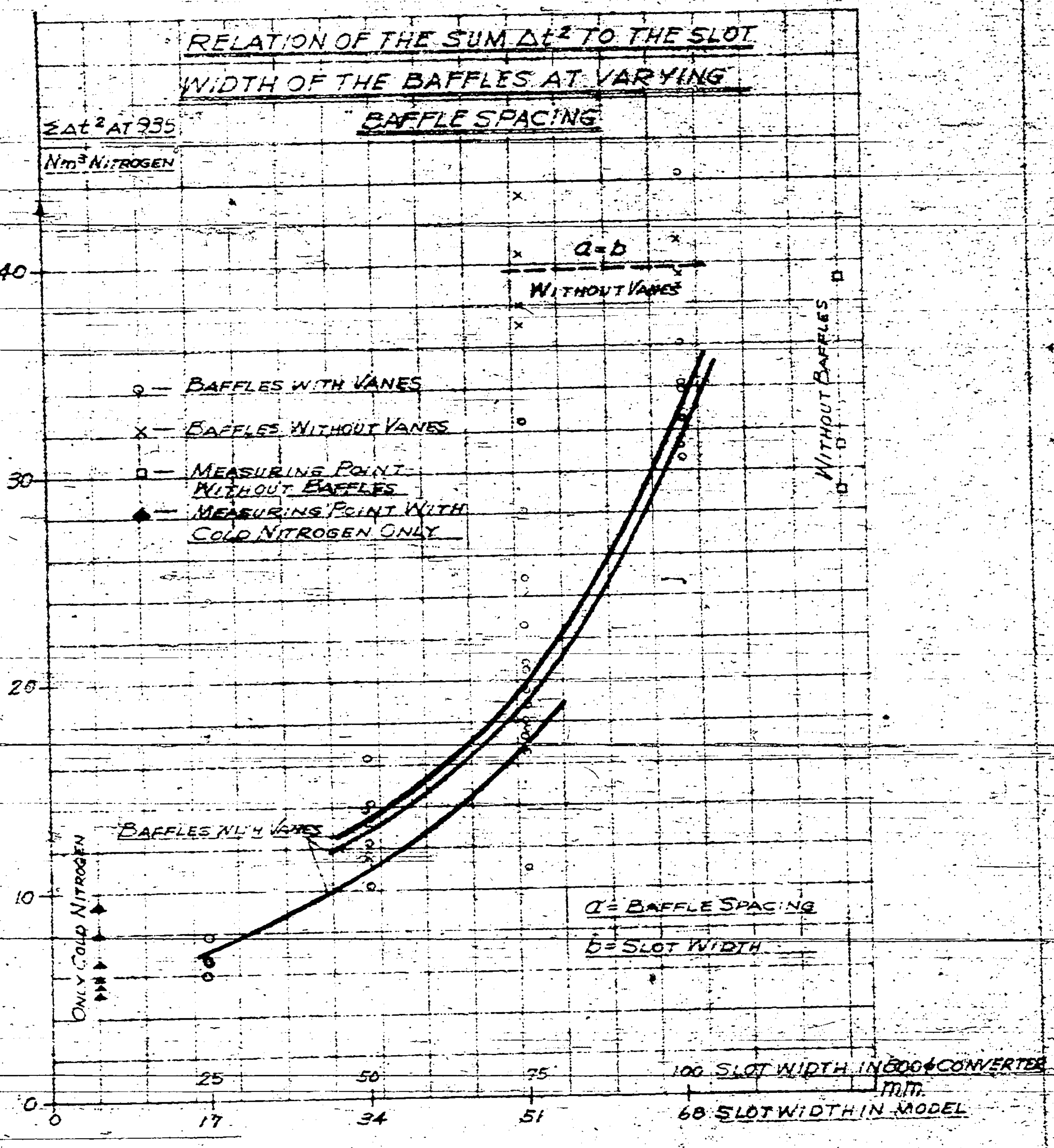
## PRESSURE LOSS IN THE BAFFLES AT 935 m³/h

NITROGEN 1 ATM, 20°C OR 30000 Nm³ GAS & 25 m³/h INJECTION,



APPENDIX-6

# APPENDIX 7



RELATION OF THE SUM $\Delta t^2$ TO THE SLOT WIDTH OF THE BAFFLES AT VARYING BAFFLE SPACING

T. O. M. Reel 9 U. S. Bureau of Mines T-121
pp. 356-365 July 17, 1942
Hydro. Dem. Plant Div.

## Discussion of Two Accidents in Politz

A bad accident occurred on June 26, 1942 in Politz, which caused 7 deaths, and a second one on June 28, with the loss of two more lives.

## Description of the Accident of June 26.

The conditions at the plant were as follows: All the 700 atm. liquid phase stalls were in operation, stall II operating with petroleum, stall 12 on tar, stalls 13 to 16 on coal. The liquid phase stalls are serviced by 3 gas circuits of 120 mm i.d. The accompanying picture shows schematically the arrangement of the circuits with the circulation pumps, stalls and oil scrubbing. Circuits I and II have been in operation since the end of the preceding year, and during that time have been alternately repeatedly stopped and started with no trouble. Circuit II was idle for six months because of repairs and was to be put in use. The circuit was flushed, blown out and filled on the preceding day. The valves 1 were carefully opened and the pressure on the pressure side equalized with the circuits 1 and 2 thru the by-pass around the valves (penciled question mark in the original). The opening of valve 3 consumed about 1 hour, and shortly afterwards the gas inlet gauge indicated a reduction in feed, and the cold gas feed went off. Converter II temperature increased from the normal 25 mv to about 27 mv. The gas inlet and the cold gas valves were turned off and shortly after that changed over to pasting oil. The temperature rose to about 40 mv. and operations of disconnecting stall 16 and opening safety valves were begun. After the valves in the pipe lines to and from the circulation were closed, gas suddenly rushed in again. The 120 mm connection pipe to converter III burst shortly afterwards above the converter and several pieces were strewn around. One of these pieces broke thru the upper part of the 8 cm thick connecting wall to stall 15 and hit there a 58 mm i.d. cold gas intake pipe, which was torn off. Gas from stall 15 streamed over the stall wall almost horizontally and reached the service gang of the open upper part of the paste press unit about 40 m. away, where the paste is screened and the storage tanks for the presses are located. The gas exploded with a flame about 80 m. indepth. 7 men working at the top of the paste pump unit were fatally injured.

The windows in the upper parts of the structures were blown out inward, in the lower part outward, which has led to the conclusion that the explosion took place above the stalls with the formation of suction near the floor.

PRESUMABLE CAUSE

The shut-off valves between circuits 2 and 3 are at a distance of about 50 m from the gas inlet of the last stall, I. It is assumed that when circuit III was put into use, the liquid, possibly contaminated with dirt, most probably from the 50 m long dead end, was pushed against the gas inlet into stall 16. Coal paste has actually been found in places indicated with arrows. This interrupted for a short while the gas path thru the intake valve and the cold gas valves, which were greatly throttled; a drop in gas intake although a considerably smaller one, was also established in stall 15.

THE ACCIDENT OF JUNE 28, 1942.

The pressure on stalls 13 and 14 was also released thru emergency valves during the explosion of June 26. The pressure on stall 14 was normally released and later started again, but in stall 13 the let-down oil was insufficient and coking began. The stall was flushed in the usual way and turned over to the repair department. The blind slides were inserted in the gas inlet and outlet. The pipe lines to the different units, such as the converters, catchpot and heat exchangers were already shut off, the thermo-couple protecting tubes removed from the converters (two protecting tubes in each converter) and converters 1 and 2 already put out of operation. Just as the converter was being excluded from operations on June 28, an explosion took place in the stall because of an inrush of gas. Two laborers were killed.

PRESUMABLE CAUSE.

The upper sketch below shows the plan of stall 13 and the arrangement of the units. As far as has been established, gas entered the stall from the corner where the heat exchangers were located. It is not as yet clear where the gas came from; possibly some obstructed tubes in the preheater or cooler came free, which caused the enclosed gas ("hidden pressure") to be liberated. Subsequent investigations have shown that all pipe lines and apparatus in question were unobstructed.

As a result of the two accidents in Pölitz the following immediate measures were taken:

1). In the stalls 13, 15 and 16 in all the vertical piping the 120/191 mm connections will be replaced as soon as possible with 120/229 mm connections. The vertical pipes remain uninsulated. The present connections can be used if strengthened by wickel armature to an outside diameter of 250 mm.

2). When a stall is flushed before being turned over to the repair department, care must be taken to flush each individual unit. To overcome any possible shorting of, say, the heat exchangers, the cold gas inlets must also be flushed. The progress of the flushing gas may be observed by temperature observations. The stall may be turned over to the repair department after these measures have been taken and satisfactory analysis have been obtained, complying with existing transfer regulation.

However, whenever there exist suspicions that the stall had been but imperfectly flushed because of obstructions, especially after trouble in operation, special precautionary measures must be taken before the transfer: attempts must be made to determine, by passing uncompressed nitrogen thru the apparatus, which parts of the stall may be obstructed. Such parts must then be isolated with the greatest precautions by shutting off the proper pipe lines.

3). The walls separating two stalls are being strengthened to 25 cm.

4). Emergency pressure relief must be immediately used even in case of a partial drop in the gas thruput, if the cold gas intake drops simultaneously. According to the present experience, the temperature in such cases rises rapidly to 40 mv., and attempts must never be made to force the gas through.

5). The circulation gas must be introduced into the coal paste thru a nozzle to make it impossible for the paste to enter the gas lines.-

There are some additional precautions to be taken to prevent similar accidents.

To avoid the formation of sections in the circulation lines in which liquids may collect, a suitable connection between the suction and the dead ends must be provided. The amount of gas normally passed thru may be kept very low, e.g. 1000 $m^3/h$; it could however be temporarily increased to equal the thruput thru a stall. The intermediate pressure relief between two shut-off valves must be arranged to permit pressure relief from the liquid in the circuit.-

Each stall must be provided with its own pipe line to the emergency pressure relief tower to permit a rapid let-down.

An automatic temperature control of the principal converter parts would be of service for a timely recognition of "running away" a converter, as discussed on April 13-14, 1942 at an operations control conference.

The stall walls may be protected from being shattered by pieces from burst pipelines by protecting them with iron in a way to permit absorption of a large proportion of the shock. Where a proper strengthening of existing stall walls can not be carried out, the open or unprotected structures in the vicinity must be protected as far as possible from open flames.

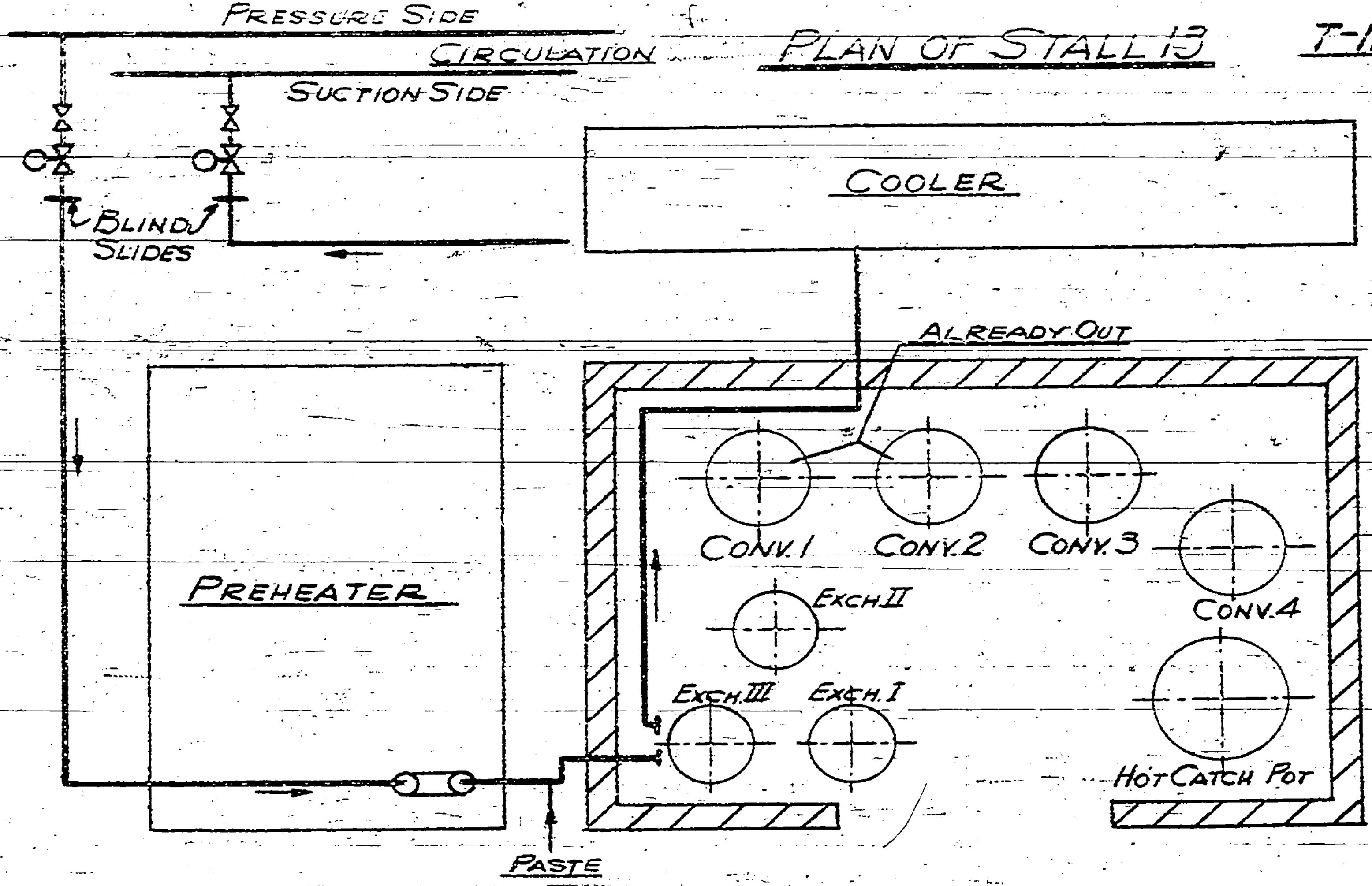
Notes in pencil: Raising stalls 54 and 17, to have the walls of the stalls exceed the height of the converter.

When a large circulation line (?) becomes filled with circulation gas and stands 1 day and cools, the possibility of collecting of larger liquid depositions must be considered. These will be brought in when the stall is started and may cause obstructions in the gas inlet valve.

W. M. Sternberg.

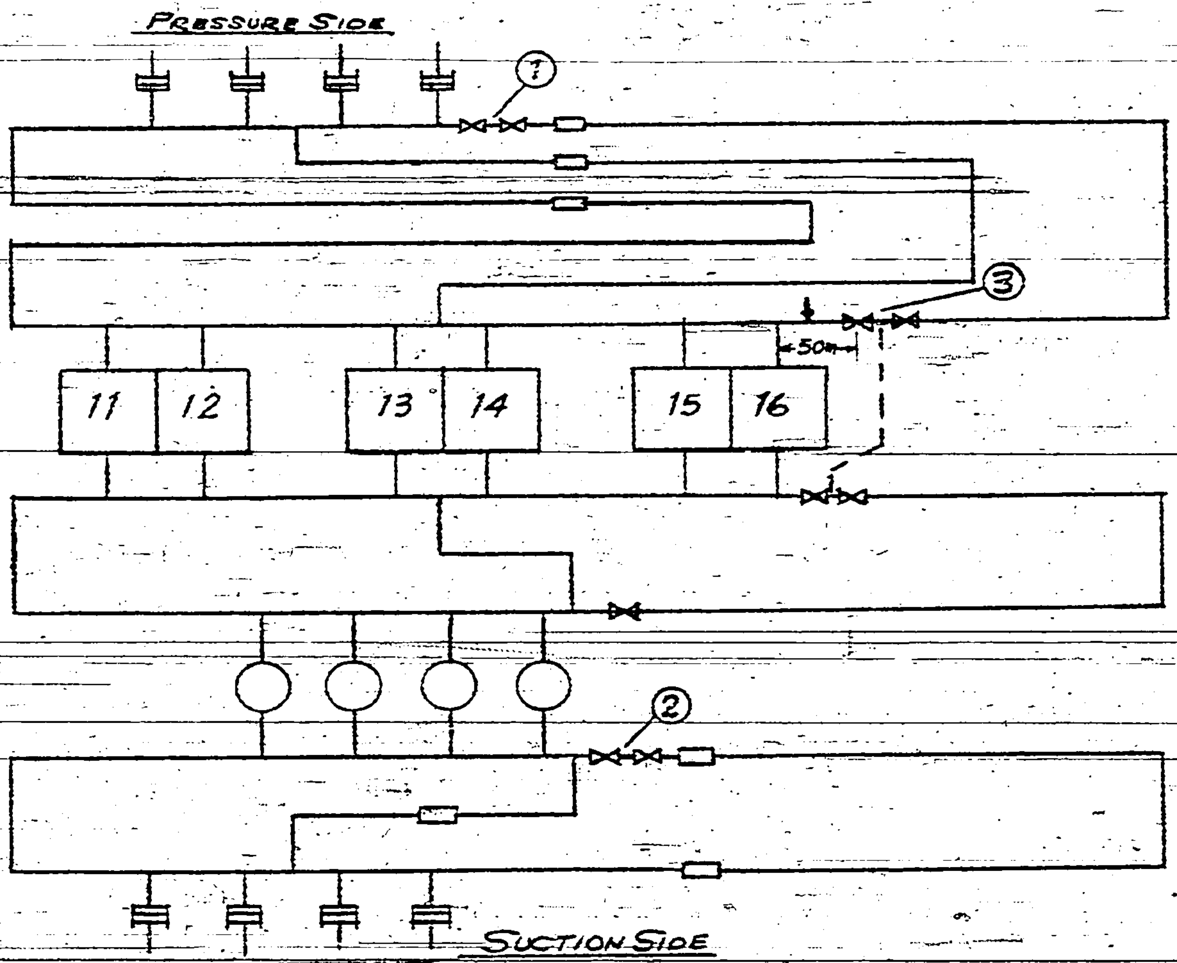
## Plan of Stall 13

T-121



## Circulation Unit of the Liquid Phase Stall in Pölitz

T-121



The Positions ① to ③ Represent the Order of Opening the Circulation Valves of the Converters

T.O.M. Reel 9
Bag 2738
Target 30/4.11
pps. 336-374

U. S. Bureau of Mines
Hydro. Demon. Plant Div.

T-122
Trld-KCBraun
10/4/46

## Experiences with 700 atm. Paste Presses at Bottrop

### By Chief Eng. Richter, Ruhröl - G.m.B.H.

Scholven, 25 April 1939

The presses were made by Maschinenfabrik-Esslingen in 1936, to the Leuna design. Their drive is oil-hydraulic with an oil pressure of 25 atm. Their rated capacity is 5 $m^3/h$ at 12 double strokes per minute and a stroke length of 600 mm. The press cylinder is connected to the drive cylinder by 4 rods. I should like to point out a flaw in design of this pump, namely the sharp constriction from the connecting flange to the cylinder proper. (Photo 1, not reproduced).

Before we started operations, tests were made on these presses at Esslingen over a period of 8 days with an extract oil at 150° C. The plungers were furnished by Mannesmann, and the stuffing boxes were cast iron, type Esslingen. (Photo 2, not reproduced).

The trials were satisfactory and we started operations.

The operating pressure is 620 atm., and the temperature 145° C. The injected feed contains about 8% solids. The plungers were water cooled. It was soon apparent that the cast iron packing was unsuitable, despite several changes and good oil lubrication. Each plunger received 50 liters lubricating oil per hour. The cast iron packings broke and damaged the surfaces of the plungers.

We then tried bronze packing with a Brinell hardness of 66, type Goetze, which proved comparatively satisfactory. In order to gain further experience, we are operating with Thermit packing at present. The arrangement of the packing is shown in photo 3.

Besides the packing, the plunger material is still causing us trouble. The Mannesmann plungers have not been satisfactory. The plungers, photo 4, have an outer diameter of 88 mm, a bore of 50 mm, length 1200 mm, an elastic limit of 33.6 $kg/mm^2$, and an elongation of 24%. The pressure load is 925 $kg/cm^2$, which is very high. The material is not suitable for such alternate stresses.

As shown in photos 5, 6, and 7 (not reproduced), all the breaks occur from the inside to the outside. The reason for this is that the cooling water heavily corrodes the plungers, poorly finished on the inside, and initiates the fatigue failures. The plungers are largely eccentric and poorly finished on the inside. Some months ago, we substituted a drilling oil emulsion for the cooling water, but plunger breaks continue to occur.

We then used cast plungers on the advice of Maschinenfabrik Esslingen, the same material used by them for crank shafts of diesel engines. Their low surface hardness of 245 Brinell is detrimental, but, as far as we have been able to determine, their life is at least as long as that of the Mannesmann plungers.

Besides that, we have tried nitrited plungers, 500-600 Brinell, which have, so far, given excellent service. We believe that they will prove economical, in spite of their high cost, which is about twice that of the cast iron.

The operating periods of the plungers and packings are still fluctuating between 700 and 2000 hours.

We had another very bad experience with the press cylinders proper. After about 3,000,000 load changes one of the 4 cylinders broke in a drilled bolt hole on the suction side. We are, therefore, forced to change the cylinders of our 4 presses one after another. The new construction is shown in photo 9. It has also been pointed out that the 4 rods connecting the drive cylinder with the press cylinder are too weak. We have measured the deformation of some of these rods in operation and found that due to the bending of the press cylinder flanges the tension rods were bent 0.4 mm, corresponding to a stress of 400 kg/cm$^2$, which is still within the permissible limit.

Materials in a 700 Atm. Stall:

We have been using N8, N10 and V2AED materials in the preheater and the stall and have had no difficulty to date, although the tube-wall temperature in the gas preheater is 520° C. and in the connecting lines 485° C., at a pressure of 600 atm. The bellows-seal connections of N8 have been very successful, although with extreme care because of the expansion and contraction of the lines. The high pressure valves furnished by Ludwigshafen, including the much used cold gas valves, have been satisfactory, except that excessive wear occurs when fluids containing some gas dissolved in it are released, as in the release of the hot catch pot. We are trying to decrease this wear by the use of throttling disks (Drossellinsen).

In general it may be said that the 700 atm. operations provide no basic difficulties.

Newman

T.O.M. Reel 181
Frames 6554 - 6566

U. S. Bureau of Mines
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T-123

# Development of the Liquid Phase Previous to 1933.

October 22, 1942.

Poison-proof catalysts for the reduction of phenols have been discovered by the end of 1924, and attempts have been made in January 1925 to hydrogenate brown coal with a fixed bed catalyst. Tar has been then successfully converted into gasoline with no coking at very low partial pressures of the feed and with small throughputs. When converting to pilot-plant operations, with the necessary increase in partial pressure and throughput, the output of the catalysts rapidly declined, because of the deposition and condensation of high molecular weight materials upon the surface of the catalysts. This has necessitated the subdivision of the process into two parts, the liquid and the vapor phase. In the liquid phase, the higher boiling, or higher-molecular weight, feed was broken down with finely divided catalysts into middle oil with a boiling point 325 to 350° C, and the oil could be converted in the vapor phase with fixed bed catalysts into gasoline.

The first industrial catalysts used in the liquid phase were K 2500 (tungsten-magnesia) and 3510. The catalyst was used, as in the vapor phase, in high concentrations (25 - 30% of the converter content) in such a way, that the converter contents were pumped over with enough make-up feed to compensate for the products formed. Make-up catalyst was added after the reaction slowed down, and the used catalyst was withdrawn.

When coal was to be used, neither the use of fixed bed catalysts nor the repumping of the converter were questioned, chiefly because the ash, unused coal and therefore also the catalyst were constantly removed from the reaction space. For that reason coal, brown coal at first, was saturated with the catalysts, such as ammonium molybdate.

Two methods of operation were used at first. Attempts have been made to introduce pre-dried coal into converters with the aid of presses or screw conveyers, while in an other method coal was made into a paste with oils or tar, and pumped in as a paste. The dry coal feed was shortly discontinued, because it has been found to be technically very difficult, and it permitted a very poor utilization of the high pressure space. The recovery of the costly tungsten and molybdenum from the residue had not been perfected, and the use of the catalysts had to be omitted in large scale production. High thruputs of the paste were then considered necessary. Tests with German coal made in 1929, as well as the tests performed later by the I.C.I., showed that lowering of the paste throughput improved the utilization of the coal, as well as the quality of the product (primarily a reduction in the asphalt content). With low throughput with brown coal it was found that good results were also obtained with economically permissible amounts of catalysts, i.e. 0.02% $MoO_3$ calculated to coal, with which the recovery of the catalyst became no longer a necessity. Utilization factors of 95% have been obtained with brown coal, while when working with no catalyst a maximum utilization of 70% was reached. The unfavorable action of the alkaline ash upon the molybdenum catalyst could be overcome by the addition of sulfuric acid to the brown coal. This resulted in still further improvements in utilization and asphalt content, in the phenol content and in splitting, as well as in the lowering of gasification. This progress in the development in Leuna resulted in a material reduction of difficulties in the utilization of the asphalt-containing hydrogenation residues.

Neutralization with hydrochloric acid in laboratory tests showed an additional advantage. This was the result of the addition of chlorine in the form of $NH_4Cl$ during the hydrogenation of coal, with molybdic acid used as a catalyst, which was subsequently replaced with tin oxalate. This combination of catalysts was first used on a large scale in large scale tests with English coals in Ludwigshafen.

The results found in the hydrogenation of coal were applied to the hydrogenation of petroleum and tars in the liquid phase by distributing molybdic acid upon neutralized grude, and adding small amounts of it to the tars or oils. This permitted an additional change in the method of operation by discarding the repumping of the converter contents, and continuously removing the used up catalyst together with but a small amount of the heaviest oils from the reaction space. Substantial yields were obtained with tars and oils as well. This process has been made use of in Leuna when operating with Volkenroda and other German oils, partly mixed with brown coal tar.

All this work was carried out at a pressure of 200 - 300 atm, and a temperature of 420 - 480° C.

Ludwigshafen investigated in small as well as in large scale tests the hydrogenation behavior of typical German brown coal and soft coal, as well as American and Dutch mineral oils and a greatest variety of brown coal and coal tars. Characteristic differences were found with the different raw materials, because the liquid phase hydrogenation modifies only partially the character of the raw material, and their structural characteristics remain to a large extent unaltered.

## TABLE 1.

| Middle oil from: | Coke oven tar | Long-flame coal | Brown coal | | Low Temp. coking tar from brown coal | Mineral oil, asphalt base |
|---|---|---|---|---|---|---|
| | | | Low-Bitum. | High Bitum. | | |
| Ultimate Analysis: | | | | | | |
| % C | | 86.3 | 85.9 | 85.7 | 87.45 | 87.4 |
| % H | | 9.5 | 10.5 | 10.6 | 11.81 | 12.0 |
| % O | | 3.0 | 3.1 | 2.7 | 0.37 | ) |
| % N | | 1.1 | 0.8 | 0.6 | 0.20 | )0.94 |
| % S | 0.2 | 0.09 | 0.01 | 0.4 | 0.17 | ) |
| g H/100 C | 9.5 | 11.0 | 12.0 | 12.4 | 13.5 | 13.7 |
| % phenols | 5 | 16 | 21 | 13 | 0.6 | Traces |
| aniline point of the phenol-free middle oil | -20° | abt. -15° | +6° | +34° | +41° | +41° |
| Spec. Grav. | 0.980 | 0.942 | 0.908 | 0.900 | 0.889 | 0.876 |
| 50% point | 240° C | 250° C | 250°C | 255°C | 275°C | 245°C |

The hydrogen content referred to 100 g. C rises from 9.5% with coke oven tar to 13.7% for low temperature coking tar from brown coal. A higher-hydrogen raw product is obtained from the oxygen-richer middle oils, as can be seen by comparing richer-bitumen brown coals with the lower-bitumen brown coals. The relatively high oxygen content of the middle oil is caused by their high phenol content. Differences in raw product are also very plainly mirrored in the aniline point of the middle oils. It rises from -20° with coke oven middle oil to +40° C with petroleum middle oil. Half the middle oils will boil over at around 250°, with the middle oil from the lowest-hydrogen oil at the lowest temperature.

The relationship between the hydrogenation products of the liquid phase with the raw materials finds, an expressions in that the oil liquid phase products from the oil residues of straight run products are very similar inside the same boiling range. The following table shows this on an example of an asphalt-base crude oil.

## TABLE II.

| | Distillation Products of an asphalt base crude oil | | | Liquid phase hydrogenation products from the heavy fraction of the same asphaltbase crude oil | | |
|---|---|---|---|---|---|---|
| | Gasoline | Middle oil | Heavy oil (residue) | Gasol. | Middle Oil | Heavy oil distillate |
| Ultimate Analysis | | | | | | |
| % C | 84.9 | 85.6 | 83.8 | 85.2 | 87.4 | 87.8 |
| % H | 14.8 | 12.7 | 10.2 | 14.7 | 12.0 | 9.9 |
| % O | 0.0 | 0.0 | 0.76 | 0.0 | ) | 0.2 |
| % N | 0.19 | 0.2 | 0.54 | 0.1 | )0.94 | 0.2 |
| # S | 0.16 | 1.6 | 4.7 | 0.006 | ) | 0.6 |
| g H/100 g C | 17.4 | 14.8 | 12.2 | 17.2 | 13.7 | 11.3 |
| aniline point, °C | +53 | +46 | - | +46 | +41 | - |
| spec. grav. | 0.730 | 0.852 | 1.020 | 0.723 | 0.876 | 0.937 |

The straight run gasolines and the liquid phase products are very similar. However, the middle oil obtained by hydrogenation is somewhat lower in hydrogen than the straight run middle oil because of the small amount of hydrogenation obtained at fairly high temperatures with very little catalyst. The hydrogenation heavy oil differs from the straight run residue in being free from asphalt.

The figures below compare the hydrogen contents and the boiling range, illustrates the different products, tells their differences and the progress of their changes during hydrogenation.

## Distillation and Liquid Phase Hydrogenation Products of Asphalt Base

| | Mineral Oil | | | | | |
|---|---|---|---|---|---|---|
| | Distillation Products | | | Hydrogenation of Heavy Fractions | | |
| | Gasoline | M.O. | H.O. | Gasoline | M.O. | H.O. |
| Spec. Gravity | 0.730 | 0.852 | 1.020 | 0.723 | 0.876 | 0.987 |
| g H/100 g C | 17.4 | 14.8 | 12.2 | 17.2 | 13.7 | 11.3 |
| A. P. °C. | 53 | 46 | -- | 46 | 41 | -- |
| % S | 0.16 | 1.6 | 4.7 | 0.06 | 0.01 | 0.6 |

## Changes in H-Content by Liquid and Vapor Phase Hydrogenation

| | Mineral Oil | Low Temp. Coking of Brown Coal | Coke Oven Tar |
|---|---|---|---|
| Raw Material | 13.5 | 11.8 | 6.2 |
| Distill. M. O. | 15.0 | 12.1 | 7.7 |
| Liquid Phase M.O. | 14.5 | 13.0 | 9.5 |
| V. Phase Gasoline, Much hydrogenated | 17.9 | 17.6 | 17.0 |

## Hydrogenation of Low Temp. Tar From Brown Coal

| | Distillation M.O. | Liquid Phase M.O. from residue of Brown coal tar | Vapor Phase return M.O. |
|---|---|---|---|
| Spec. Gravity | 0.930 | 0.860 | 0.815 |
| An. pt, °C | 23 | 18 | 46 |
| boiling range | 195-325 | 195-325 | 185-285 |
| % phenols | 24 | 5 | 0.3 |
| % S | 1.6 | 1.1 | 0.01 |

Trsl. - W. M. Sternberg

Newman

T.O.M. Reel 181
Frames 6567 - 6572

U. S. Bureau of Mines
Hydro. Demon. Plant Div.

T-124
Oct. 23, 1944

## Development of the Liquid Phase Since 1933

After the hydrogenation of brown coal had reached a certain stage, the center of hydrogenation experimental work was shifted to soft coal. A successful large scale test was performed in 1934 on the hydrogenation of Ruhr flame coal. At the occasion of this test, suitable apparatus was developed for the centrifuging and kilning of the residues of coal hydrogenation industry. Foundations were simultaneously created for the erection of the first soft coal hydrogenation works, which has been started in Scholven in 1936.

Tests with higher pressures in particular with 700 atm, were undertaken in order to apply the hydrogenation coal utilization methods to the older coals as well. The great improvement in the hydrogenation at this high pressure resulted in the use of cheaper catalysts, replacing tin and chlorine. A higher temperature may be used at higher pressures, which in turn resulted in greater utilization of the coal, better yields, lower asphalt content, the latter being particularly important in the utilization of the residue. The gasification is less at 700 atm. in spite of the high temperature, than at 300 atm. Were tin and chlorine also used at 700 atm, instead of iron catalysts, still greater advantages could be gained at 700 atm. These advantages may be seen in table 1, which reproduces results of tests in 10 li converters.

TABLE 1.

EFFECTS OF PRESSURE ON THE HYDROGENATION OF RUHR COAL
(82.7% C)

| Pressure | 300 atm. | 700 atm. | 700 atm. |
|---|---|---|---|
| Catalyst | tin - chlorine | iron | tin - chlorine |
| Reaction Temperature | 465 | 475-480 | 473-480 |
| % Coal utilization | 93 | 96 | 97 |
| Production of oil, k/li/h | 0.18 | 0.27 | 0.32 |
| % gasification Gasification÷(oil + gasification.) | 25 | 21 | 19 |
| Asphalt content of the HOLD, % referred to pure coal | 18 | 11 | 9 |

This development of the hydrogenation of soft coal benefited also the hydrogenation of tars, pitches, cracking residues, etc. 700 atm. have been used for the first time on an industrial scale in Welheim for the hydrogenation of pitch, and in Gelsenberg for the hydrogenation of soft coal.

An examination of the hydrogenation products obtained at 700 atm. (table 2) shows that the character of the material to be hydrogenated is reflected in the products obtained. The hydrogen content of the middle oil increases from coke oven tar to the cracking residues, as does the aniline point; the phenol content corresponds to the phenol content of the original material; the relationships with heavy oils are similar.)

TABLE 2

PROPERTIES OF THE 700 ATM. LIQUID PHASE PRODUCTS FROM DIFFERENT RAW MATERIALS.

| Raw Material | Coke Oven Tar | Soft Coal | Low Bitumen. Brown Coal | Cracking Residues. |
|---|---|---|---|---|
| Middle Oil: | | | | |
| Ultimate analysis. | | | | |
| % C | 88.51 | 87.28 | 86.05 | 87.00 |
| H | 8.95 | 9.54 | 9.37 | 11.07 |
| O | 1.82 | 3.08 | 3.90 | 1.14 |
| N | 0.66 | 1.06 | 0.55 | 0.16 |
| S | 0.06 | 0.04 | 0.13 | 0.63 |
| g H/ 100 C | 10.12 | 10.93 | 10.90 | 12.72 |
| % phenols | 2.5 | 15.3 | 20.1 | 0 |
| A.P. of phenol oil | -25 | -20 | -10 | |
| Specific gravity | 0.988 | 0.974 | 0.962 | 0.907 |
| Heavy Oil: | | | | |
| % C | 90.71 | 89.27 | 88.62 | 88.62 |
| H | 7.46 | 8.26 | 8.40 | 9.46 |
| O | 1.10 | 1.64 | 2.62 | 0.64 |
| N | 0.61 | 0.77 | 0.28 | 0.12 |
| S | 0.12 | 0.06 | 0.08 | 1.16 |
| g H/100 C | 8.22 | 9.25 | 9.46 | 10.67 |
| Specific gravity | 1.053/50° | 1.038/50° | 1.030/50° | 0.994/50° |

The data previously given always referred to the same basis, - the complete coversion of the raw material into gasoline and middle oil. The hydrogenation conditions in this case are very sharply defined, and the hydrogen added is very high. An extreme method of operations with very little hydrogen added is represented by the extraction with coal middle oils which give off hydrogen. All the different hydrogenation methods may be placed between these extreme cases. Depending on the conditions chosen, there is formed chiefly middle oil, heavy oil, or high asphalt bitumens. An intermediate step found application in the development of the fuel oil process, which was done at the request of the Navy to produce fuel oil from domestic materials. Conditions have been successfully found to have plants use high throughputs and produce additional amounts of fuel oil instead of gasoline.

Table 3 shows the utilization of Upper Silesian coal for the production of gasoline and middle oil, compared to two methods for the production of 35% and approximately 50% heavy oil (fuel oil). The difference between the fuel oil process and the gasoline - middle oil process consisted, aside from the high throughput, in a somewhat lower hydrogen absorption. With the same degree of utilization of coal, the oil production is increased 50%, with a lower gasification.

The coal throughput is held within such limits which permit ready overcoming the asphalt formed by the usual methods of utilization of residues, centrifuging and kilning.

The process for the heavy oil production has been first tested on an industrial scale in Ludwigshafen. This test has provided the necessary foundation for the Blechhammer plant and produced the fuel oil to be tested by the Navy. The quality of the products satisfied the requirements of the Navy.

TABLE 3

DIFFERENT METHODS OF HYDROGENATION OF COAL

| Method for: | Gasoline + Middle Oil | Gasol. + Middle oil + little heavy oil | Gasoline + M.O. + much heavy oil |
|---|---|---|---|
| Temperature °C | 476 | 478 | 480 |
| Pure coal thruput | 0.43 | 0.62 | 0.63 |
| Pasting oil | 100% heavy oil | 85% heavy oil<br>15% middle oil | 73% heavy oil<br>27% middle oil |
| Utilization, % | 96 | 95.5 | 96 |
| Total production | 0.26 | 0.40 | 0.41 |
| Composition of oil: | | | |
| % gasoline | 23. | 20 | 21 |
| % middle oil | 77 | 40 | 32 |
| heavy | - | 35 | 47 |
| Gasification % | 23 | 20 | 18.5 |
| Asphalt in heavy oil from HOLD | 14.7 | 18.0 | 19.3 |

A further increase of the thruput resulted in a new process of utilizing the asphalt-containing residues of hydrogenation as binders in the production of coal briquettes. In this way poorly coking coals, for which formerly no binders were available, are transformed into solid coke which can be well utilized in water gas producers. The possibility to utilize the tars obtained in the liquid phase of hydrogenation, results in a combination method of low temperature coking and hydrogenation, as has first been done in the Upper Silesian plant Blechhammer.

The purpose of the so-called extraction hydrogenation is the production of high-molecular weight asphalts as the chief product, and represents the mildest form of hydrogenation among the methods mentioned. In this process, the coal is pasted with middle oil and is hydrogenated with a high throuput with small amounts of hydrogen, producing thus high-molecular weight bitumens, which can be separated from the ash by filtration. These completely ash-less products are valuable raw materials for the manufacture of electrode carbon for the aluminum industry. The extraction hydrogenation differs from the Pott-Broche extraction by the use of gaseous hydrogen at high temperature and pressure. Higher thruputs and yields are obtained than in the extraction. The process is distinguished by the large number of possible modifications in the properties and nature of the resulting products. Depending on the choice of conditions, the proportion of bitumen and the additionally produced light oils may be altered.

Distillation of the light oils from the unfiltered product of the extraction hydrogenation produces a useful binder for briquettes, the so-called anhydrous coal.

We may further mention that when molybdenum became scarce during the war, the molybdenum catalysts were replaced with iron catalysts in the 300 atm. hydrogenation of brown coal, tars and oils.

Signed Rank.

TABLE 4

COMPOSITION OF HYDROGENATED COAL - - -

| Works | Leuna | Rheinbraun | Scholven | Gelsenberg | Pölitz |
|---|---|---|---|---|---|
| Grade of coal | brown coal | brown coal | coal | coal | coal |
| % ash in dry coal | 12.8 | 5.9 | 4.0 | 3.0 | 6.8 |
| V.M. in pure coal | 57.9 | 53.5 | 38.5 | 37.5 | 37.8 |
| % C in pure coal | 71.9 | 68.7 | 82.8 | 83.8 | 81.9 |
| Available hydrogen, g H.100 g.pure coal | 4.1 | 2.4 | 4.5 | 4.6 | 3.9 |

## TABLE 5

## PROPERTIES OF FUEL OILS

| | Navy Specifications | Hydrogenation Fuel oil from coal. |
|---|---|---|
| Specific gravity | over 1.030 | 1.041 |
| Viscosity/20° | max. 35° E | 15.5° E. |
| Min. heat Value, Kcal/li | over 9000 | 9600 |
| Coking test | below 6.0 | 0.8 |

W. M. Sternberg

T-123

## HYDROGEN CONTENT AND BOILING RANGE

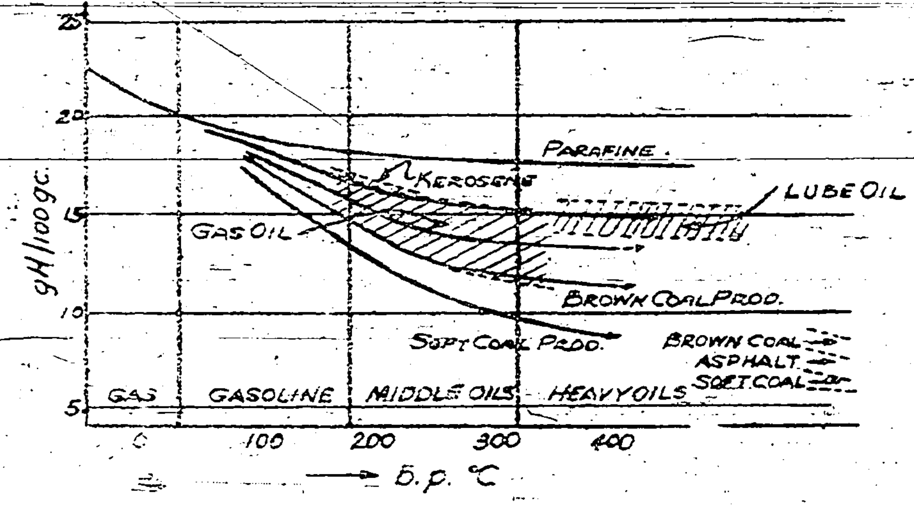


FIG. I

This drawing was inadvertently omitted from T-123. Please attach to copy in your possession.

U. S. Bureau of Mines
Hydrogenation Demonstration Plant Div.

Newman

TOM Reel 5
Bag 2747
Target 30/4.08
Pps. 52-74

U. S. BUREAU OF MINES
HYDRO DEMON. PLANT DIV.

T-125
Trsld KCBraun/jw
10/7/46

# Investigation of Occurrence and Avoidance of Fatigue Breaks in Machine Parts at Gelsenberg

The high loads on the machines at Gelsenberg have caused many breaks since the start of operation. Numerous investigations into these breaks by the I.G. laboratories have indicated that they were due to fatigue almost without exception.

## A. Investigations of Materials:

The investigated machine parts were in all cases made to VC Mo 125, corresponding to DIN-provisional standard 1663. The later investigations showed conformity to the stresses and chemical composition of the materials provided for in the standards, except one press body made of special steel. The parts were heat treated to a strength of 50-60 kg/mm$^2$ and a minimum elastic limit of 30 kg/mm$^2$. Elongation and reduction in area, as well as notched-bar impact values, were fairly high, with some exceptions. The press bodies, damage #6, varied considerably from the standard in the chromium and molybdenum contents, 0.47% Cr and 0.02% Mo; supposed to be a special steel. But in this case, also, the mechanical materials test values were within specifications, so that it was assumed that the analysis did not effect the durability.

Investigations into the structure showed, in most cases, small cracks squarely through the grains, occurring more or less frequently. These fine cracks were identified as flaking cracks. They occurred preferably within the range of the segregations, mostly small in themselves, though they also occurred outside of the segregation zone. It should be mentioned that in several later investigations of broken parts no flakes were found.

Generally speaking, it might be concluded from a compilation of the mechanical or metallographic investigations so far conducted that, in order to avoid fatigue breaks, the repeatedly observed fine cracks or segregations must be avoided. But how this is to be accomplished, or if there was a causal relation at all between the flaws and the breaks, is not shown in the reports. It might well be argued that the fine cracks are the result and not the cause of an over-stress and that this stress will then naturally appear at the weakest points of the structure.

In any case, these careful investigations led to no diminution of the damages. Irregular spots and even local loosening in steel can not be entirely avoided, but they are detrimental only when they are on or near the surface and in an unfavorable relative location to the points of maximum stress. We, therefore, tried another angle in order to get a picture of how far the weak points of the construction, in themselves or in connection with the tendency to failure of the material, influenced the number of breaks. For this purpose, we made a count of the weak points based on the reports of damages. The result of this investigation is compiled separately for the individual machine parts in the following chapters.

## B. Weak-Points Investigation:

### I. Stuffingbox Housings for Paste Presses.

### Number of load changes endured.

A total of 21 stuffingbox housings were damaged. Examination of the damaged parts indicated fatigue breaks in all cases. In order to separate the breaks into those caused by a steady load and those caused by an intermittent load it was first necessary to determine the number of load changes endured up to the break. Fig. 1 shows the life in operating hours with a conversion scale for the number of load changes, calculated on the assumption of 450 load changes per hour, arranged in the order of frequency of occurrence. The life duration is scattered very broadly between 500 and 20,000 operating hours, corresponding to 200,000-10,000,000 load changes. These load changes are still within the range of the fatigue strength usually observed in fatigue breaks due to steady load. This range may be assumed to extend up to 10,000,000 in construction parts, while in simply formed test bars at steady load no breaks normally occur after a few million load changes. It may, accordingly, be assumed that the normal operating load on any part of the stuffingbox housing of present construction and of presently used materials is within the range of the fatigue strength, that is, already so high that fatigue breaks must be expected.

### Intensity of Stresses:

Calculating the stress @ 700 atm. of hollow bodies according to the theory of form change energy gives a maximum tangential tension of over 16 kg/mm$^2$ on the rim of the inner surface of the stuffingbox housing, which decreases to 4.7 kg/mm$^2$ on the rim of the outer surface. Compared to the stresses usual in machine construction, which normally include a high safety factor, these stresses must be considered very high, even though they are still within the fatigue strength values of test bars of uniform cross-section. The fatigue strength of the machine part can not be calculated within reasonable accuracy. It is also probable that the local stresses are higher, though very little higher, than the fatigue strength of the part, the comparatively high number of load changes endured indicates that. However, according to experience, the lower the stress above the fatigue strength, the greater the range of life duration. This explains why certain parts last longer than others. Small variations, in the loading, variations in the depth of notches, or small surface flaws, in such cases are the deciding factor of shorter or longer life.

## Count of the Weak Points:

For the experimental selection of parts best suited for special purposes, the principle of the weak point count, that is, in this case, the determination of the location of the most frequent breaks, has been verified. In the 21 damaged stuffing boxes only longitudinal cracks occurred, of which 17, or 81% of the total, were through the lubricating oil hole. In 2 cases, or 9.5%, the cracks barely missed the oil hole, in one case it was on the side, in another case on the bottom, of the stuffing box housing, figure 2. In all cases the break is wider on the inside than on the outside though it never extends over the full length.

These findings point to a relation between the oil hole and the location of the breaks. However, the notch effect of the hole alone can not be the main cause, since, in that case, no cracks should occur close to it, but all would run through it. It was, therefore, to be expected that some other fundamental cause related to the hole influenced the break. Since the stuffing box housing reaches a temperature of about 120° C. in operation, while the lubricating oil, at about 30° C., enters the stuffing box comparatively cold, the effect of an unfavorable temperature distribution must be assumed. Even if the temperature difference is not very great, it will, nevertheless, have a deciding influence on the durability, in conjunction with the mechanical notch effect of the hole and the variable inner pressure.

## Remedial Measures:

Even the operating department admits that the flushing oil admitted through the flushing oil hole would suffice for lubrication. The suggestion was, therefore, made to forego the lubricating oil supply and eliminate the oil hole entirely in new machines. After adopting this measure, only 2 breaks have occurred on the present machines, and none at all on new machines on which the oil hole in the stuffing box housing was omitted, after approximately 6 million load changes.

An additional suggestion was intended to lower the tangential stresses causing the breaks or to distribute them more uniformly over the cross-section. Experience in the building of gun barrels, subjected to high internal gas pressure, and therefore similarly stressed, has shown us that a more uniform distribution of stresses is obtained by sub-dividing the cross-section and shrinking on the constituent rings, figure 2. If we assume that the inner surface of both halves be equally stressed, the stress on the inner rim of the box is reduced from a maximum of 16 kg/mm$^2$ to 10-11 kg/mm$^2$, where the calculated required absolute shrinkage is only 0.067 mm. With this reduction in the dangerous rim tension considerable improvement in durability is to be expected.

## II. Press Cylinders for Coal Paste Presses:

Seven breaks in press cylinders have so far occurred. Their life, at 2400 to 23660 operating hours, corresponding to 1 to 10.5 million load changes, is on the average considerably greater than the stuffing box housings, see figure 1. The breaks are still within a range of load changes which justifies the assumption that they are due to normal operating stresses, considering the effect of wear and corrosion.

### Weak point count:

All of the 7 breaks in the cylinders indicate a comparatively long longitudinal crack, extending from the inner to the outer surface, narrowing down towards the outside. In 3 cylinders the crack is at the rounded base of the flange on the side of the eccentric coal inlet. In 2 other cases the crack is more towards the middle but still close to the preceding main weak point, so that 2/3 of the press cylinders broke near the same point, figure 3. A similar crack occurred in the side wall proper and the 7th in the lower inside edge but did not extend to the outside.

It is remarkable that the side wall cracks occurred only after a very high number of load changes or the highest so far experienced before a break, while with one exception, the break in the main weak point occurs much sooner.

### Remedial Measures:

The clustering of the cracks on the upper, and their absence on the lower, side point to a one-sided loading of the cylinder. This unsymmetrical loading may be explained by the eccentric location of the inlet and outlet openings for the coal paste. There is no reason why these could not be arranged concentrically.

However, with such an rearrangement breaks in the side wall could still occur, though these occur, as shown in the foregoing evaluation, less frequently and then only after a much greater number of load changes. In general, this would constitute a basic improvement in safety and durability.

A more thorough elimination of the breaks could be obtained, just as with the stuffing box, by shrinking on and outer over an inner cylinder, which would greatly reduce the tangential stresses.

## III. Valve Head of the Coal Paste Presses:

Three breaks have occurred here after 130,000, 4 and 5 million load changes, respectively. Two broken valve heads show the same point of break, a crack extending from the inner sharpest corner of the hollow space to an adjacent threaded hole, figure 4. It was probably caused by the sharp corner, so unfavorable for high pressure flow.

### Suggestion for Improvement:

The coal paste is sucked into the valve head from a line perpendicular to the suction cylinder and forced through an opposite outlet opening. In the valve head, therefore, 2 lines join a third line at right angles. Besides the sharp corners formed by this junction, this causes an unfavorable flow condition for the coal paste, which makes a right angle turn at every stroke. It is suggested to arrange suction and discharge at an angle less than 90° to the valve axis, which will result in less sharp corners, figure 4. Even a comparatively small departure from 90° will permit a better rounding off of the dangerously sharp edge.

## IV. Pump Body of the Press Pump.

### Number of Load Changes

Sixteen pump bodies on the press pumps have so far been broken, of which 10 operated at 300 atm. and 6 at 700 atm. Their construction is practically identical. Their life, at 100 to 3000 operating hours, is less than for any of the parts discussed so far. But since the number of hourly load changes is greater, 5100/h, the number of sustained load changes, 500,000 to 15,000,000, is just as great and as variable as in the broken parts of the coal paste presses, figure 5. It should be noted, that the life of the bodies working at low pressures tends towards higher values.

The weak point count showed cracks, which with but one exception, originated at the inner edge of the hollow space of the pump body, figure 6, while their exact location along the inner edge varies. Of a total of 19 cracks 7 (37%) occurred at one edge of the suction valve space, while 4 (24%) occurred at one edge of the valve seat. No rounded surfaces are provided on the drawings for the inner edges of the valve spaces. The drawings merely note that all sharp edges should be rounded off by hand. But since these edges represent points of local peak loads on the already heavily stressed inner space, rounding off the edges by hand is not good enough, special tools must be used to provide a spherical hollow space.

Suggestions for Improvement:

Assuming that the pressure valve will operate satisfactorily in a horizontal position, the pump body can be made simpler, better suited to resist the strains on it, and more favorable to the flow, see bottom figure 6. In this proposed construction the pressure oil passes through the pump body in only one direction, instead of the old right angle flow, with only 6 corners, instead of the former 9, which, at least in part, offer more favorable conditions for rounding off by direct connection of larger bores. It is to be expected that this suggestion will eliminate at least part of the recognized weak points, and considerably ameliorate others. In addition, by simplifying the body, it measurably reduces its cost.

The operating department had proposed to reduce the high tensile stresses on the inner surface of the pump bodies by artificial surface hardening. However, the effect of such surface hardening is soon dissipated by wear and corrosion because the hardening does not penetrate deeply enough. Also, at temperatures of over 500° C. the beneficial effect of the surface hardening is soon destroyed, nor is such a surface treatment able to resist, for long, the high alternate impact stresses from zero to a maximum.

## V. Flushing Oil Press Cylinder:

### Number of Load Changes:

The 6 broken press cylinders of the flushing oil presses so far investigated showed a life duration between 700 and 9000 operating hours up to the break, figure 7. With a load change of 720/h, this corresponds to 500,000 to 6,500,000 load changes, or about the same as most of the parts discussed so far.

### Weak Point Count:

In all but one of these breaks, or 83%, the cracks occurred on the edges of the inner space, figure 8. Since the cylinder is symmetrical, the damaged points of the right and left half may be combined. The sharper lower edge accounts for 50% of the breaks, the upper edge for 33%.

Suggestions for Improvement:

This condition can be considerably improved by an increased radius of curvature of the spherical surface or by relocating the valve bore. This will necessitate increasing the depth of the cylinder, so that there will be enough material left between the inner space and the threaded holes, figure 8. In any case, an increased life of the cylinder may be expected from this change. Since the number of load changes endured before the break have already reached the limit, above which no breaks occur with the same operating load, it is quite possible that this threshold value may already be exceeded by this small change in shape, and that breaks will then occur only in rare cases with a combination of several unfortunate circumstances.

## VI Stuffing Box Housing for Flushing Oil Presses:

### Number of Load Changes

The operating life of the broken boxes vary between 8000 and 12000 hours or between 5,500,000 and 8,500,000 load changes, which is in the upper range of the broken parts previously discussed herein.

Damaged Points:

Three stuffing box housings have been broken so far. These breaks were similar to those on the stuffing boxes for coal paste presses, figure 3, though they were not bunched at any particular point. Their cause may be assumed to be the same, that is, high tangential tensile stresses on the inner rim of the bore.

Suggestions for Changes:

The suggested remedy for these boxes is the same as for the coal paste press stuffing boxes, that is, a shrunk-on outer over an inner cylinder for better stress distribution.

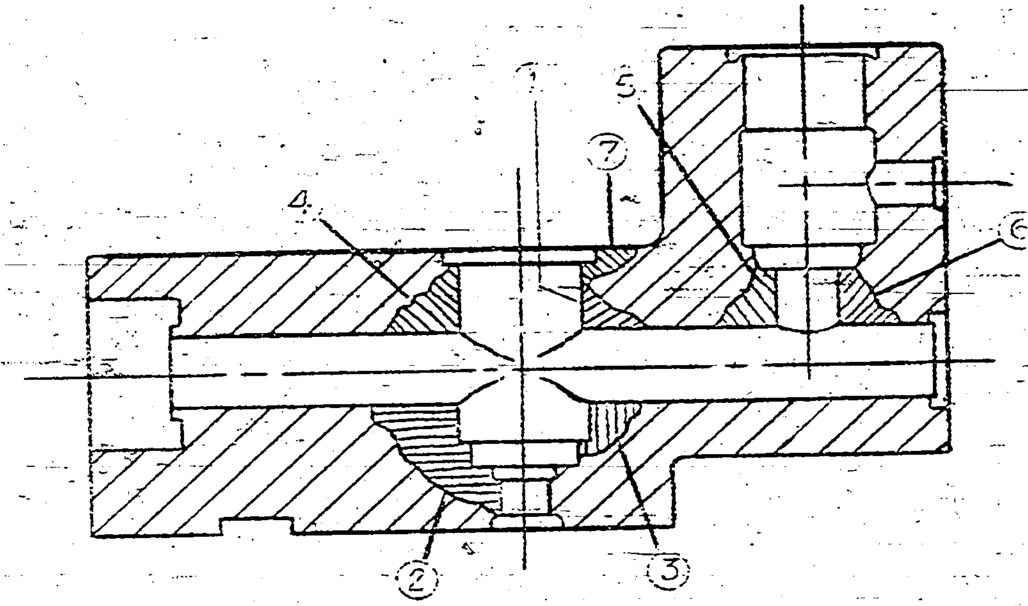
Summary:

The former method of metallographic investigation of materials merely confirmed the visible existence of fatigue breaks, and sought their cause in each individual case in local slag inclusions or flakes. Accordingly, relief could only be obtained by better materials, which gave us little consolation, since flawless materials do not exist.

On the contrary, the present investigation was based on the observation that breaks in similarly shaped parts often occur at the same place, and tried to find the points of greatest danger by a weak point count, that is, the points at which breaks occurred most frequently, in order to determine by this method the form and direction of the most severe operating strains. This resulted in suggestions for changes in construction, which would give longer life even when using existing materials.

The proposed changes are at present on trial. No breaks have occurred so far on any parts in operation on which the suggested changes have been made, but the final judgment must await more extended operating experiences.

## Weak Point Count on Pump Bodies of Press Pumps



| | Number | % |
|---|---|---|
| Crack at Point (1) | 7 | 37 |
| " " " (2) | 4 | 21 |
| " " " (3) | 2 | 10.5 |
| " " " (4) | 2 | 10.5 |
| " " " (5) | 2 | 10.5 |
| " " " (6) | 1 | 5.2 |
| " " " (7) | 1 | 5.2 |
| Total | 19 | 100 |

## Suggestion for Improvement

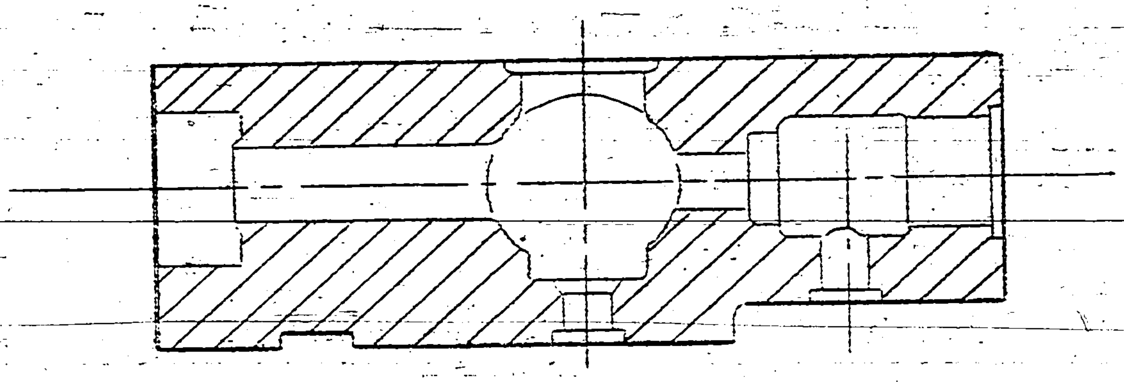
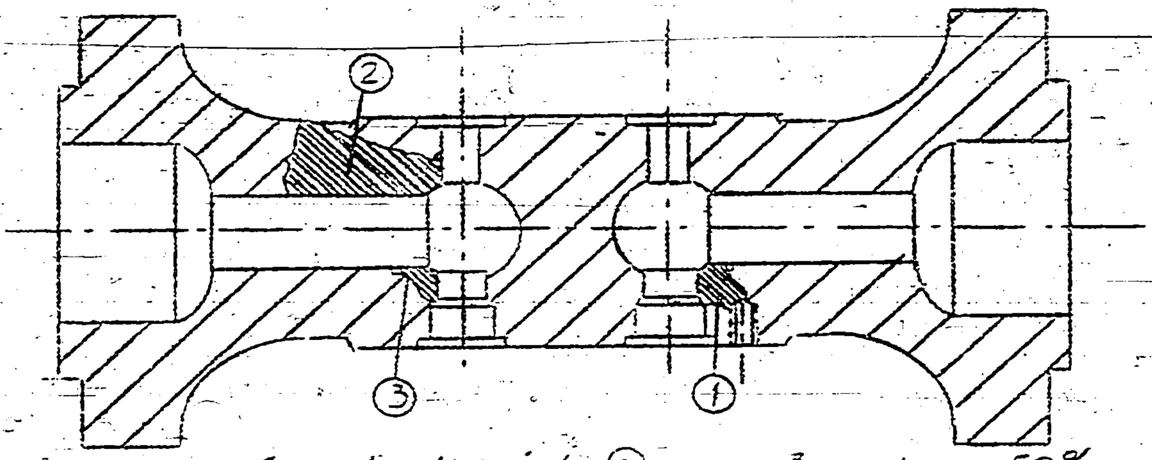


FIG. 6

# Weak point count on press cylinders of flushing oil presses



| | | | |
|---|---|---|---|
| Crack at point | ① | 3 | 50% |
| " " " | ② | 2 | 33% |
| " " " | ③ | 1 | 17% |
| | Total | 6 | 100% |

Suggestion for improvement
Point 1.

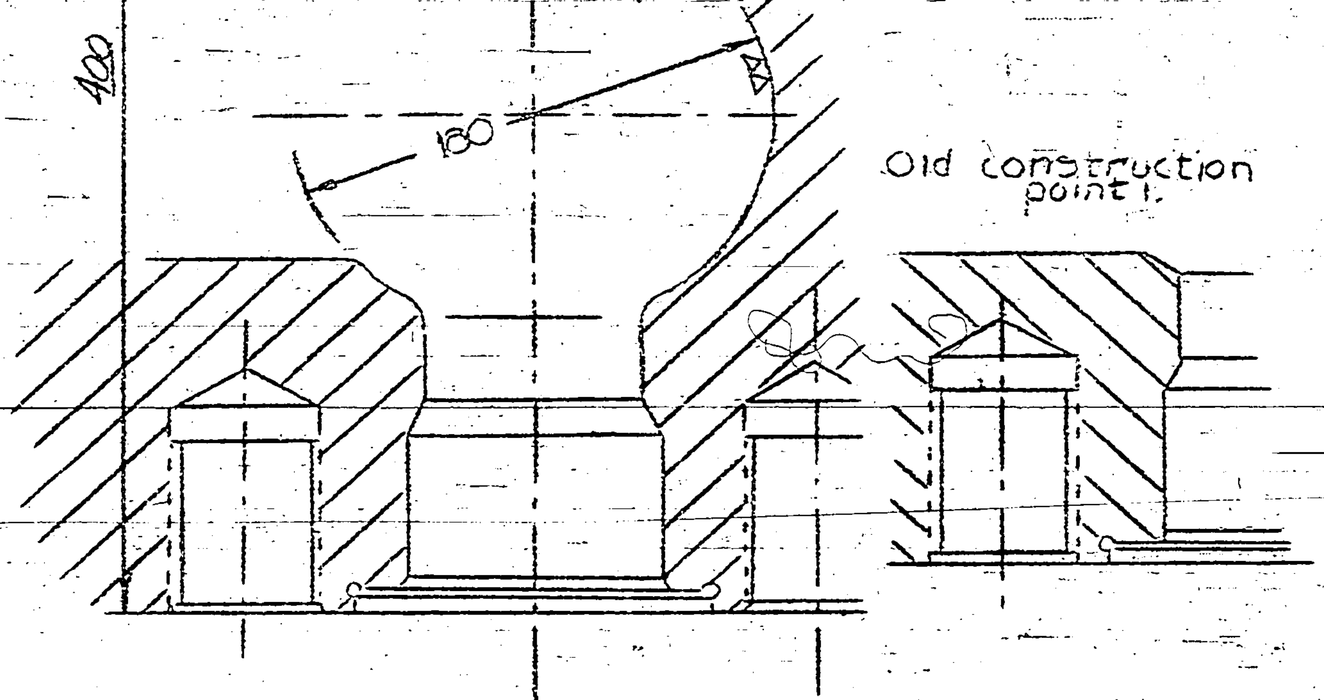


FIG. 8

U. S. BUREAU OF MINES
HYDROGENATION DEMONSTRATION PLANT DIVISION

These drawings were inadvertantly omitted from T-135, "Investigation of Occurrence and Avoidance of Fatigue Breaks in Machine Parts at Gelsenberg."

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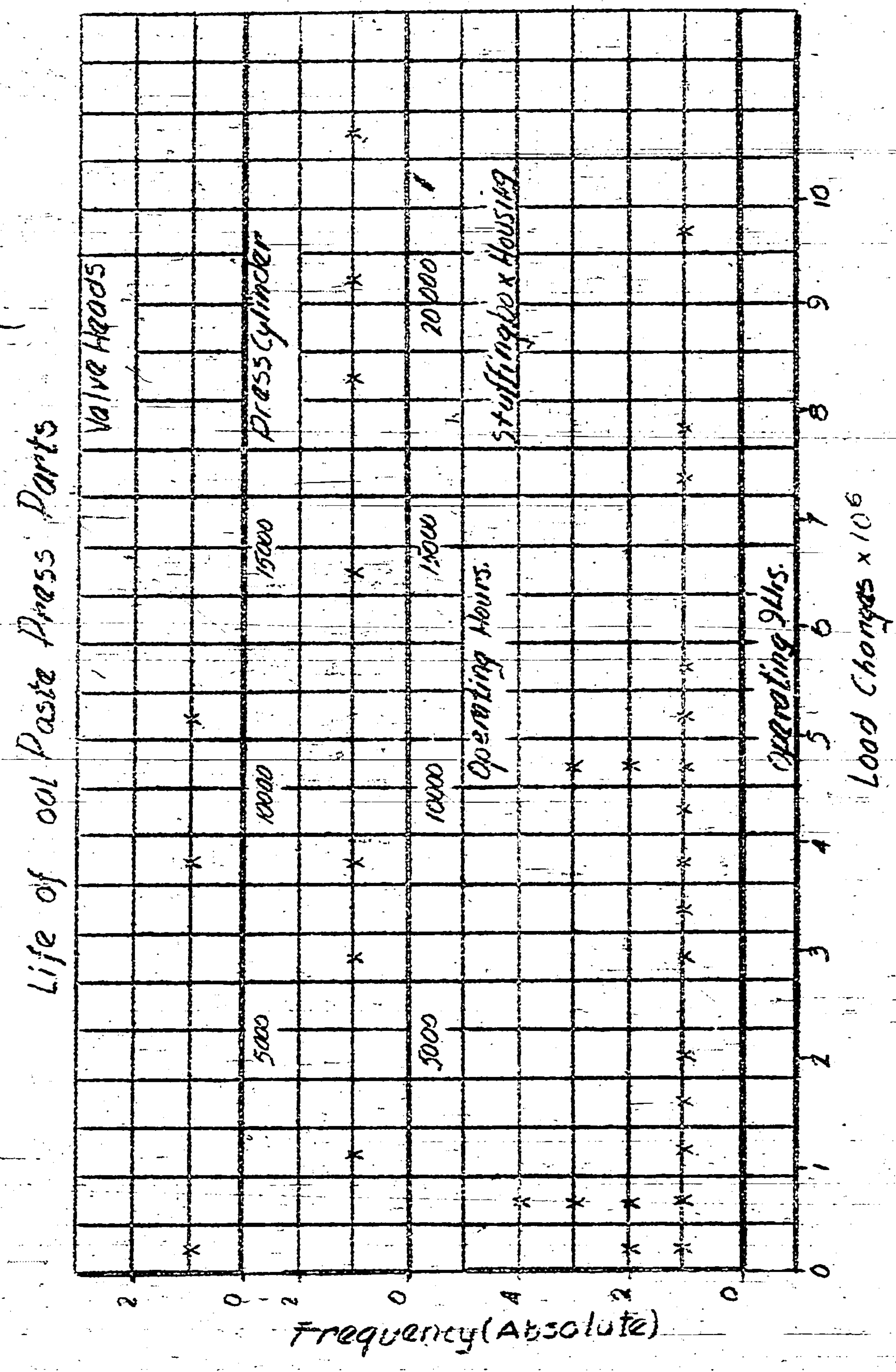
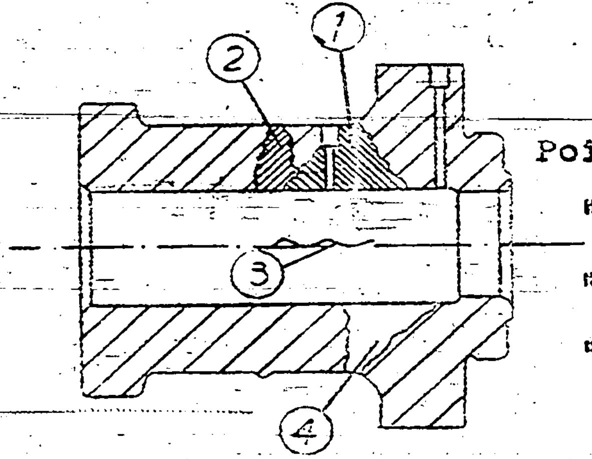
Newman

T-125



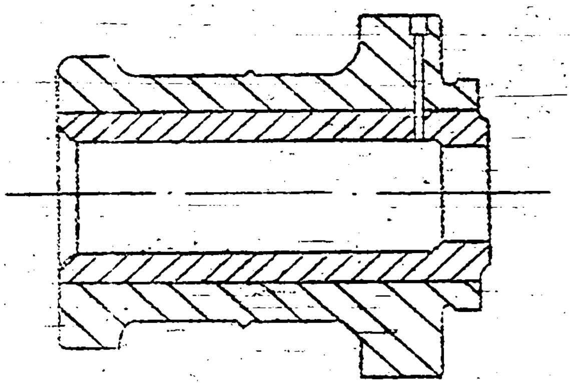
F IG-1

## Weak Point Count on Coal Paste Press Stuffing Boxes



| | | | Number | % |
|---|---|---|---|---|
| Point | ① | Long. Crack thru hole | 17 | 81 |
| " | ② | " " near hole (top) | 2 | 9.5 |
| " | ③ | " " on side | 1 | 4.75 |
| " | ④ | " " bottom | 1 | 4.75 |
| | | Total | 21 | 100 |

## Suggestion for Improvement

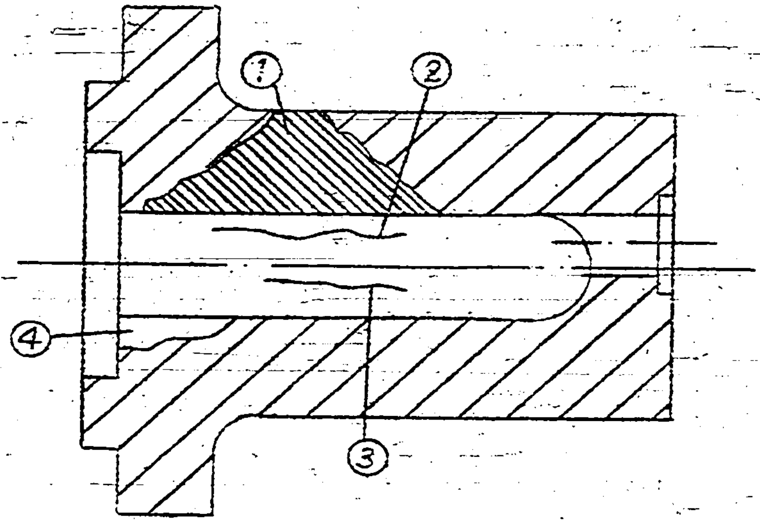


**Dimensions**

| | |
|---|---|
| O. D. | 400 mm |
| I. D. | 200 mm |
| O. D. of Sleeve | 280 mm |
| Shrinkage | 0.067 mm |

Fig. 2

## Weak Point Count on Coal Paste Press Cylinders.



| Point | | Number | % |
|---|---|---|---|
| ① | Long. Crack | 3 | 43 |
| ② | " | 2 | 28.5 |
| ③ | " | 1 | 14.25 |
| ④ | " | 1 | 14.25 |
| | Total | 7 | 100 |

### Suggestion for Improvement.

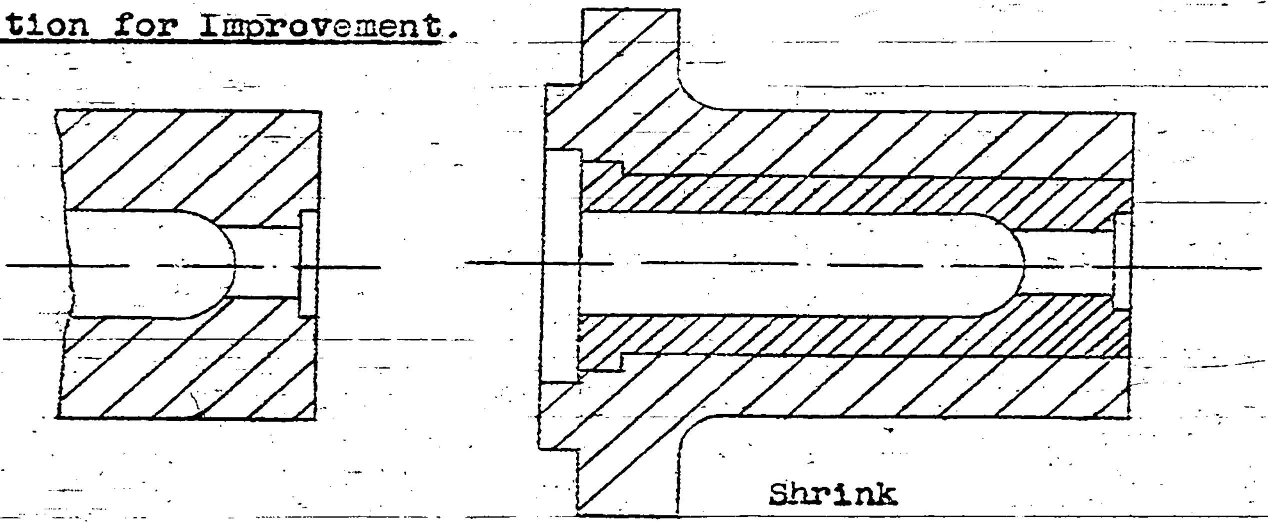
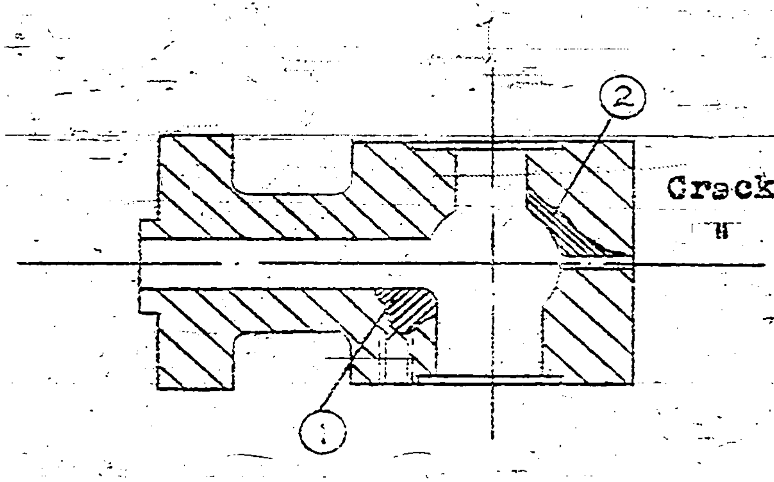


Fig. 3.

## Weak Point Count on Valve Heads of Coal Paste Presses



| | Number | % |
|---|---|---|
| Crack at Point ① | 2 | 67 |
| " " " ② | 1 | 33 |
| Total | 3 | 100 |

### Suggestion for Improvement

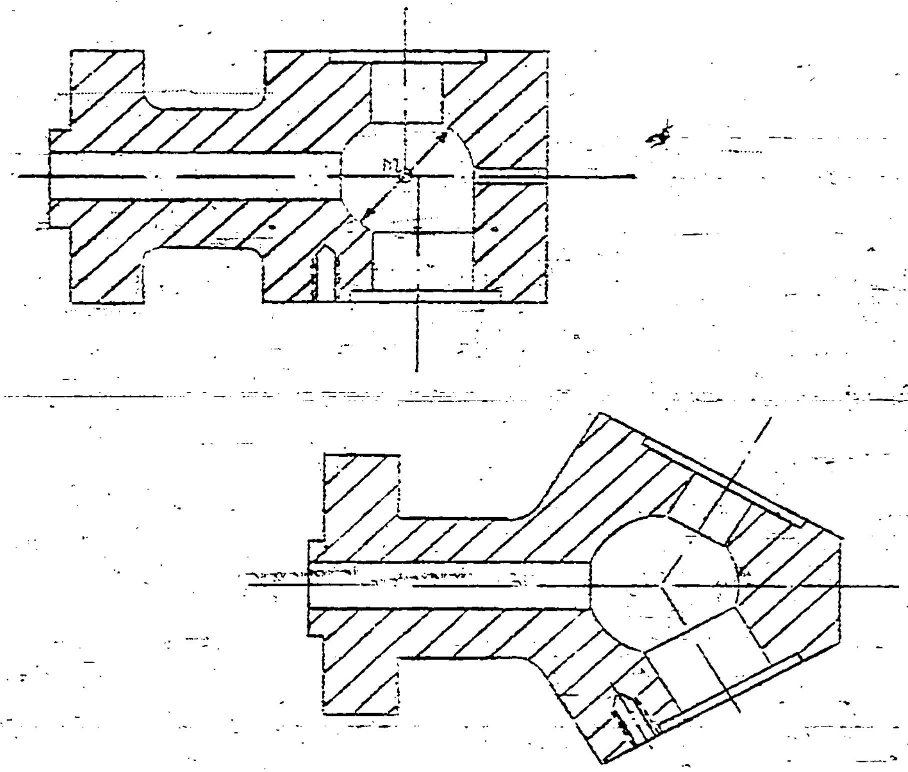


Fig. 4

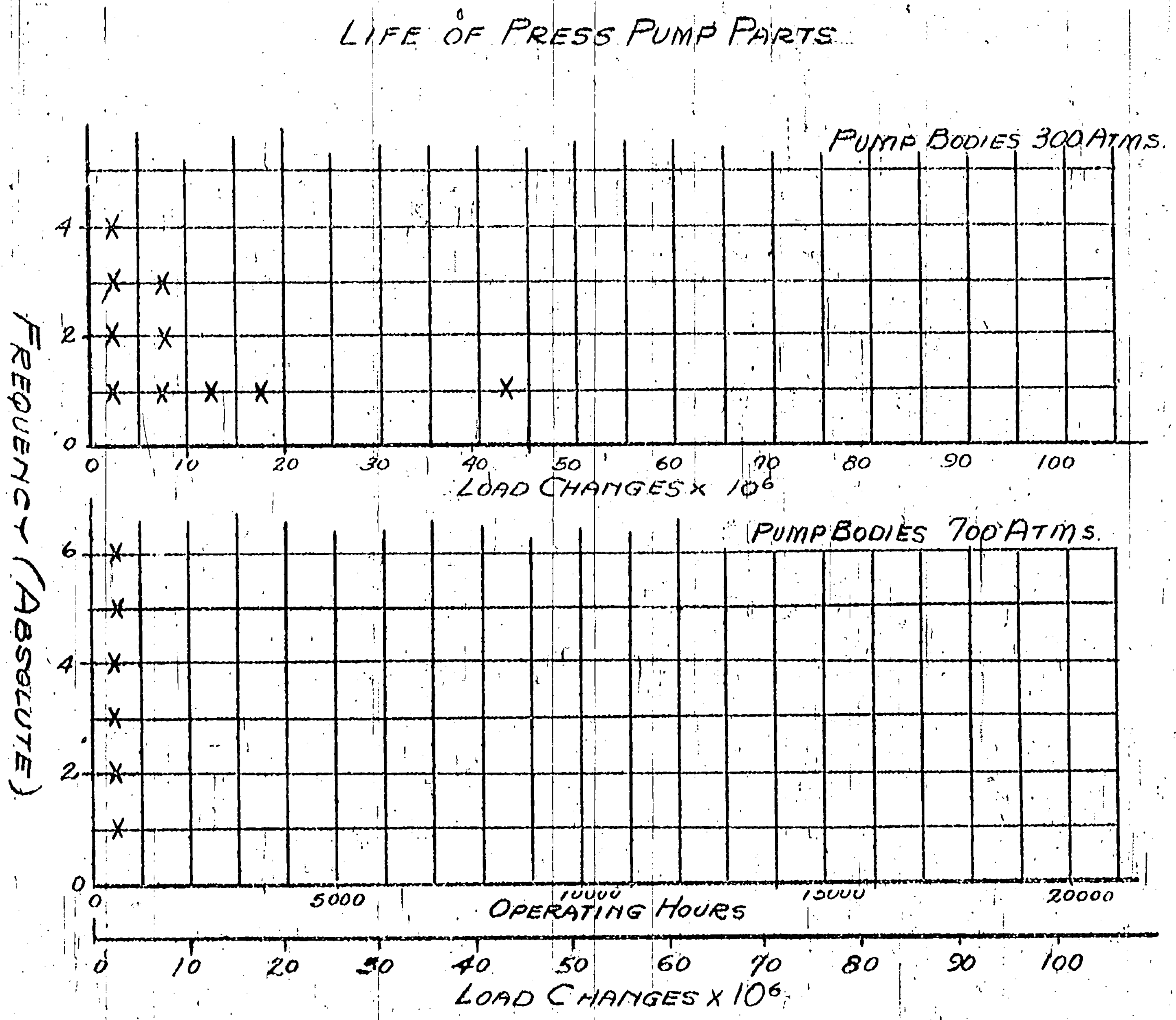

LIFE OF PRESS PUMP PARTS
PUMP BODIES 300 ATMS.
4
2
0
0
10
20
30
40
50
60
70
80
90
100
LOAD CHANGES x 10^6
PUMP BODIES 700 ATMS.
6
4
2
0
0
5000
10000
15000
20000
OPERATING HOURS
0
10
20
30
40
50
60
70
80
90
100
LOAD CHANGES x 10^6
FREQUENCY (ABSOLUTE)

FIG. 5

# LIFE OF FLUSHING OIL PRESS PARTS

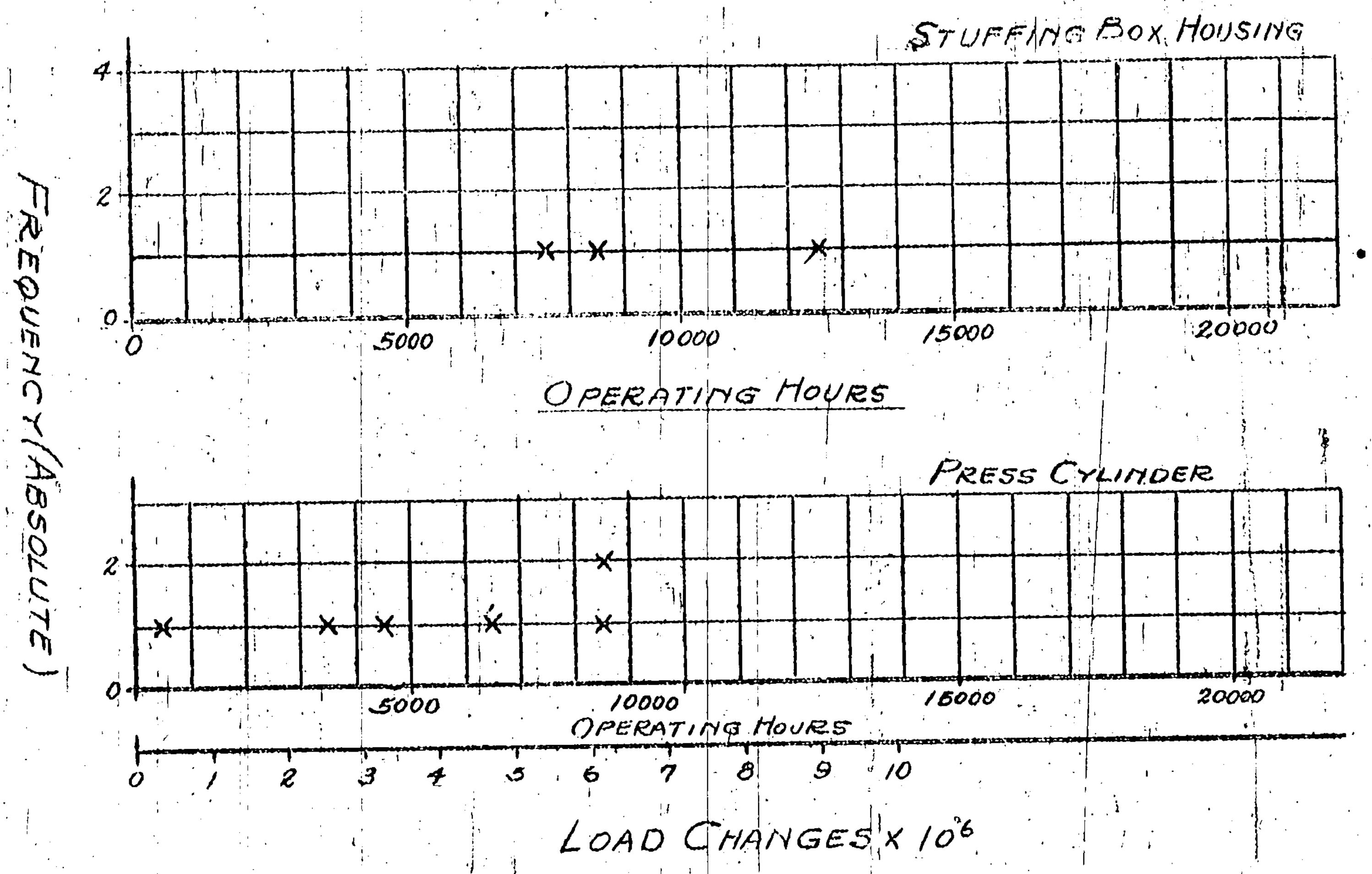


FIG. 7

T.O.M. Reel 181
Frames 6734-6754

U. S. Bureau of Mines

Hydro. Demon. Plant Div.

T-127
(7 Sheets of
Drawings)

# 6434 Catalyst (VK) in Flowing Circulation Gas

By Schwab

## Contents - Summary

Since the catalyst 6434 has been introduced, phenomena have been observed never seen before. This catalyst causes a continuous deterioration of heat exchange, which requires a steadily increasing amount of outside heat in spite of the large heats of reaction; the outside heat supplied by a given preheater soon reaches the maximum value the preheater may transmit. This drop in heat transfer, especially in hot heat exchangers, has been observed in almost every case. When the exchangers were opened, dust was found in the tubes, and that dust was definitely produced by the catalyst. Scales were frequently observed in the inlet, as well as in the exchanger tubes, especially in Leuna where the feed was sulfurized with elementary sulfur.[a]

Experiments described below carried out in Leuna disregarded the sulphur problem and were concerned exclusively with the 6434 catalyst.

This catalyst is used in pill form with a diameter of about 10 mm and 10 mm high, with the upper and lower surface of the cylinder spherical. The pills, when new, are porous and become hardened after use, and some recovered catalyst was used with this "new" catalyst. The recovered catalyst had been in operation for 58 days in Leuna in the converter 216 of Stall 11. In addition to this two kinds of catalyst, a third one was subsequently added (Section 3); it had been pretreated in Ludwigshafen. This catalyst had been heated

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[a]). Detailed reports: Kimmerle, Leuna, 9/6/37; Kuppinger, Leuna, 10/22/37.

to about 400° C in nitrogen (later in hydrogen) in order to increase its resistance to mositure. This pretreated catalyst kept its shape much better and was extremely insensitive towards water.

## I. Direction of the Flow°

The most usual direction of flow of gas through a converter was from below upward not only because of the blends built in the construction of that date, but also because of the more favorable temperature distribution with this direction of flow. The first experiments were designed originally to show the effect of the direction of flow upon the formation of dust, and were carried out as shown in Figure I. The gas obtained from the gasoline circuit was compressed to 260 atmospheres in a circulation pump and used in a circuit of its own. The gas was somewhat reduced in pressure, measured, and then lead through tower I, through which it passed downward, and through tower II, where the direction of flow was the reverse. This arrangement offered the advantage of feeding both towers under absolutely identical thruput proportions. The dust was deposited on two double bundles of an absorbent (Nesselstoff) and weighed. The determination of dust made in that way was very accurate. The second bundle normally showed no increase in weight. The amount of gas, as well as the resistance in the columns of the catalyst and through the first dust absorbing bundle, could be continuously supervised by means of pressure gauges. The catalyst towers consisted of 120 mm high-pressure tubing. Coke was placed above and below the catalyst which formed a column 1 m in length and contained about 9 kg of catalyst.

The catalyst was blown through with nitrogen from above downward, as usually done in these operations. It was found in one determination that even when the blowing was done carefully, over 0.3 per cent of the total catalyst taken was blown out from the tower as a cloud of catalyst dust. In the later experiments, which lasted between 35 and 60 hours, the amount of dust found behind the first tower (with a down-flow) was negligibly small in comparison with the amount back of tower II with the upward flow, and in addition to dust there was also a large amount of coke and catalyst carried over. The dust from tower I amounted to 2.3 gms in the first test, and less than 0.2 gms in the succeeding tests, the amount of dust from tower (upward flow) equalled 88 and 21 gr in the two tests, without considering the catalyst and coke carried over, the amount of which was of the order of 1 kilogram. The tests were accelerated by increasing the rate of flow to 0.56 m/sec, based upon free cross section. (All velocities are referred to the free cross section, the actual velocity inside the catalyst was about 2.4 times greater.)

2-°). Section I and II are based largely on the reported discussions on December 9, 1937

This velocity still had a tendency to carry some catalyst over, and it was subsequently found that 0.48 m/sec was the limiting permissible velocity. With 0.43 m/sec velocity, no catalyst was carried over; after 39½ hours of gas flow the absorbant bundle back of tower I remained completely clean, the increase in weight was 0.12 gm, while the bundle behind tower II contained 18.9 gm of clean dust.

## II. Velocity of Flow

These experiments showed distinctly the advantage of downward flow at high velocity, and they were followed by tests at atmospheric pressure, intended to explain the effect of velocity in upward flow. Glass tubes of 52 and 178 mm diameter showed that the layer of catalyst, which at first remained quiet, got into motion as the velocity of the gas increased. Just as in some subterranean stream, the pills in the middle of the tube had the greatest amount of motion. As the velocity increased further, the pills on the surface moved more strongly and finally the surface would periodically erupt and the pills would be thrown upward up to 50 cm high.

All these phenomena illustrate an equilibrium between the downward acting gravity of the pills and the upward pushing pressure of the gas in motion, and is affected by the shape of the pills. We will give the suspension velocity of a perfectly cylindrical pill independent of the size. The direction of the flow upon the pill is from the base (circle), since it will be more quickly set in motion with pressure so applied, then upon its cylindrical side. The resistance coefficient used was the theorectical value of 0.91. The theoretical velocity of suspension is then Vsch = $\sqrt{\frac{2.g\zeta act.4}{\gamma act.0.91}}$ (m/sec), where $\zeta$act. was the net weight of the pills with consideration of the upward push in kilograms, d the diameter of the pills in meters, and $\gamma$ act the actual weight of the flowing medium in kg/m$^3$. The value obtained by calculation is not exactly equal to the actual suspension velocity, because pills are not true cylinders, and the edges exert a great influence upon the flow. Any deviation from a sharp;edged cylinder results in an increase in the suspension velocity. To gain an idea of it, a few aluminum cylinders were made 10 mm in diameter and 10 mm high and exposed to the air current. The first piece of this kind required 1.07 times the suspension velocity in air, derived by calculations to suspend it a height of m. After a few repetitions, this rose to 1.14 times the theoretical value because the edges of the cylinder have become rounded by numerous collisions. Aluminum cylinders with very slightly broken edges required at first 1.18 times the theoretical velocity to float away, later 1.22 times that value. Furthermore, we have usually found that catalyst pills required between 1.40 and 1.55 times the theoretical suspension velocity. The use of theoretical velocities as references permits us to compare atmospheric pressure experiments with conditions under high pressures. The data for the individual catalyst pills in the operating stalls are not accurately known, and average values were used in computations, namely 9.35 g. for the weight of the pill, and 11.2 mm for the diameter.

It has been found in experiments at atmospheric pressure, that the surface of the filled layer of catalyst was beginning to move at 15% of the theoretical suspension velocity, and if the velocity was further increased and reached 20% of the theoretical value, the catalyst pills were tossed upward, a condition existing in the carrying-over. This result was applied to the first tests, and the value of 0.48 m/sec found there was found to be very close to 20% of the theoretical suspension velocity. The ratio of actual velocities (always referred to the free cross section) found in Leuna, Böhlen and Magdeburg for stalls operating with the 6434 catalyst for maximum thruput, to the theoretical suspension velocities is shown below. The equipment and connections in front of all the stalls which had been previously used are shown on fig. 2 representing the flow in 6434 stalls. One may see the large number of tests run in Leuna. Unfortunately, the picture here becomes very confused, because the feed sulfurized with elementary sulfur as well as the catalyst dust act very unfavorably upon the heat exchange, with a general formation of scales in the outer pass of the exchanger (upon the tubes). The amount of gas and of the injection feed have been given in the first columns of the fig. 2 to permit a more accurate definition of the gas flow. The actual specific weight $\gamma$act in kg/m$^3$ and the effective velocity at the outlet of the last converter will be defined by these values as well as the specific gravity, pressure and temperature. The theoretical suspension velocity has been always calculated from the formula given above. Finally the relative value (in %) was obtained for the actual and theoretical suspension velocities, which shows to what extent velocities referred to the free cross section differ from those velocities at which single pills would vibrate.

The testing of the maximum relative values in stall 12 at Leuna, with three 800 mm converters gives striking results. The high gas: feed ratio required at first indicates a high theoretical suspension velocity (2.4 m/sec), but it results in a more rapid growth of the effective velocity, so that the maximum relative value of over 16% of the theoretical suspension velocity is extraordinarily large. This resulted in an exceptionally rapid and strong fouling of the heat exchangers, which greatly affected the heat transfer number as well as the resistance, and could be partly remedied by the addition of water. The K value in exchanger I dropped uniformly in 4 months from 400 to 160, and remained at that level for 1½ months.

Stall II was first equipped with three 1200 mm converters. The diagram shows, that behind the converter I with an upward flow from below, the same relative values were obtained as in the original construction of stall 12. The resistances created and the subsequent dismantling showed an actual entrainment of the catalyst. The stall with three 800 mm converters was next connected from above downwards. This should have deprived the catalyst of any chance of motion and therefore of abrasion, while the load was high. The K values of the exchanger I dropped the first month from 350 to 200, and then stayed at that value for 1½ months. The load remains so high, considered from the standpoint of flow, with a relative value of 15.9%, that it would have caused an acute fouling of the exchanger with an upward flow according to all available experience.

Conditions were very similar in the two Brabag plants, Bohlen and Magdeburg. The A-feed stall which was always working at an extreme load has a steady transfer value in the heat exchanger I, while the load of the B-feed stall, which was not small, and amounted to 10% of the relative value, required no changes in the heat exchanger I and showed a very slow decrease in the K values (iron sulfide). It is of particular interest, that acute disturbance to be attributed to the catalyst were experienced in the two A-feed stalls operating under almost exactly equal flow relationships. In Bohlen a fourth converter had been added on August 1937 in stall 3 with relative values between 13, 4 and 13.9% of the theoretical suspension velocities, and this resulted in a sudden deterioration of the K values, connected with a rise in resistance. Stall 4 in Magdeburg behaved quite similarly on September 26, 1937. The catalyst was carried over and obstructed the pipe with a relative value of theoretical suspension velocity equal to 13.6%.

Considering all the results in the table fig. 2, the limits for the carrying-over of the catalyst fluctuate between certain velocities. In the tests performed in Leuna, under high pressure as well as under atmospheric pressure, the catalyst was carried over only with 20% of the theoretical suspension velocities, this happened in Leuna (stall II) at 16.7% and in Magdeburg at 13.6%. There are several reasons for it. When considered purely from the standpoint of theory of flow, the shape of the pills is of deciding importance. In the tests, the catalyst was always strongly abraded. However, tests with aluminum model pills have shown, that under such conditions a higher effective suspension velocity is required. Spheres will only begin to vibrate later. The diameter of the tube introduces further geometrical considerations, because as the diameter increases, the possibility of bridge formation, with a resulting inner strengthening, is reduced. In the tests the diameters were however 120 and 178 mm, while the narrow converter of stall II in Leuna was 655 mm wide, and 860 mm was the diameter of the Brabag converter. We must also mention the effect of the method of operation, especially for the carrying-over, less so for abrasion. When the upper layer of the catalyst is in a state of motion, a small additional push by cold gas is sufficient to cause entrainment. It is very interesting, therefore, that from considerations of flow the stall 4 in Magdeburg was not in the same conditions on August 16, 1937 as on September 26, 1937, when it no longer could overcome the effects of thruput (cold gas additions) raised from $30\ m^3/h$ to $33\ m^3/h$ (according to the converter log).

## III Wet Circulation Gas.

The effect of the cold wet circulation gas upon the catalyst was studied from purely theoretical flow tests and computations. In the meantime tests were begun with the "pretreated" 6434 catalyst heated in Ludwigshafen to 400°C, and two preliminary tests were at once started by subjecting 1 sample each of a "new" catalyst, (delivered in 1937), "pretreated" and "recovered" catalyst to an uncontrolled slow flow of cold circulation gas at 220 atm for 19 and 33 hours. The ultimate strength of the "new" catalyst indicated a great drop of about 50%. The "pretreated" catalyst had also lost in strength, while the losses of the "recovered" catalyst were inside the limits of scattering of results. (The results are shown in table 2).

100 whole pills of the three kinds of catalyst were subjected separately to a controlled flow of 0.2 m/sec in a 45 mm high pressure tube. The filling and the pressure relief of the apparatus was done in the 4½ hours usually required in operations, and the catalyst was always acted upon by the circulation gas longer than the actual duration of the test (= time of flow). As shown in fig 3., the gas was taken from the gasoline circuit and had opportunity to give up its mositure in a double necked flask of $0.68\ m^3$ capacity when flowing at the temperature of the test thru a coil and thru the apparatus with the samples of the catalyst The coil and the apparatus were enclosed in containers which could be used as water baths, making it possible to raise the temperature in later sets of experiments. The amounts of gas were continuously measured at its return to the suction side of the circuit.

In the two sets of experiments, the first one was run in the cold, at room temperature. The circulation gas flowed thru the two necked flask and the catalyst at the prevailing temperature. The temperature of the gas in the flask was always lower than the temperature of the gas circuit. The liquid collected in the flask was continuously decompressed. The duration of the test (duration of flow) lasted from 0 to 42 hours in the 7 cold tests. In a second series of tests the temperature of the gas was raised 40° in the double necked flask.

For the purpose of evaluation, the catalyst, after being kept in the circuit for a longer or shorter time, was subjected to ultimate strength tests, determined in the Merserburg testing laboratories on 10 pills. However, the tendency to form dust is not identical with ultimate strength, and a technique of direct abrasion measurements was developed, in which the abrasion was produced by mutual rubbing of the pills. After preliminary tests, a 2-chamber drum, 100 mm in diameter and 25 mm wide was prepared (fig 4); with 20 pills per chamber and with 70°rpm, the pills keep rolling down against each other. It has also been found experimentally, that under such conditions the abrasion between 0 and 100,000 revolutions was represented very accurately as a square root of some function. A standard was set for 50,000 revolutions of 20 pills (= 20-30 gm), and small deviations recalculated by the above function. In actual measurements 2 samples of 20 pills were first blown free from dust, dried for 24 hours over $P_2O_5$, accurately weighed and placed into the two chambers of the drum. After the test the pills were again blown free from dust, re-dried for 24 hours over $P_2O_5$, and accurately reweighed. The difference was the abrasion. The drum was blown out after each measurement.

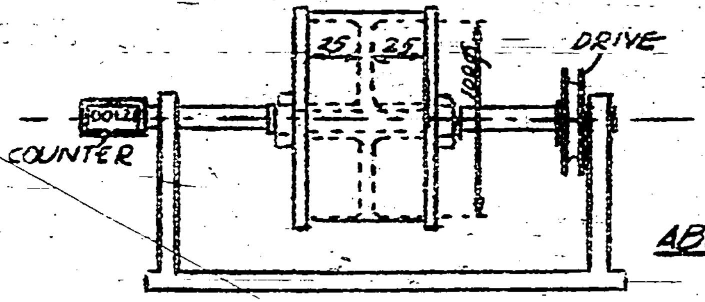


FIG.4

ABRASION DRUM

In spite of this always very uniform procedure, the "pre-treated" catalyst as delivered invariably showed a slight increase in weight after 50,000 revolutions in contradiction to all the other cases. This increase was always the same and the drying, which was satisfactory in all the other cases, has not been further improved. Abrasion experiments in the two chambers were run separately and recalculated to 50,000 revolutions. The average value of the two measurements was the final abrasion value.

When considering the results, we must bear in mind that all three kinds of catalyst, as delivered, i.e. before use in the tests, gave greatly scattered results, especially in ultimate strength tests. When the runs were made samples were invariably tested before use. The average values obtained as well as the range of scattering of results of strength tests are shown in curves (figs. 5 and 6) and in the table I.

Table I. Average values of catalysts before use in the experiments.

| | Ultimate strength (kg/cm$^2$) | Abrasion (gr. after 50,000 rev.) | Weight of 20 pills in grains |
|---|---|---|---|
| "new" | 150 (126-163) | -0.585 | 28.4 |
| "pretreated" | 241 (208-260) | /0.290 | 20.4 |
| "recovered" | 193 (155-225) | -0.241 | 23.7 |

In the first series of tests, the three samples arranged in series were acted upon by a cold stream of circulation gas with a velocity of 0.2 m/sec. The mechanical resistance of all 3 catalysts was thereby reduced. The ultimate strength became lower, abrasion larger.

Table II. Results in cold circulating gas.

| | Hours of passage of gas | Preliminary Tests | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | 19 | 33 | 0 | 3 | 6 | 12 | 20 | 40 | 42 |
| "new" | Strength | 98 | 85 | 152 | 148 | 135 | 100 | 94 | 92 | 90 |
| | Abrasion | -- | -- | -1.8 | -2.12 | -2.25 | -2.90 | -3.52 | -5.27 | - |
| "pretreated" | Strength | 185 | 197 | 206 | 208 | 224 | 214 | 208 | 179 | 164 |
| | Abrasion | -- | -- | -0.001 | -0.15 | -0.44 | -0.76 | -0.76 | -1.01 | -1.26 |
| "recovered" | Strength | 175 | 177 | 200 | 191 | 194 | 190 | 188 | 163 | 180 |
| | Abrasion | -- | -- | -0.72 | -0.83 | -0.86 | -1.23 | -1.30 | -1.80 | -2.03 |

In the next series of tests, to protect the catalyst, the gas was heated 40° on the way between the catchpot and the catalyst. The results obtained after longer interaction were studied.

Table III. Results with warmed circulating gas ($\Delta t = 40^\circ$ C)

| | Hours of Passing Gas: | 12 | 24 | 43 | 50 |
|---|---|---|---|---|---|
| "new" | Strength | 216 | 196 | 209 | 189 |
| | Abrasion | -0.14 | -0.15 | -0.34 | -0.41 |
| "pretreated" | Strength | 254 | 241 | 257 | 235 |
| | Abrasion | -0.05 | -0.03 | -0.25 | -0.18 |
| "recovered" | Strength | 217 | 219 | 203 | 225 |
| | Abrasion | -0.40 | -0.46 | -0.57 | -0.71 |

The results obtained in the cold and warm circuits were plotted in figs 5 and 6 against the duration of the test, plotting also in every case the results obtained before the start of the test and after its completion. The effects upon ultimate strength is shown in fig. 5. 4½ hours were always used for production of the pressure and for exhausting, and this was in addition to the actual time of the run, and this time the samples were subjected to the action of the circulating gas. The values and their range of scattering were plotted to the left of the ordinate. The scattering indicates a lack of uniformity of the material, and one expects the new results also to be scattered, but surprisingly, the scattering was slight.

The strength of the "new" catalyst dropped very rapidly right from the start of the test in cold circuit, and that drop was strongly affected by time during the first 20 hours and only becomes flattened out after that. The "pretreated" catalyst also shows a decrease in strength as the cold gas is made to pass over it, and this decrease is as large, as with the "new" catalyst. The least effect is found with the "recovered" catalyst, which is explained by its having been strengthened with use as well as saturated with oil. These values obtained in preliminary tests are satisfactorily confirmed by the more recent values. The same sheet of curves shows the results of the second series of tests with the gas circuit preheated to 40° C. No effect of length of tests is to be observed with any of the three catalysts. In the "new" catalyst in particular an increase in strength over the initial value can be observed, probably caused by the removal of moisture absorbed by the pills in the course of time. The "pretreated" catalyst had been shipped in airtight containers from Ludwigshafen a short time previously, and retains its original strength. This difference in the tendency of the catalysts treated cold or warm to retain their strength is of extraordinary interest and the gain in strength by a preheating to 40° C has therefore been checked twice.

A more sensitive test for the catalysts has however been developed in the abrasion tests. The effect of length of the test has again been plotted (fig. 6). Each point represents values furnished by 40 pills, as against only 10 pills in the ultimate strength test. The average values before use have again been plotted to the left. The increased values in the "pretreated" catalyst resulting from insufficient drying has already been discussed. The results confirm and strengthen those obtained in strength tests. All catalyst showed a strong dependence from the length of action of the cold circulation gas, and the "new" catalyst is particularly strongly affected. The resistance of the "pretreated" catalyst is best. The series of tests in the warm gas ($\Delta t = 40°$ C) show in the much lower abrasion values a much smaller effect of the length of the treatment, the "new" catalyst is materially improved by the action of the warm gas, as has also been shown in strength tests. The "pretreated" catalyst is hardly at all abraded. The improvements by a slightly warmed gas is shown in these tests are even greater than in the ultimate strength tests.

## IV. Starting a 6434 Stall.

Three points must be considered with the 6434 stall which were unimportant with 5058. The tests have definitely shown, that the downward flow results in important advantages by removing all possibility of motion, and therefore of abrasion, from the light catalyst. The stall 11 in Leuna was, in accordance with these results, connected from above downwards. The success has been definite by permitting operation of this stall at almost 16% of the theoretical velocity. Such loads invariably resulted in acute fouling of the heat exchanger I, which manifested itself mostly in deterioration of resistance and of the heat transfer. The poorer temperature distribution with downward flow through wide converters must be overcome by a suitable construction of blends.

An other very important measure is the blowing out of dust before use of the converter filled with the catalyst. The present Ludwigshafen "pretreated" catalyst has greater strength and is considerably less abraded, which greatly reduces the amount of dust produced during filling the converter, than with the former "new" catalyst (as delivered in 1937). Tests show particularly clearly the effect of the circulation gas used during filling. The gas continuously passed during filling must be at a higher temperature than the high pressure units at room temperature, and must be fed from the warm circuit. In view of the high hydrogen content, no cooling is to be feared when pressure is released, the gas cools when the stall is filled, and this results in condensations upon the catalyst which have been shown by the above experiments to result in a marked damage to the pills. The amount of harm is extraordinarily great with the former "new" catalyst, smaller with the "pretreated" catalyst, but still remains considerable. Chances of condensation upon the catalyst must always be avoided.

The starting of the stall filled with the 6434 catalyst as recommended below is based on these considerations. The stall is filled at 30 atm. with gas at a temperature of not over 40° C from the circulation pipe line with 230 atm pressure. This will reduce the moisture content of the saturated catalyst to at most 0.00635 below 4° C. At higher temperatures the gas is relatively dry and has no tendency for condensation. The intermediate pressure selected must be still lower in the winter during the cold weather. A marked heating of the converter partially filled with catalyst must take place before the addition of more catalyst. This heating can only be accomplished by recirculation of gas thru connections with the preheater. A special circuit must therefore be provided for the starting of the stall; a small turbine blower is well adapted for that purpose. Fig. 7 shows a scheme of such a stall with a blower between the suction and pressure sides in an already existing pipe line (exhaust to the outside). It is important here to locate the connection on the suction side behind the catch pot to permit the separation of the water, and on the pressure side in front of the intake gauge, which permits the regulation of the amount used. The blower should enable the circulation of 260 m$^3$/h at 30 atm with $\gamma_{eff.} = 6.5$ kg/m$^3$ against 2-3 atm resistance in the stall. With the low pressure only about 8000 m$^3$/h (measured at atmospheric pressure) are available for heat transfer, against 20,000 m$^3$/h at high temperature under 220 atm (stall II was available during January 1938). In spite of all that, the stall can be started as formerly. The rise in temperature of gas in the preheater and the drop in temperature of the converter will become 2.5 times as great with the same preheater capacity. But the temperature conditions in the heat exchangers will not be materially affected by it.

The temperature relationship for two cases of heating the stall II on January 19, 1938 are shown in Fig. 8. The heavy lines show temperatures at 5 o'clock. The exact temperature below 40° C in the exchanger II and in the gas cooler are unknown. The region between the preheater and the three converters is important. 20,000 m$^3$/h of gas reached the preheater from the exchanger I at 110°C, the first converter at 160°, and left the last (3rd) converter at 130° C. In the case discussed above (8000 m$^3$/h) the temperature changes are represented by broken lines. Taking into consideration the increased radiation of the hotter parts, the gas will reach the first converter at 225°C and leave the last one at 145°C. The heat transfer per hour would then remain unaltered. The lines at the right show the corresponding temperatures at 10 o'clock (140-210-176°C and 140-295-200°C).

The rapidly increasing ability of the gas to take on water and carry it out without condensation upon the catalyst is of greater importance than the question of temperature differences. The table below shows the saturation with water (in kg) by 1 m$^3$ of gas at different temperatures:

| Temperature °C | 40 | 80 | 120 | 160 | 200 |
|---|---|---|---|---|---|
| kg/m$^3$ of water | 0.0509 | 0.293 | 1.124 | 3.262 | 7.763 |

Were the stall incompletely dry at the start, the gas will have an increasing capacity for moisture. In the least favorable case, if the insulation is still moist in exchanger I, the gas will be saturated with moisture when leaving the exchanger I (el. 18). This gas however streams thru the preheater and reaches the converter very dry. The gas gives up only so much of its heat there, that when leaving the last converter (el. 208) there still is an appreciable excess of temperature over the el. 18, and this excess of temperature must still be taken care of by the heat exchanger I (fig.8). Under the least favorable conditions the gas may have been saturated at that temperature, without taking into consideration the drop in pressure in the converters. No condensation is possible under such conditions. With present pretreated absolutely dry catalyst, no moisture from that can reach the converter. The moisture present in the warm gas must be condensed and separated from the gas in the catchpot, because of the lowering of the temperature in the exchangers and especially in the gas cooler. No apprehension about the operation of the catchpot should be entertained on the strength of our present experience with the separation of water of reduction produced with other catalysts.

After the stall had thus been heated to 250-300° C and dried, the blower can be turned off and the pressure increased to 220 atm. Fig. 9 (below Fig. 8) shows the changes of temperature and pressure with time. The stall is first filled to 30 atm in the usual operating time, and heated to about 250°C. When the stall is next filled to 230 atm. the temperature drops by about 35°-40° C (including the heat of radiation). The preheating can then be continued. Moisture from the circuit is taken up with no difficulties by the warm gas. When the amount of gas is further increased 2.5 times during subsequent heating (measured at atmospheric pressure), the temperature of the preheater outlet and the converter inlet will be correspondingly lowered. The least temperature change will be observed when the temperature of the last converter approaches the operating temperature, without affecting the excess temperature of converter I caused by the reduced amount of gas. It remains however always true, that the gas leaving the last converter must be warmer than at the inlet to the preheater, and therefore dry (as long as no moisture is given off by the catalyst).

Signed Schwab.

Trsld W.M. Sternberg

T-127

# Effect of direction of flow in the gas circuit with 6434 catalyst

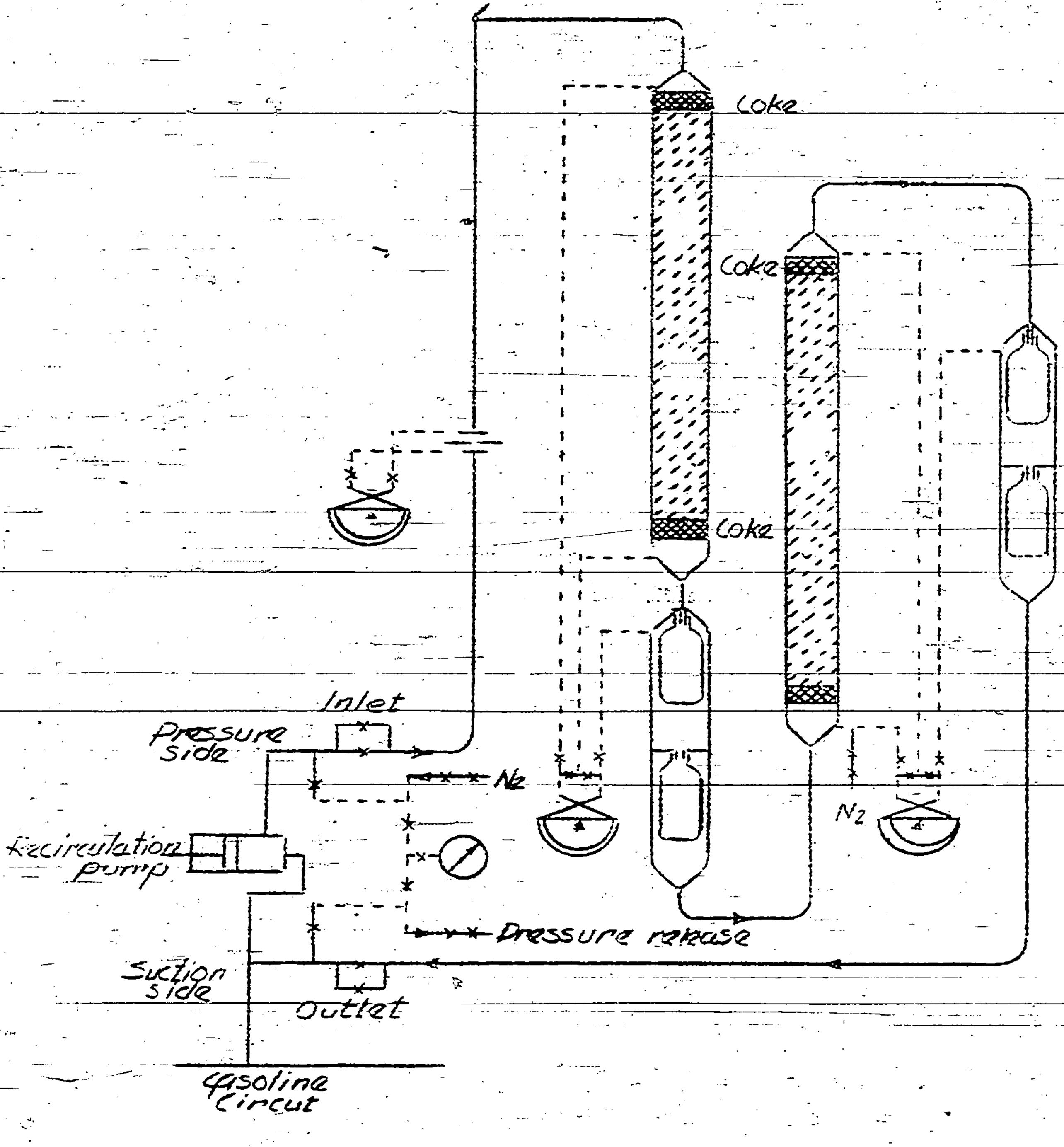


FIG 1

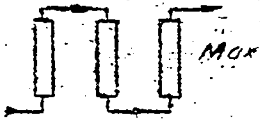
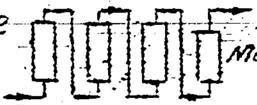
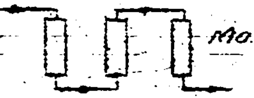
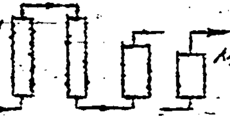
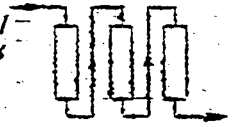
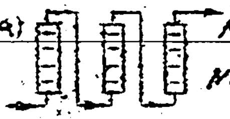
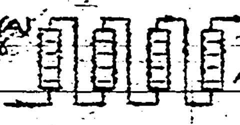
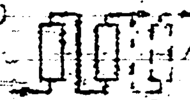
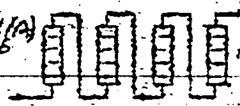
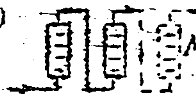
| | | | INLET GAS | COLD GAS | INJECTION | | EFF VELOCITY | THEORETICAL VELOCITY | RELATIVE VELOCITY | REMARKS (HEAT EXCH) |
|---|---|---|---|---|---|---|---|---|---|---|
| | | | m³/h | m³/h | m³/h | Kg/m | m/sec | m/sec | % | |
| LEUNA | | | | | | | | | | |
| STALL 12<br>3 x 800 ϕ |  | Maximum | 34000 | 9000 | 17 | 490 | 0349 | 2.39 | 16.7 | STRONG FOULING |
| STALL 12<br>3 x 1200 ϕ |  | Maximum | 30,000 | 16,000 | 44 | 856 | 0.182 | 1.78 | 10.2 | STEADY SLOW DROP |
| STALL 11<br>3 x 1200 ϕ |  | Maximum | 32000 | 6000 | 25 | 64.5 | 0.156 | 2.08 | 7.5 | SLOW DROP |
| STALL 11<br>2 x 800 ϕ<br>2 x 1200 ϕ |  | Maximum | 35000 | 200 | 26 | 74.0 | 0.322 | 1.93 | 16.7 | CATALYST CARRIED |
| | | | | 9000 | | 64.0 | 0.169 | 2.05 | 8.1 | OUT OF CONV I |
| STALL 11<br>3 x 800 ϕ |  | | 20000 | 10000 | 26 | 64.2 | 0.284 | 1.79 | 15.9 | UPWARD FLOW<br>K VALUE CONSTANT AT 200 |
| BÖHLEN | | | | | | | | | | |
| STALL 3 (A)<br>3 x 1000 ϕ |  | Normal | 30000 | 25000 | 24.1 | 74.1 | 0.238 | 1.93 | 12.1 | VERY RAPID DROP |
| | | Maximum | 35000 | 22000 | 27.7 | 74.3 | 0.249 | 1.92 | 13.0 | |
| STALL 3 (A)<br>4 x 1000 ϕ |  | Maximum | 35000 | 29000 | 30 | 83.7 | 0.239 | 1.79 | 13.4 | ACTIVE FOULING |
| | | Maximum | 30000 | 23000 | 37.3 | 101 | 0.227 | 1.69 | 13.9 | OF HEAT EXCH. |
| STALL 4 (B)<br>2 x 1000 ϕ |  | Maximum | 25000 | 13000 | 22 | 73 | 0.165 | 1.86 | 8.9 | NO DROP |
| MAGDEBURG | | | | | | | | | | |
| STALL 4 (A)<br>3 x 1000 ϕ |  | Maximum | 25000 | 17000 | 26.2 | 75.5 | 0.189 | 1.91 | 10.4 | |
| STALL 4 (A)<br>4 x 1000 ϕ |  | Maximum | 39000 | 20000 | 31.6° | 72.0 | 0.268 | 1.96 | 13.6 | CATALYST |
| | | | 36000 | 18000 | 32.6 | 75.4 | 0.258 | 1.91 | 13.6 | CARRIED OVER |
| STALL 3 (B)<br>2 x 1000 ϕ |  | Maximum | 23000 | 15000 | 22.4 | 67.8 | 0.198 | 2.02 | 9.8 | NO DROP |

FIG. 2

T-127

6434 Catalyst with gas circulation flow
Effect of cold and hot circuit
Arrangement of test.

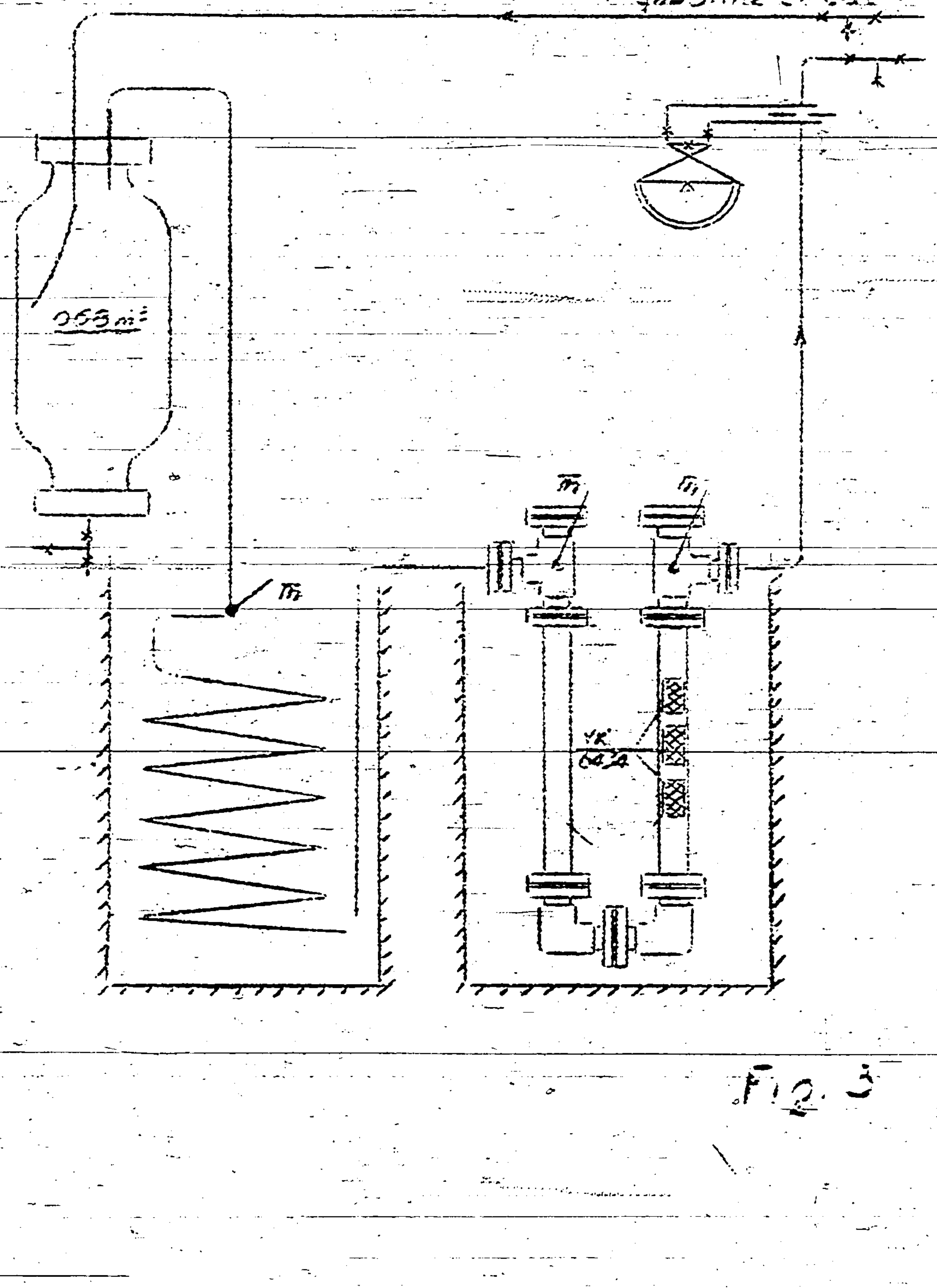


Fig. 3

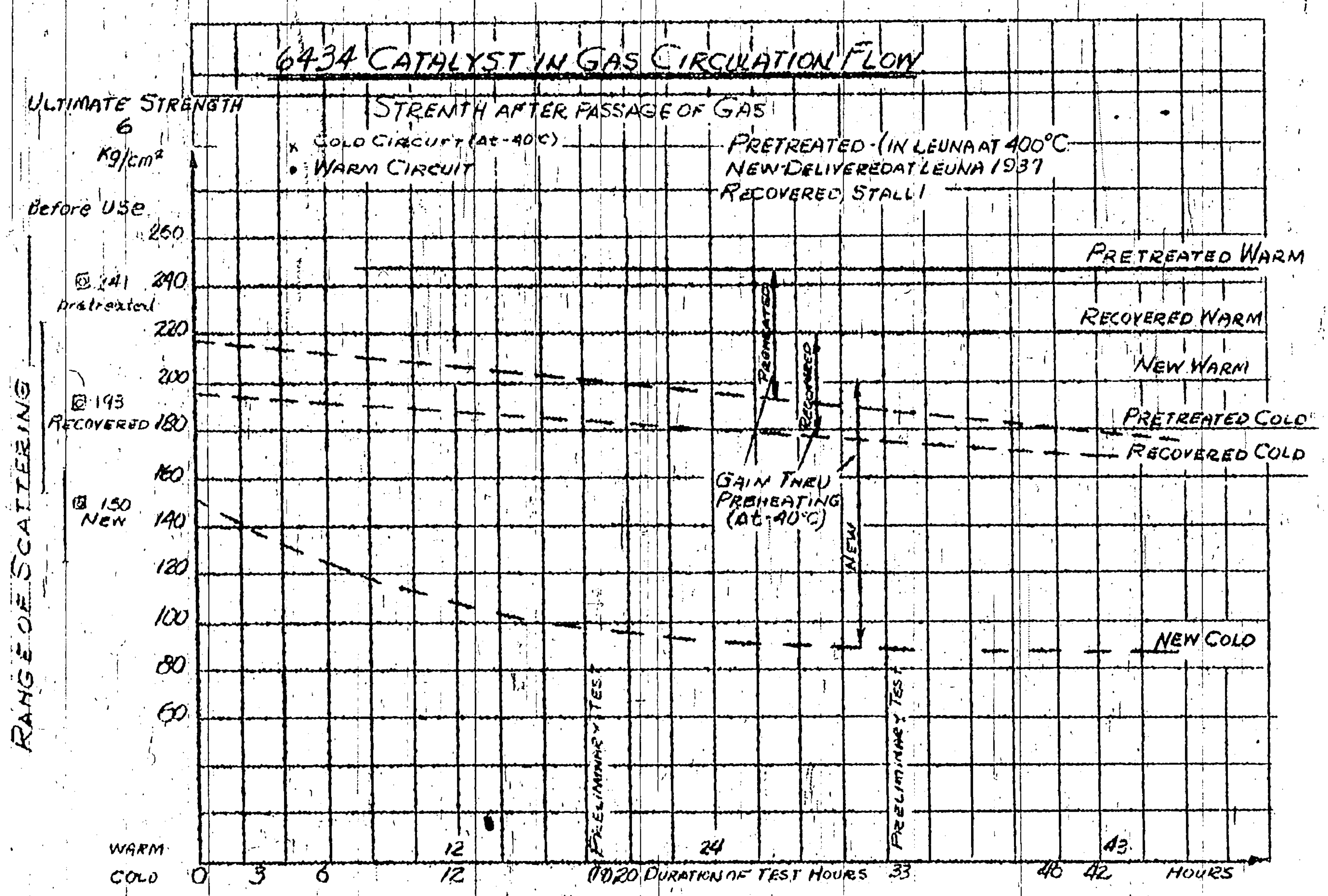

6434 CATALYST IN GAS CIRCULATION FLOW
STRENTH AFTER PASSAGE OF GAS
ULTIMATE STRENGTH 6 Kg/cm²
x COLD CIRCUIT (At -40°C)
• WARM CIRCUIT
PRETREATED - (IN LEUNA AT 400°C
NEW - DELIVERED AT LEUNA 1937
RECOVERED, STALL I
Before Use
⊡ 241 pretreated
⊡ 193 RECOVERED
⊡ 150 NEW
RANGE OF SCATTERING
260
240
220
200
180
160
140
120
100
80
60
PRETREATED WARM
RECOVERED WARM
NEW WARM
PRETREATED COLD
RECOVERED COLD
NEW COLD
PRETREATED
RECOVERED
NEW
GAIN THRU PREHEATING (At -40°C)
PRELIMINARY TEST
PRELIMINARY TEST
WARM
COLD
0
3
6
12
12
(19) 20
24
DURATION OF TEST HOURS
33
40
42
43
HOURS

FIG. 5

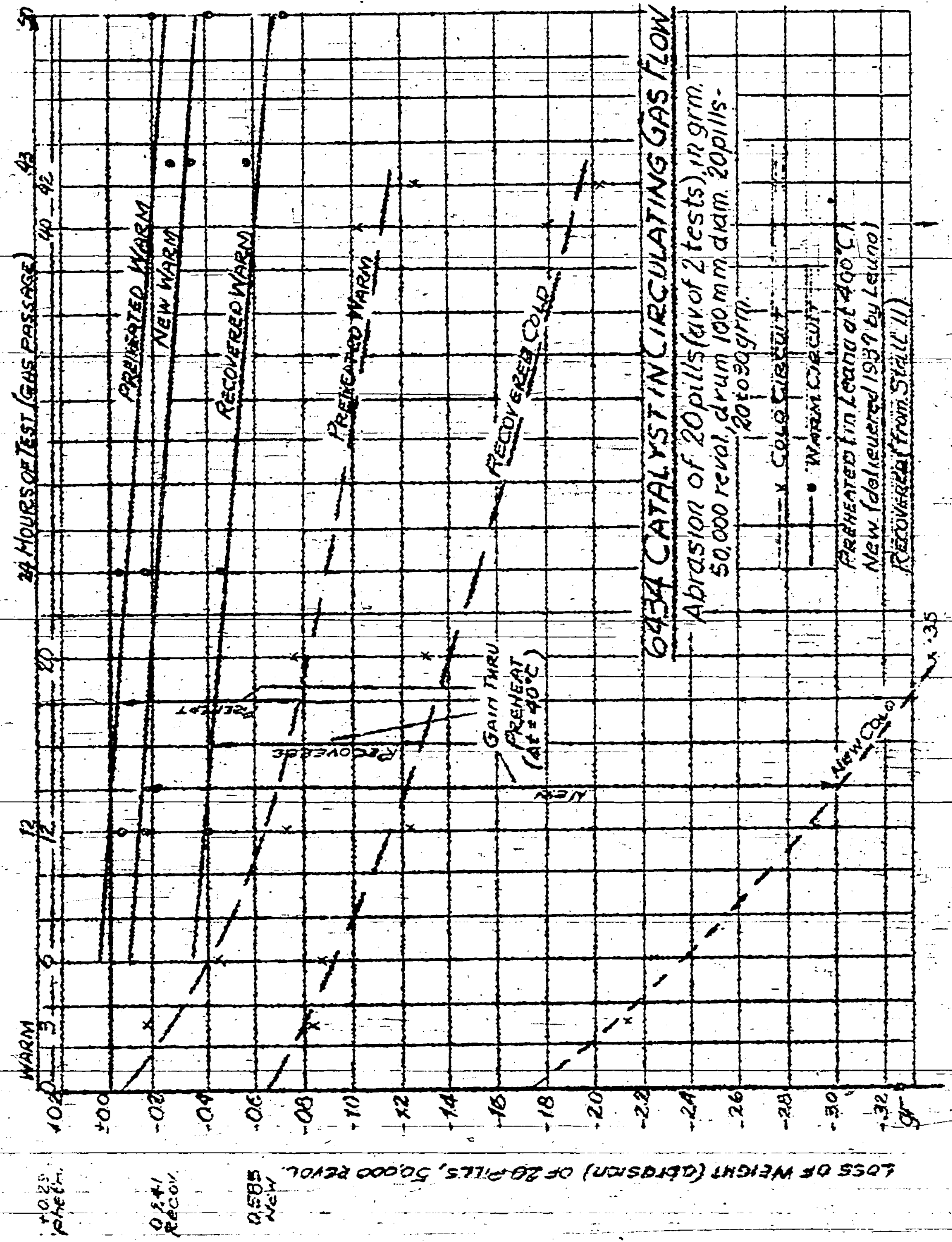

6434 CATALYST IN CIRCULATING GAS FLOW
Abrasion of 20 pills (av. of 2 tests), in grm.
50,000 revol., drum 100 mm diam. 20 pills - 20 to 30 grm.
x COLD CIRCUIT
• WARM CIRCUIT
PREHEATED (in Leuna at 400°C)
New (delivered 1939 by Leuna)
RECOVERED (from Stall 11)
24 HOURS OF TEST (GAS PASSAGE)
WARM
3
6
12
20
24
40
42
48
50
PREHEATED WARM
NEW WARM
RECOVERED WARM
PREHEATED WARM
RECOVERED COLD
NEW COLD
GAIN THRU PREHEAT (at 400°C)
PREHEAT
RECOVERED
NEW
+.35
+.02
±0.0
-.02
-.04
-.06
-.08
-.10
-.12
-.14
-.16
-.18
-.20
-.22
-.24
-.26
-.28
-.30
-.32
gr
LOSS OF WEIGHT (abrasion) OF 20 PILLS, 50,000 REVOL.
+0.23 Preh.
0.541 Recov.
0.585 New

Fig 6

# 6434 CATALYST IN CIRCUL GAS FLOW

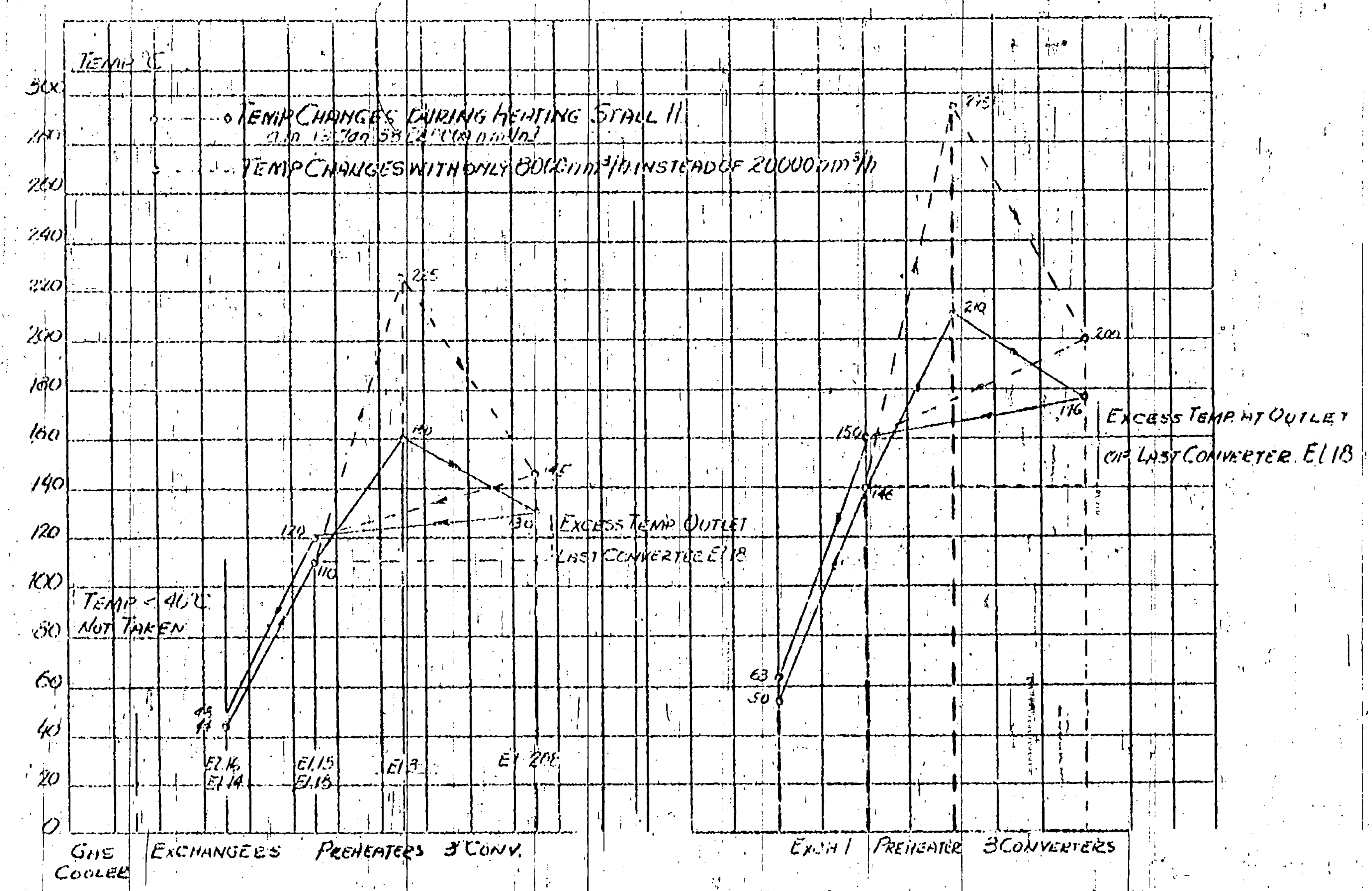


FIG. 8

T-127

## STARTING OPERATIONS OF A STALL WITH CATALYST
(WITH CIRCULAR BLOWER)

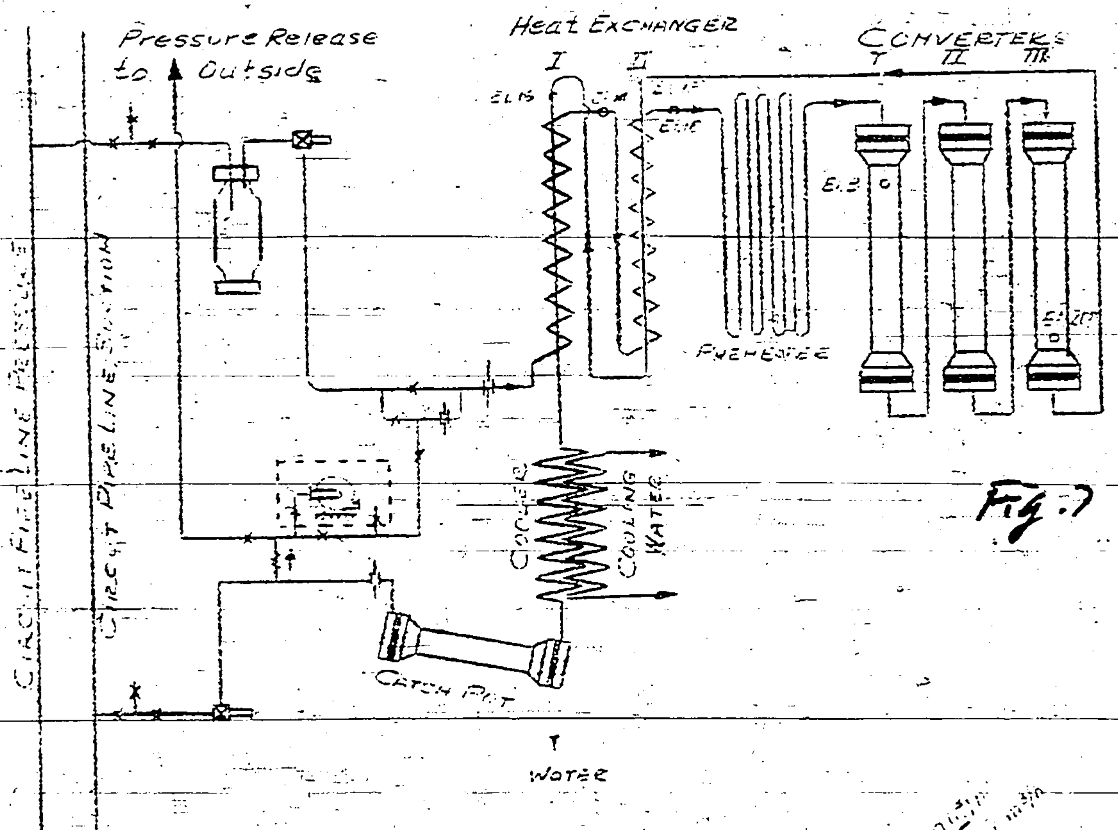


Fig. 7

## PRESSURE TEMPERATURE CHANGES
of Vapor Phase Stall with Blower

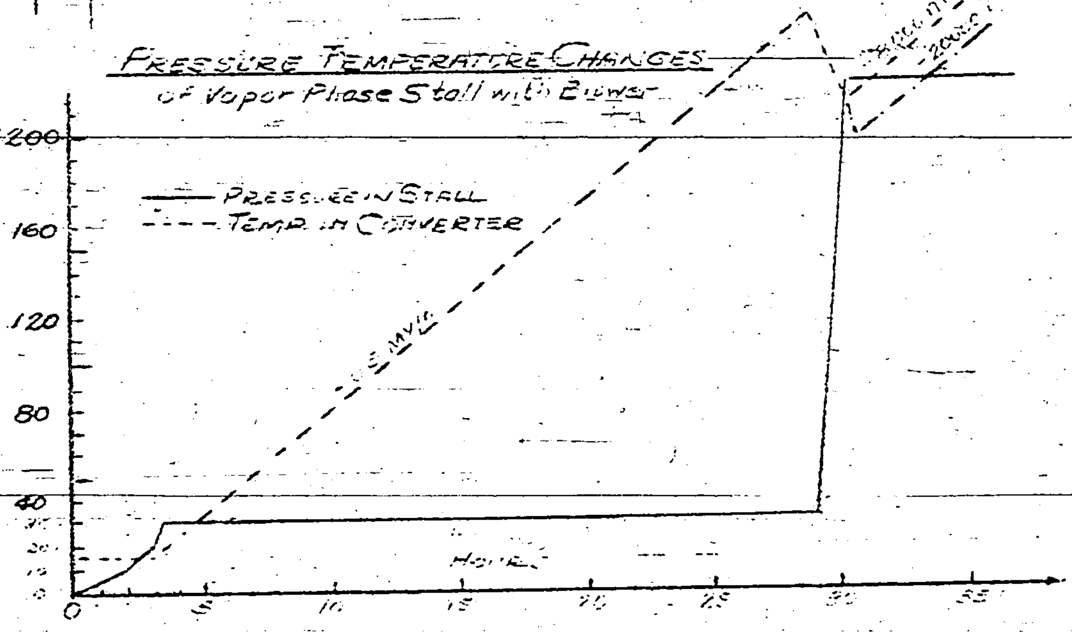


FIG 3

Newman

T.O.M. REEL 129
Pgs 680-725

U. S. BUREAU OF MINES
HYDRO. DEMON. PLANT DIV.

T-128
Trlsd KCBraun/pay
10/9/46

# Abstract of Report on High Resistances on the Suction Side of Heat Exchangers for 5058 Stalls.

(See also T-131)

Leunawerke, 10 October 1938.

High resistances have recently been observed on the suction side of the heat exchangers for the 5058 vapor-phase stalls.

Results of examinations of dismantled heat exchangers are compiled below. We are attempting to find the causes of the fouling by a study of the findings on dismantling, in connection with the operating characteristics of the heat exchangers still in operation.

## I. FINDINGS ON DISMANTLING.

### 1). Stall 16, Heat Exchanger II, 812/33 (See Fig. 1)

Dismantled 20. Feb. 1938, after 493 operating days.

Operating Periods and Injection Feed:

From 20 September 1936 to 19 March 1937=180 days, A + B middle oil + bituminous coal tar middle oil.

From 20 March 1937 to 1 January 1938=282 days, A middle oil.

From 19 January 1938 to 20 February 1938=31 days, A + B middle oil + bituminous coal tar middle oil.

Heat Transmission and Resistance.

The heat transmission to the end of December 1937, that is over a year, held to 200 Kcal/m$^2$/$^\circ$C/h and then fell to 160 in January 1938. The resistance on the suction side of the heat exchangers was normal up to this time at 1.5-2 atm. A decided rise to 10 atm. in the resistance on the suction side did not occur until February 1938. At the same time the heat transmission dropped to 80 Kcal/m$^2$/$^\circ$C/h. In this last operating period A + B middle oil, containing bituminous coal tar middle oil, was run.

Findings on Dismantling:

The outside of the bundle was clean, only very meager FeS deposits. (See photo).

Inner Bundle: (See Foot Note)

a). The upper tube sheet was partly covered with a white salt deposit. Besides, the tube sheet was heavily corroded, indicated by stalagmites 1 cm high.

b). The lower tube sheet was also heavily corroded and covered in the middle with white salt deposits.

The clogging of the tubes was determined by resistance measurements, which equalled over 800 mm oil when passing $200 m^3/h$ of nitrogen.

Of the 151 tubes, 139 were clogged, 7 others were restricted, and only 5 were entirely free (See Fig. 2).

Analysis:

The white salt deposit on the tube sheets is $NH_4Cl$ and contains no $CO_2$. The deposits inside of the tubes is FeS and $NH_4Cl$.

2). Stall 13, Heat Exchanger II, #828/46

Dismantled 7 April, 1938, after 254 operating days.

Operating periods and Injection Feed.

From 14 July 1937 to 23 July 1937=9 days, A / B middle oil / bituminous coal middle oil.

From 29 July 1137 to 3 December 1937=125 days, A/B middle oil / bituminous coal middle oil.

From 18 December 1937 to 7 April 1938=120 days, A middle oil without bituminous coal middle oil.

Heat Transmission and Resistance.

For the first 2 months the heat transmission held to 370, then fell to 200 by December 1937 and held to this figure to the dismantling. The resistance rose intermittently from 2 to 5.5 atm. between the end of October and the middle of November, then temporarily dropped back to 3.5 atm, only to rise again to 6.5 atm. in January 1938. Just before the shut-down the resistance on the suction side was 9.5 atm. At the shut-down on 3 December 1937, the heat exchanger was flushed out with water. The flushed-out residue consisted of FeS-Zn. It is possible that ammonium chloride was dissolved in the flushing water and did, therefore, not show in the analysis of the deposited residue. Presumably, FeS was deposited

(Note:-The author speaks of "Inner Bundle" and "Outer Bundle". What he seems to imply is "inside" and "outside" of tubes).

when running A/B middle oil ⁄ bituminous coal middle oil. The Steep rise in January must be attributed to previous deposits piled together.

Findings on Dismantling.

Outside of Bundle: The tubes were practically clean, had only small FeS deposits.

Inner Bundle: The upper tube-sheet was encrusted with FeS on one side, otherwise the tubes were clean on top. The lower tube-sheet was also clean, as far as could be seen before taking it apart.

Findings on Disassembly

Of the 151 tubes, 43 were completely clogged up and a large part of the tubes were heavily constricted. Both tube-sheets had heavy rust deposits.

Analysis: The borings from the inner bundle tubes consist of FeS and Zn. They contain only very little Cl, compared to the previously described heat exchanger.

3). Stall 7, Heat Exchanger I, #832/23.

Dismantled 25 June 1938 after 943 days, operating largely on A ⁄ B middle oil ⁄ bituminous coal tar middle oil.

Heat Transmission and Resistance.

For over 2 years, just as in Heat Exchanger II, following, the heat transmission varied between 350-500 Kcal/m$^2$/$^o$C/h; and then dropped to 200-250 just before dismantling. The resistance on the suction side was 1.0-1.5 atm. to March 1938, and then rose to 3 atm. before dismantling.

Findings on Dismantling.

Outside of Bundle: Some tubes have an FeS crust to 1.5 mm thick, others show no corrosion, indicating varying quality of galvanizing. The corrosion is heavier on the hot than on the cold end. The tubes are also covered with a layer of black, sooty deposit.

Inner Bundle:

The Upper Tube-sheet. Many of the tubes are clogged up with washed together FeS crusts.

The Lower Tube-sheet has a thick rusty deposit and efflorescences of white salt. A large number of the tubes are clogged with white salt deposits partly hanging from the lower tube-sheet.

When they were taken apart, 98 of the 151 tubes were found to be clogged, that is, their resistance was above 800 mm. The clogging occurred principally in the lower third of the bundles, that is, the cold end, and consisted of $NH_4Cl$, which indicates that $NH_4Cl$ was already precipitated in the cold end of the hot heat exchanger.

Stall 7, Heat Exchanger II, #827/18.

Dismantled 25 June, 1938, after 1010 days, operating on the same product as heat exchanger I, preceding.

Heat Transmission and Resistance.

Until December 1937, or over 2 years, the heat transmission held to 250, then slowly dropped to 120 just before dismantling.

Similarly, the resistance on the suction side rose in December from 2.5 to 5.0 atm, which was then maintained to the shut-down.

Findings on Dismantling:

Outside of Bundle: The tubes are only slightly fouled at the bottom with a thin smudge of block soot increasing towards the top.

Inner Bundle: Upper and lower tube-sheet. A large number of tubes is clogged with a rusty deposit. The lower funnel is heavily corroded and shows nuclei of corrosive attacks. Of the 151 tubes, 117 were found to be clogged, that is, their resistance exceeded 800 mm.

Analysis: The residues consist largely of FeS. Compared to the heat exchanger in stall 16, they contain very little $NH_4Cl$.

The $NH_4Cl$ had already been deposited in the cold end of H.E.I. and then produced corrosion and FeS formations in H.E.II, where condensed water is injected.

Stalls 9 and 10.

Heat exchangers I and II of these stalls gave performances in practice similar to the foregoing. They are, therefore, not reproduced here.

Heat Exchangers still in Operation

Stall 13. Since 12 April, 1938, this stall has been running A-middle oil, which contains bituminous coal-tar middle-oil since the 14 May, 1938.

Heat Exchanger II. (On the 6 October, 1938; after 292 operating days). During the first 78 days of operation the resistance held to 2.5 atm, when it rose in jumps to 9 atm on the suction side and later dropped back to 6.5 atm.

Heat Exchanger I: (On the 6 October, 1938, after 547 operating days). Its resistance was 2 atm. without perceptible fluctuations. The heat transmission of both exchangers together is 300 Kcal/m$^2$/$^0$C/h. A separate calculation of each exchanger is not possible because one exchanger element has dropped out.

Stall 16. - Since the 30 March, 1938, this stall is operating with 2 new heat exchangers, running A-middle oil, which contains bituminous coal middle oil since the 19 May, 1938.

Heat Exchanger II: (On the 6 October, after 195 operating days). The resistance on the suction side the first 60 operating days, to the end of May, was 3 atm, then rose intermittently to 6-6.5 atm, which it maintained to the beginning of August. Since then, the resistance has dropped again and is now 4 atm.

The heat transmission held to 300 to the end of May, then dropped to 150 simultaneously with the steep rise in resistance, and rose again to 300 with the decreasing resistance. Apparently we have succeeded in flushing out the clogged tubes, at least in part.

Heat Exchanger I. (On the 6 October 1938, after 195 operating days). Its resistance has held to 2.5-3.0 atm. since the start. The heat transmission to the middle of June 1938, was 550, and it has since dropped slowly to 300.

Stall 9. Operating with 2 new exchangers since the 25 June, 1938.

Heat Exchanger II. (On 6 October, 1938, after 105 operating days). We made our first attempt here to prevent clogging by different connections. It is so connected that the incoming feed passes through the inner bundle from bottom to top and the catch pot product through the outer bundle from top to bottom. See

Figure 4. This connection has, however, not been satisfactory. The resistance on the suction side rose after only 30 days from 1.5 to 4.5 atm. and then still further to 7 atm. at present. The heat transmission has slowly dropped from 250-300 at the start to 160 Kcal/m$^2$/$^0$C/h. This resistance could not be lowered even after temporarily increasing the water injection for 7 hours to 5 m$^3$/h.

Heat Exchanger I. (On the 6 October, 1938 after 105 operating days). Standard connections. The heat transmission dropped from 700 to 450. The resistance is still normal at 1 atm.

Stall 10. Operating with 3 new heat exchangers since the 3 October. Exchanger II is connected the same as in Stall 9, except that the suction side is connected so that the direction of flow is from bottom to top. This will form a sump on the suction side of the cold exchanger, from which it is hoped that, due to the constant motion and whirling, no salt segregations will be deposited or that they will be easier to flush out because of the better water mixture.

## Chlorine Content of the Injection Feed to 5058 Stalls.

Because large quantities of $NH_4Cl$, partly in almost stoichiometric relation, were found in the fouled exchangers, the chlorine content of the injection feed will now be considered.

It has been found that bituminous coal tar middle oil, which formerly contained 0.015-0.02% Cl, shows repeated sharp peaks in its Cl content within the past years. This oil, mixed with A + B middle oil, was injected until May 1938. Since then it is mixed with A - middle oil. The high peak of 0.08% Cl in the bituminous coal middle oil in July 1938, however, is not reflected in a corresponding increase in the Cl-content of the A-middle oil.

Since the deposits in the heat exchangers consisted formerly of $NH_4HCO_3$, and deposits of $NH_4Cl$ occurred only once, temporarily, in 1934, the higher Cl-content of the injection feed, and particularly of the bituminous coal tar middle oil, is probably responsible for our recent troubles.

## $H_2S$ Contained in the Inlet Gas to Gasoline Stalls.

The greater FeS formation on the suction side of heat exchangers, compared to former observations, may be explained in the following manner:

Since the introduction of the 6434 catalyst, whose injection feed is charged with briquet sulfur or $H_2S$ in order to maintain the activity of the catalyst, the $H_2S$ content of the circulating gas has risen from 0.04% (Vol.) to 0.07-0.08% (Vol.).

### Explanation of the Fouling by FeS on the Suction Side of Heat Exchanger II

The $NH_4Cl$, which is probably produced in the converters by double decomposition of the organic chlorine compounds with $NH_3$, is mixed at the suction inlet of the cold heat exchanger with the condensed water (1000 liter/h) injected for the purpose of removing the salts. The concentrated $NH_4Cl$ solution formed partly dissolves the galvanizing and the heat exchanger material. The zinc and iron chloride formed combines with the $H_2S$, now present in larger quantities, to form FeS, which fouls the inside of the tubes and can not be removed, even by water injection. This explanation is verified by the constitution of the FeS-deposits found in the tubes of the cold heat exchangers. These do not consist of FeS-crusts or shells but of FeS in the form of powder or crumbs.

### Means for Removing the Fouling on the Suction Side of Heat Exchangers.

#### I. By better Distribution of the Condensed Water Injected into Heat Exchanger II.

As found in the dismantling of H.E. II of Stall 10, the clogged tubes are principally near the center of the tube bundle, which leads us to presume that the injected water spreads to the periphery of the tube bundle and does not reach the center tubes. (See figure 3). When it becomes possible to flush all tubes uniformly with water we may expect that the $NH_4Cl$ or FeS formed will have no chance to be deposited, because it will be flushed out immediately after formation.

#### II. By Injection of a Soda Solution into the Suction Side of the Cold Heat Exchanger.

The conversion of ammonium chloride into sodium chloride would prevent the corrosive character of the $NH_4Cl$ and with it the heavy FeS formation.

In Scholven, 800 liters/h of a 0.04-0.07% soda solution is injected into the A-product stalls on the suction side between H.E.I. and H.E. II. A comparison of conditions between Leuna and Scholven A-middle oil stalls shows that Leuna uses from 5 to 7 times as much soda for neutralizing the chlorine. It is surprising that the Scholven middle oils on a pure bituminous coal basis show a lower chlorine content than our middle oils of a mixture of brown coal with relatively little bituminous coal tar middle oil, because the products processed in Welheim, pitch, anthracene oil, etc, show chlorine contents of 0.03 to 0.07%. It must be assumed that the chlorine compounds in Scholven are already removed in the liquid phase.

Sometime ago Leuna tried this injection of soda solution and also NaOH. This caused a deposit of $Na_2CO_3$ on the upper tube sheet, due to the evaporation of the water, and further increased the resistance.

III. By Lowering the $H_2S$ Content of the Circulating Gas.

The heavy FeS formation could be reduced by washing the circulating gas for 5058 stalls, though this would mean a separation of the circulating systems for the 5058 and 6434 stalls and can not be done with the existing circulating lines.

IV. By a Change of Flow in the Cold Heat Exchanger, in case the present arrangement in Stall 10 works out successfully.

## SUMMARY

Examination of dismantled heat exchangers indicate that many times during the past year high resistances on the suction side of the cold heat exchangers for the 5058 stalls have occurred, which were caused by a high chlorine content of the injection feed. These resistances imply a steep drop in the K-value of the heat exchangers.

The $NH_4Cl$ starts to separate on the suction side in the bottom third of Heat Exchanger I. The cold exchanger shows either heavy deposits of $NH_4Cl$ or FeS, or a mixture of both salts.

The higher $H_2S$ content of the circulating gas, appearing since the introduction of the 6434 catalyst, favors the formation of FeS on corrosion by ammonium chloride.

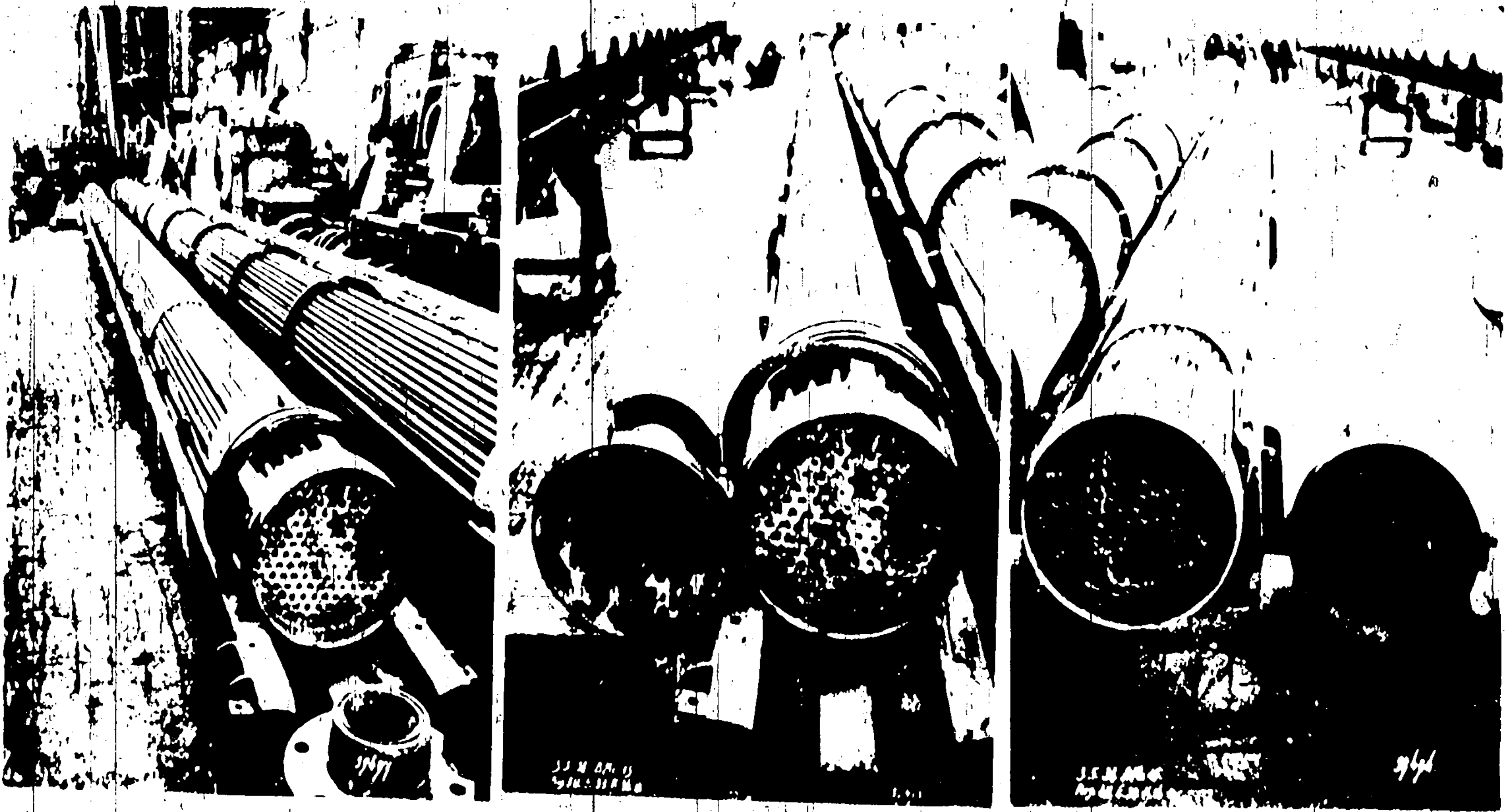
Measures for removal of these deposits are indicated herein.

(Signed) Kimmerle.

T-128

Stall 16.
Kammer 16.

Heat Exchanger II Nr. 812/33, dismantled 20. Feb. 1938 after 493 operating days.
Regenerator II Nr. 812/33 ausgebaut am 20. Februar 1938 nach 493 Betriebstagen.



Unterer Rohrboden mit Salzbelag
Lower Tube-Sheet with Salt Deposit.

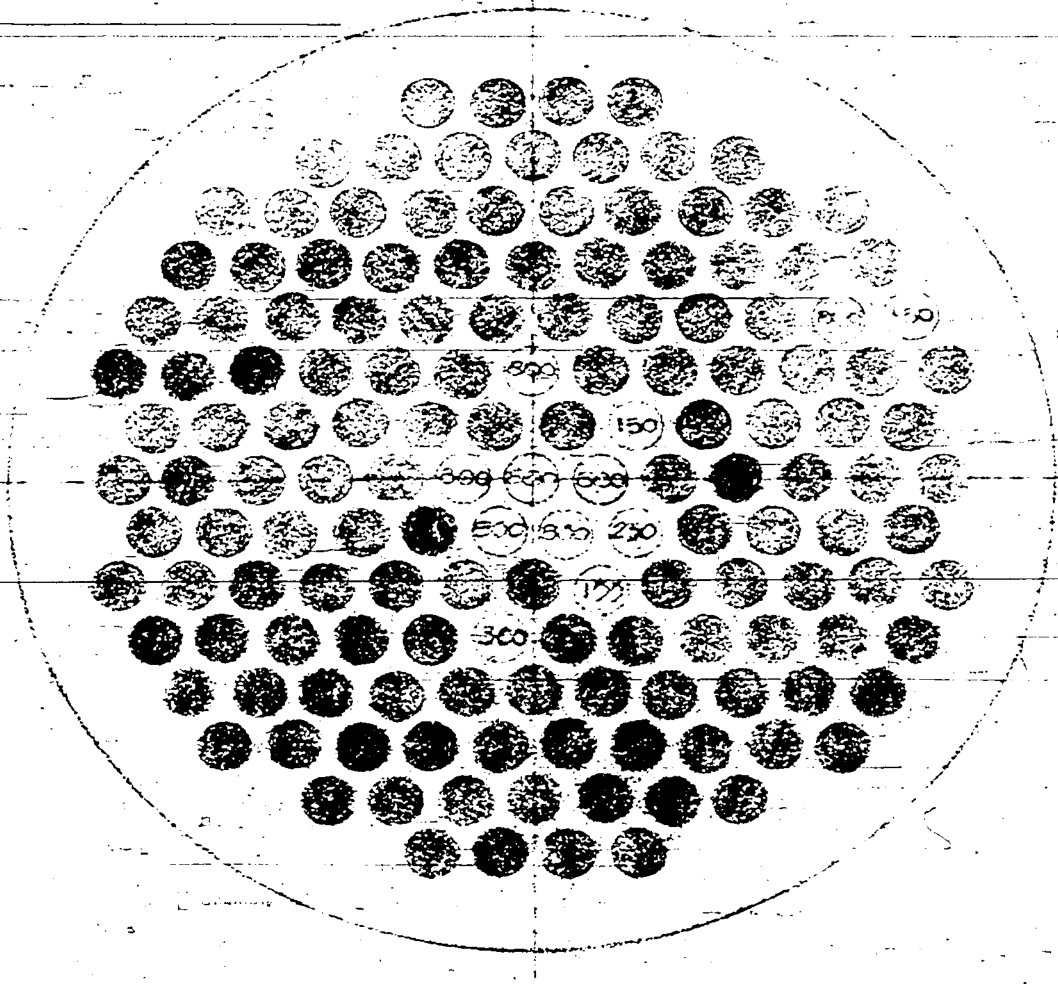
Unterer Rohrboden und Trichter mit Salzbelag
Lower Tube Sheet and Funnel with Salt Deposit.

Oberer Rohrboden
Upper Tube-Sheet.

FIG. 1.

Still 16
Heat Exch. II #812/33

133 Tubes clogged, over 800 mm oil resistance. Inserted figures indicate tube resistances.

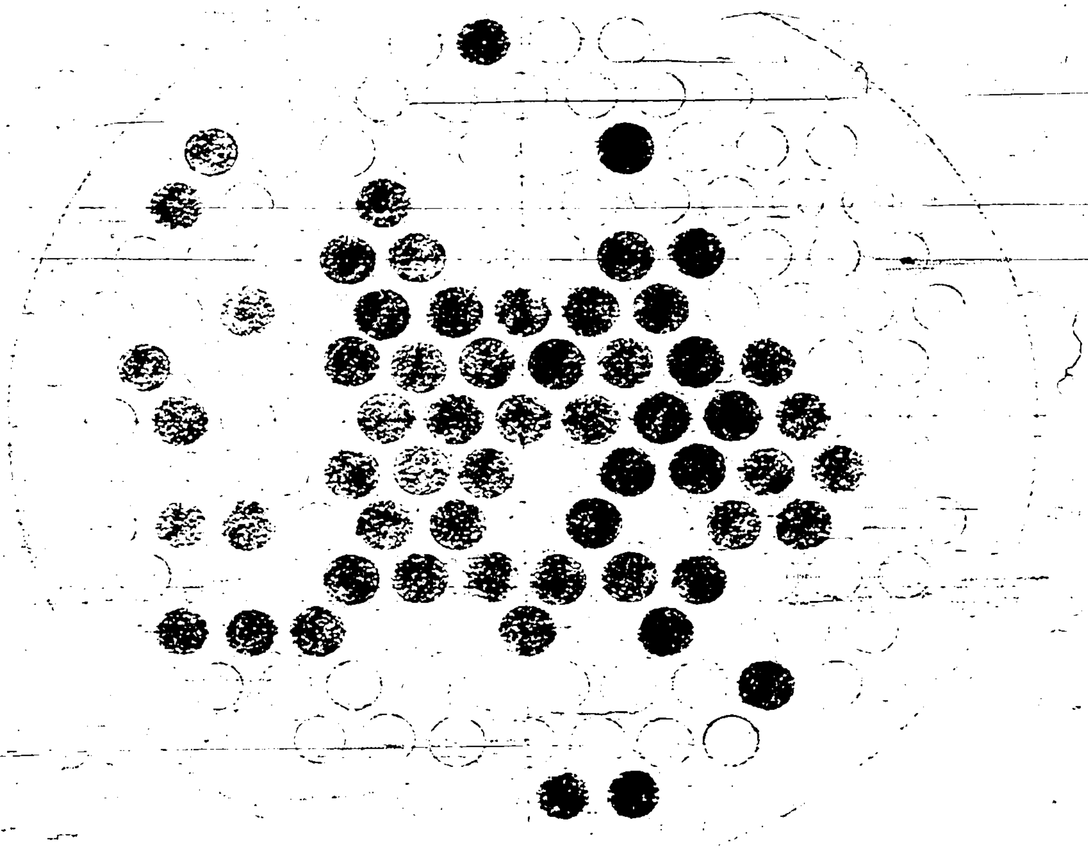


Arrangement of tubes in 500 mm ⌀ Heat Exchanger
151 tubes 14/23 mm⌀

FIG. 2

T 125

Stn. 10
Heat Exch. II #818/10



Arrangement of Tubes in [illegible] Heat Exchanger
[illegible] 181 Tubes [illegible]

FIG-3.

Dudley

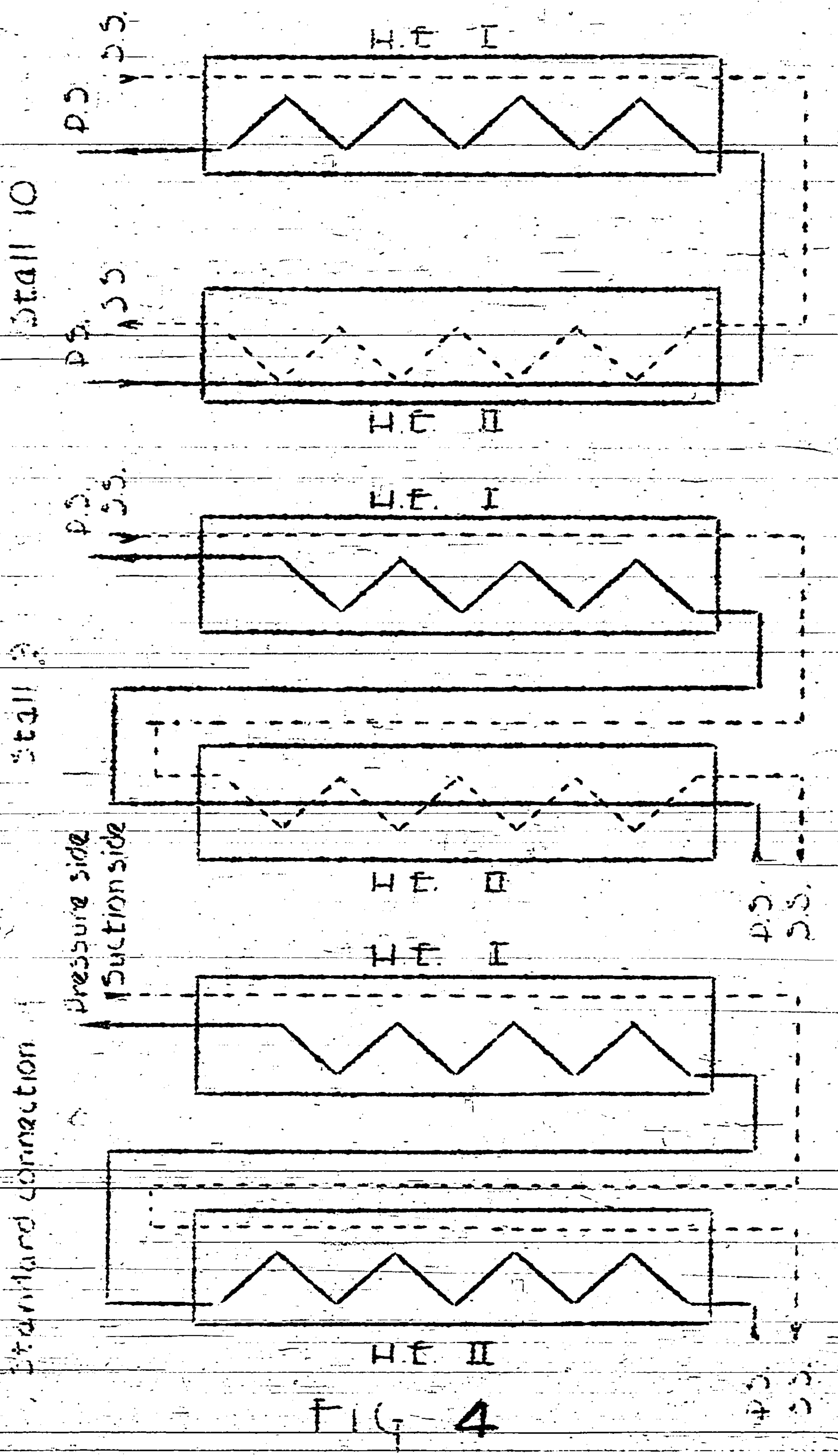

H.E. I
D.S.
S.S.
Stall 10
D.S.
S.S.
H.E. II
H.E. I
D.S.
S.S.
Stall 9
H.E. II
D.S.
S.S.
H.E. I
Pressure side
Suction side
Standard connection
H.E. II
D.S.
S.S.

FIG 4

TOM Reel 180
pp. 849-851

U. S. Bureau of Mines
Hydro. Demon. Plant Div.

141

T-129

# HIGH PRESSURE OPERATING PROBLEMS

By Dr. Kimmerle and Dipl. Ing. Schwab

Me 870, 11 May 1939

## INDEX

1. - Resistance in 5058 Stalls:

It is probable that the increased injection of water into the cold heat exchangers will prevent resistances caused by ammonium salt deposits. However, the resistance in the 500 mm dia. heat exchangers is already about 3 atm., when new, due to the high gas volume in the stalls with 1200 mm dia. converters, so that the pressure difference on the suction side of the exchangers alone is 6 to 7 atm. It is intended to check these resistances again. The stalls are, therefore, already put out of use with a pressure difference of about 0.6 atm.

The hydraulic resistance is considerably smaller. The pressure difference on the inlet side (pressure side) is only 0.6-1.0 atm. for each exchanger.

It is, therefore, intended to provide one stall experimentally with larger dia. exchangers. Possibly 800 mm dia. converter jackets may be used.

2. - Recirculating Lines:

In order to eliminate the large quantities of oil in Me 803-805, because of the fire hazard, the installation of recirculating lines (Ringleitungen) for coal paste and pasting oil from Me 801 to Me 803-805 was discussed. Such recirculating lines would be of particular advantage when Insichfahren, because with the present arrangement the level must be held in each individual measuring vessel. (Insichfahren, literally "running in, by or within itself", seems to imply idling, recicling or operating without feed). Recirculating lines are also desirable for reasons of economy of operating personnel.

It is intended to investigate the possibility of increased capacity in Me 801, possibly in two different places. When we succeed in keeping the letdown from Converter I of the coal stalls in continuous operation, it will be possible to "idle" (Insichfahren) the coal stalls also without seriously endangering the stalls. The silos and measuring vessels are already out of service for B-middle oil because of sulfuring the product. It is also proposed to build direct lines for the A-product, by-passing the silos and measuring vessels.

3. - Electrically Operated Valves:

So that we can quickly shut off our fresh-gas lines in case of trouble with the gas compressors or in the gas cleaning equipment, we intend to install electric driven valves. Because of delay in delivery of these valves, the installation of check valves should be investigated.

The ratchet valves for shutting off the stalls from the recirculating lines should also be electrically driven because of the dearth of operators.

All electrically controlled shut-off elements on the circulating and fresh-gas lines should be operated from a central control panel.

4. - Gas Circulating Pumps:

At present all eight circulating pumps are in operation.

For Circuit I, 5 pumps @ 265 RPM.

For Circuit II, 3 pumps @ 210 RPM.

Every circulating pump has to undergo a general overhaul annually requiring from 4 to 6 weeks. For this reason, only four pumps are at present available for Circuit I. In case of failure of one pump, the other three can not supply the required gas. Since it is essential that sufficient gas be supplied to the liquid phase, because of the coking danger, one of the pumps on Circuit II must be switched on to Circuit I in an emergency. The gas to the 6434 stalls must, therefore, be reduced in Circuit II, and the injection into 5058 stalls must be cut back. The switch-over requires at least 1/2 hour. We hope to bridge over this period by crowding the remaining three pumps in Circuit I.

5. - Preheater Coils:

Since Stall 6 has already run 88 days on 27 $m^3/h$ injection, the tube bends in the gas preheaters should be investigated for wall thickness with mesothorium.

6. - Irregular Coal Stall Operation:

The operating department is of the opinion that the irregular operation of the coal stalls is due:

1.) - To variations in coal paste composition.

2.) - To the gas used for cooling the letdown, 30-40% of the total gas supply, which is not heated uniformly in fluctuations in letdown quantity produced. Since this gas from Heat Exchanger II is mixed with the coal paste and inlet gas, fluctuations occur in the heat exchanger and converter temperatures.

To eliminate this influence, a stall without letdown heat exchange is to be designed.

KCBraun/jw

10-11-43

U. S. Bureau of Mines
Hydro. Demon. Plant Div.

Newman

## Water Injection with Spray Nozzles Into Heat Exchanger II of 5058 Saturation Stalls

Leuna Werke, 11 Sept. 1940

On the suction side of Heat Exchanger II of 5058 saturation stalls an ever-increasing resistance due to salt deposits was encountered after operating for some time. To prevent this, 1000 liters/h of water was injected on the suction side between Heat Exchangers I and II. Careful investigation has shown that this quantity of water is not enough to saturate the gas; between 3000 and 4000 liters/h must be injected into Exchanger II.

The first problem to be solved was, how to distribute this water uniformly over the exchanger tube-sheets in order to prevent local temperature differences, which would tear the weld between the tubes and tube-sheet. To avoid this, the water should be injected by spray nozzles, which would distribute it uniformly over the exchanger tube-sheet. The following experiments were made with several spray nozzles on a standard exchanger containing 186 tubes. These were divided into 36 tube groups, arranged in 6 concentric columns of 6 groups each, as shown in Figure 1. The water discharged from these tube groups was collected in separate measuring vessels. The experiment was so arranged that the distance between nozzle mouth and tube-sheet could be varied to suit. It was also possible to vary the water pressure for variable water volumes. Two sight glasses in the exchanger neck made it possible to observe the nozzles in operation.

The experiments were made principally with the following four spray nozzles:

1). Schlick - 1/2"

2). Richter - 1/2"

3). Körting - 8 mm.

4). Leuna - 7 mm, developed by us in the course of the experiment. See Figure 2.

In three of the nozzles the water enters tangentially into the nozzle inserts in which it assumes a rotating motion and leaves the nozzle mouth in a conical stream. In the Körting nozzle this is accomplished by a triple spiral. The hole in the center of the inserts distributes the water over the middle of the tube-sheet.

To get a picture of the distribution of the injected water, the water collected in the 36 measuring vessels was measured and the average amount per tube determined for each experiment.

Experiments were made with each type of nozzle at varying water pressure but constant distance between nozzle and tube-sheet, and again with constant water pressure and varying distance between nozzle and tube-sheet.

The experiments indicated that the 1/2" Schlick nozzle distributes much water over the middle of the tube-sheet at low pressure, 0.5 atm., and constant distance of 200 mm., while towards the periphery the water volume first decreases and then again increases to a maximum on the outside. At the higher pressure of 2 atm., the distribution is more uniform, although the water volume in the extreme outer column is again much higher, so that the corrected mean water volume is only 56%, (perfect distribution = 100%). Varying the distance produced a similar effect.

The 1/2" Richter nozzle and the 8 mm Körting nozzle have similar characteristics, although with different water pressures and volume. The water distribution over the middle of the tube-sheet is very poor, for both nozzles, first increases towards the outside, then decreases, and again rises to a maximum on the periphery.

The experimental distances between nozzle and tube-sheet seem to indicate that the Schlick and Richter nozzles have a comparatively steep spray cone, while the Körting nozzle has a shallow spray cone. The latter, therefore, is more sensitive to changes in the distance between nozzle and tube-sheet. These three nozzles have the additional disadvantage, for our purpose, of too fine a spray.

Because these three nozzle designs did not meet our requirements for water distribution, experiments were made with the Leuna nozzle developed by us. After many experiments it was made with a nozzle opening 7 mm dia., a central hole 4 mm dia., and two slots 5 mm wide x 8 mm long in the insert.

This nozzle does not meet all our desires for uniform water distribution proportional to pressure and distance, but it, nevertheless, is an improvement over the others. Except for the outer periphery, it does give a fairly uniform water distribution over the greater part of the tube-sheet. (See Figure 3). The accumulation of the water on the outer periphery is probably due to some water deflected from the more central portion of the tube-sheet towards the outside. In practical operation, this condition will very probably be considerably relieved because of the comparatively dense gas at the high operating pressure, so that a more favorable water distribution over the tube-sheet may be expected than the tests would indicate. If we follow this line of reasoning and disregard the water on the outer tube column, we get a fairly good water distribution over the entire tube-sheet, where the corrected mean water volume at 210 mm nozzle distance and 3 atm. is 90%, at 5 atm. 94% and at 10 atm. 85%.

The given pressures are typical operating pressures, when 2000-4000 liter/h water are injected into the heat exchanger. Since the injected water pressure is high, compared to the other nozzles, this nozzle will also give a favorable performance with the pressure fluctuations in the heat exchanger normally occurring within certain limits. Neither does it require constant regulation in operation in order to inject an approximately uniform water volume. It was also observed that this nozzle spray is coarser than the others, which would justify the assumption that not all the water will be vaporized before it reaches the tube-sheet but will form a film that will largely prevent salt deposits in the tubes.

All indications, therefore, point to a superior nozzle, which will give satisfactory results. This nozzle will now be generally installed, and it is hoped that results will justify our expectations.

(Signed) Schwab

KCBraun/jw

10-14-46

T-130

# HEAT EXCHANGER EXPERIMENT

Arrangement of tube groups
for spray nozzle water distribution

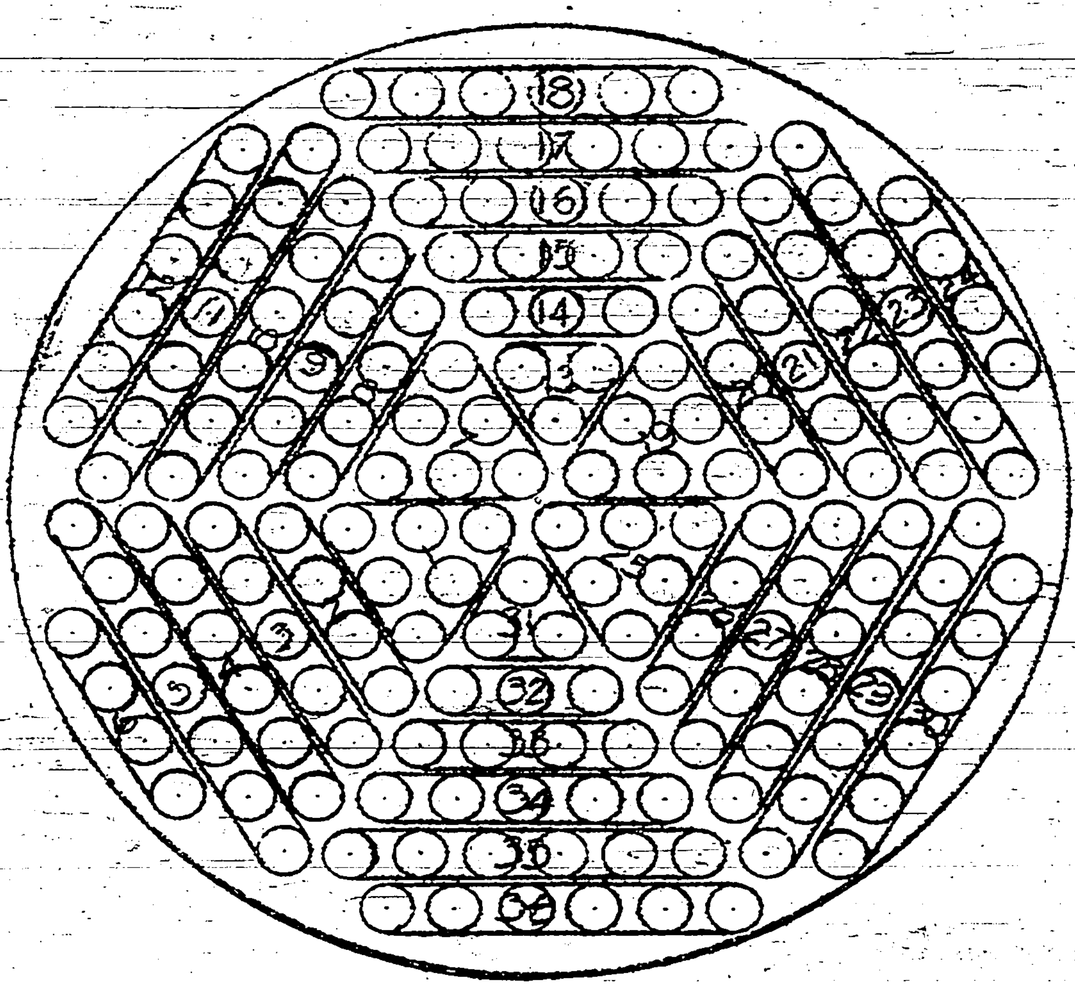


FIG. 1

U. S. BUREAU OF MINES
HYDROGENATION DEMONSTRATION PLANT DIVISION

These drawings were inadvertently omitted from T-130. "Water Injection with Spray Nozzles Into Heat Exchanger II of 5058 Saturation Stalls."

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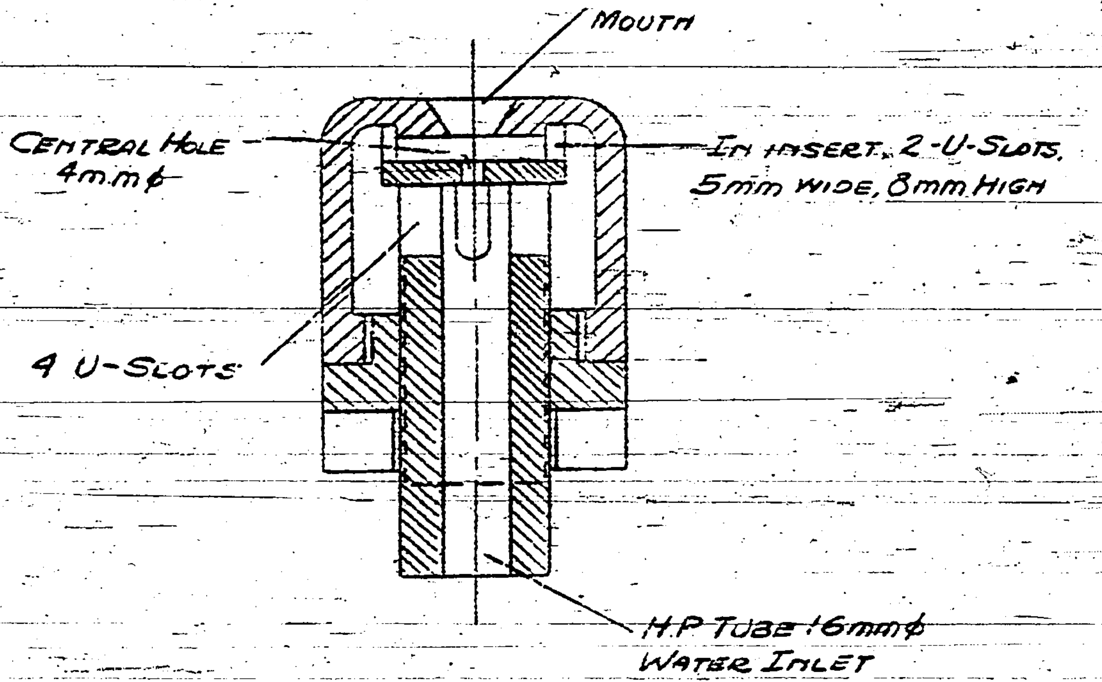
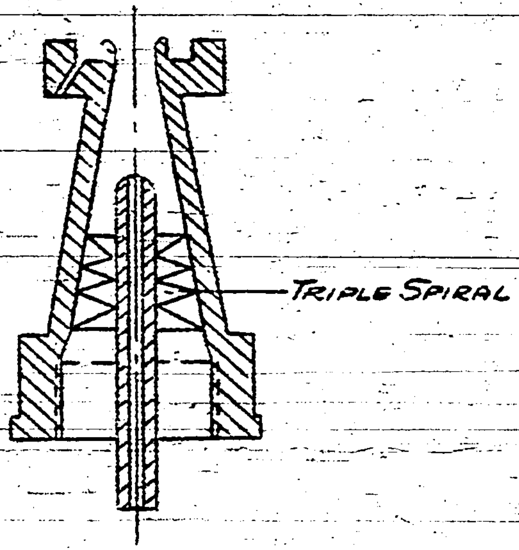
# BASIC NOZZLE CONSTRUCTION

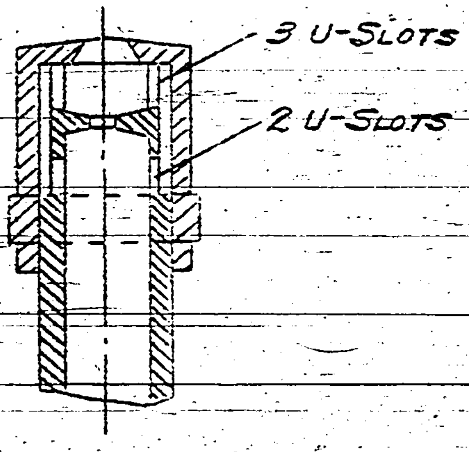
LEUNA NOZZLE 7mm. ϕ



KORTING NOZZLE 8m.m. ϕ



SCHLICK NOZZLE 1/2"



RICHTER NOZZLE 1/2"

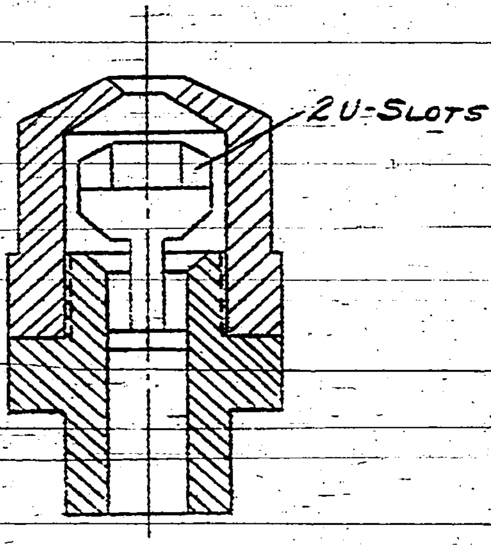
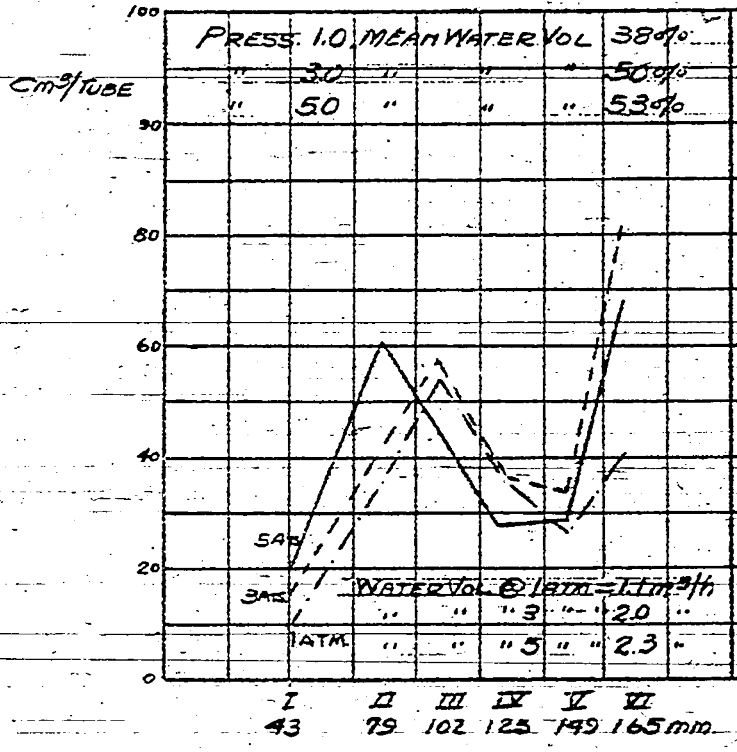
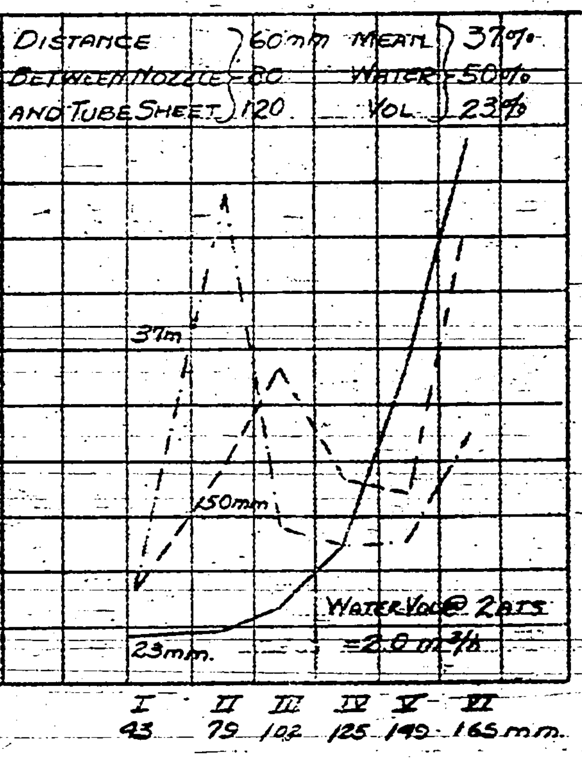


FIG. 2.

KORTING NOZZLE 8mm ϕ

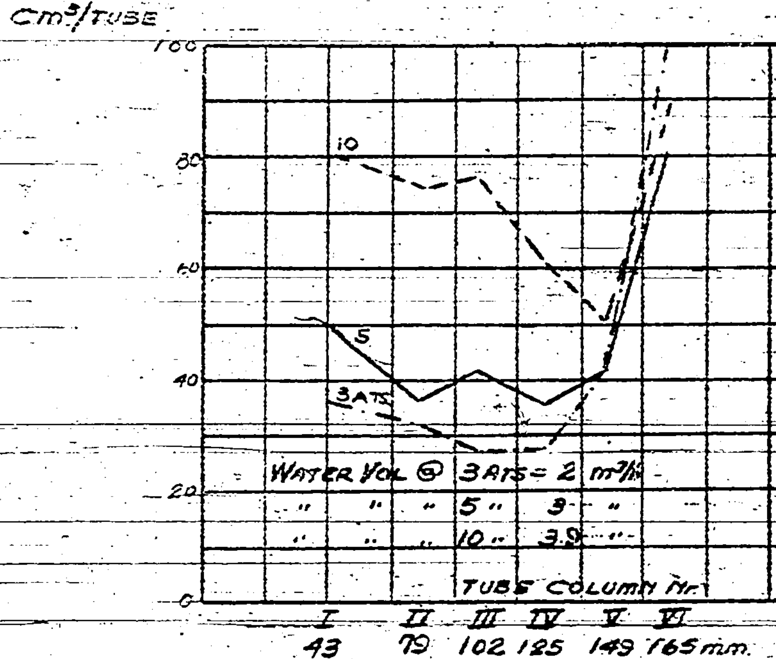


KORTING NOZZLE 8mm ϕ



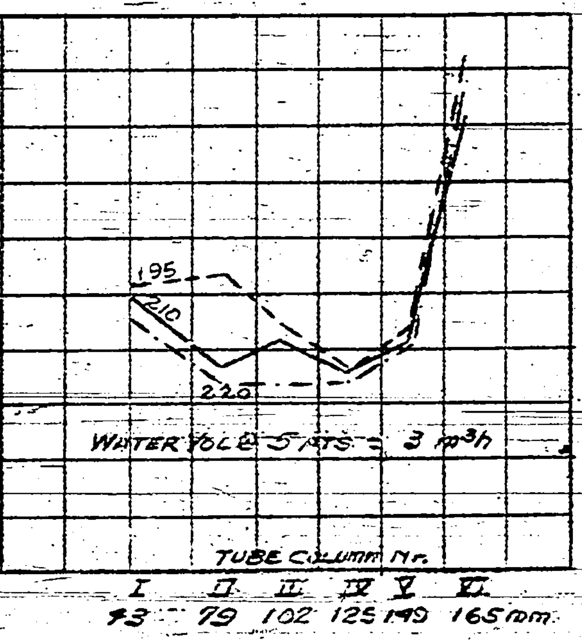
LEUNA NOZZLE 7mm ϕ

INFLUENCE OF THE WATER PRESS. ON THE WATER DISTRIBUTION AT A CONSTANT DISTANCE OF 210mm BETWEEN NOZZLE AND TUBESHEET.



LEUNA NOZZLE 7mm ϕ

INFLUENCE OF THE DISTANCE BETWEEN NOZZLE AND TUBESHEET AT CONSTANT WATER PRESS OF 5 ATS.



PRESS. 3 ATS, CORRECTED MEAN WATER VOL 42%
" 5 " " " " " 50%
" 10 " " " " " 62%

DIST. BETWEEN NOZZLE & TUBE-SHEET } 195 mm, 210 mm, 220 mm } CORRECTED MEAN WATER VOLUME } 40%, 50%, 44%

FIG. 3

# INSTALLATION OF THE WATER-INJECTION NOZZLE
## STALL 9, HEAT EXCH. 2

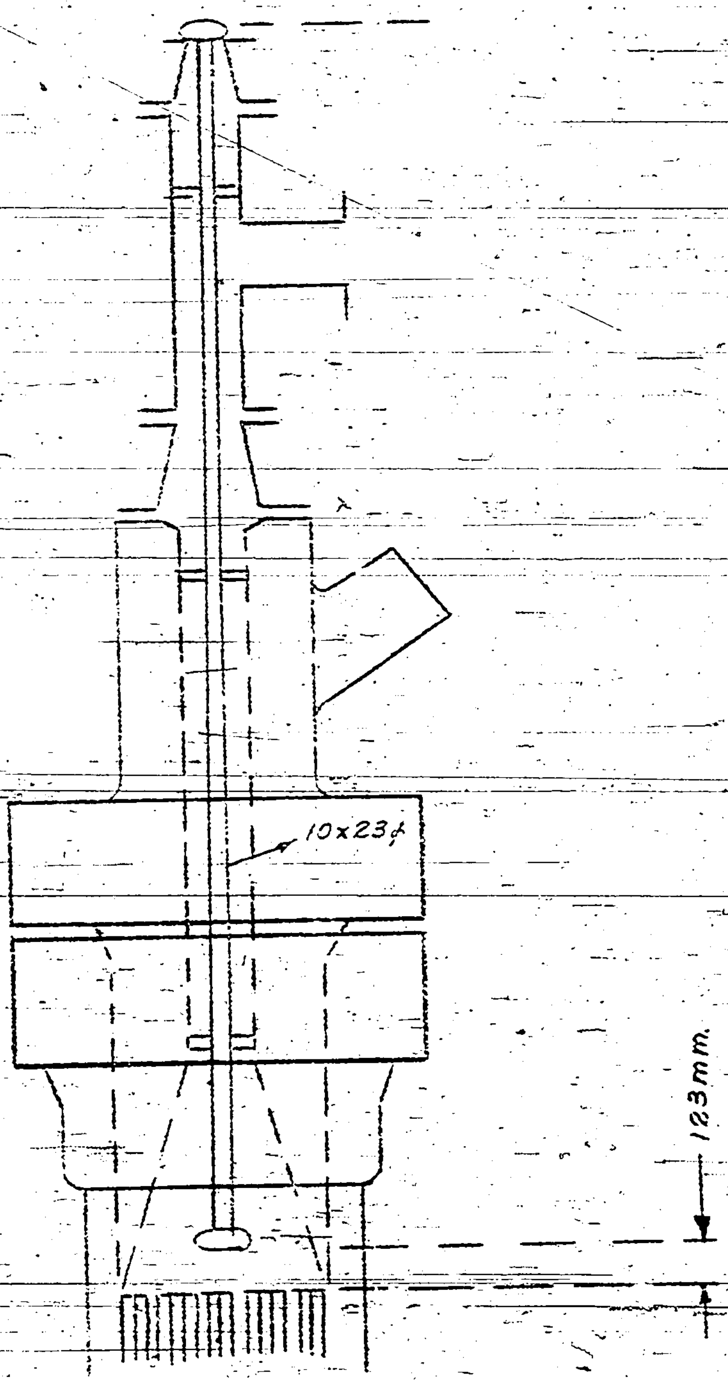


FIG. 4

TOM Reel 124
pp. 726-776

U. S. Bureau of Mines
Hydro. Demon. Plant Div.

T-131

## Fouling on the Suction Side of 5058 Heat Exchangers.

(See also T-128)

Leuna, 8 April 1941

Just as in the recirculating lines, salt deposits have been observed for years on the suction side of the heat exchangers behind the converters. They consisted of ammonium carbonate formed of one molecule each of $NH_3$, $CO_2$ and $H_2O$. The corresponding hydrogen-sulfide combination was, however, never found. By means of occasional, later continuous, water injections on the suction side of heat exchanger II, these deposits could largely be removed and their new formation made more difficult by reducing the $NH_3$ content of the circulating gases.

When towards the end of 1937 fouling occurred, which could not be removed so simply, these produced such high resistances in the heat exchangers that the thru-put in gas and product had to be reduced. The findings on dismantling differed from those found before.

For example, in heat exchanger II of Stall 16, 139 of the 151 tubes were clogged up after 493 operating days. The pressure loss on the suction side had risen from 1.5 to 10.0 atm. At the same time, the injection had to be reduced from 14 to 8 $m^3/h$.

In heat exchanger II of Stall 16, the resistance to flow increased from 3 to 9 atm. with decreasing injection and gas thruput volume after 254 operating days.

Heat exchanger I of Stall 7 on dismantling after 943 operating days already showed salt deposits on the lower tube-sheet. The pressure difference rose from 0.6 to 3.3 atm.

Heat exchanger II of Stall 10 also showed an increase in pressure loss from 2 to 6 atm. after 980 operating days. Heat exchanger I also showed $NH_4Cl$ deposits on the lower tube-sheet.

The fouling substances consisted of ammonium-chloride and ferrous-sulfide. The proportion of both compounds was variable and differed in color and general appearance, from white salt, consisting principally of $NH_4Cl$ to a black substance consisting largely of ferrous-sulfide. Remarkable, also, is the occurrence of distinct quantities of zinc oxide, which was also found when there was no $NH_4Cl$, which had been dissipated in some manner by succeeding processes.

The question now arises, where does the chlorine come from and why didn't we have trouble before? It has been shown that A-middle oil, and bituminous coal tar middle oil mixed with it, contains chlorine. It is organically combined and cannot be washed out with water, but is liberated in hydrogenation as partly dissociated $NH_4Cl$. In this form, it strongly attacks the walls and forms Fe and Zn compounds, which, in turn are separated as insoluble FeS and ZnS by the simultaneously present hydrogen-sulfide. The Cl is then again liberated in the form of HCl and can begin its work of destruction anew. If water is present at the same time or a zone of condensed reaction water should later be formed, the $NH_4Cl$ will no longer be found at the point of primary attack but only its traces in the form of FeS, ZnS and ZnO.

Compared to former operating periods, the thruput per stall had now been markedly increased, because, in place of 2-800 mm converters, 4 were installed or even the latter were replaced by 1200 mm converters. The water injection of 1000 liter/h was, however, retained.

In addition, the introduction of the 6434 catalyst with the attendant sulfuring of the B-product, doubled the $H_2S$ content at the entrance to the gasoline stalls, from 0.04 to 0.08%.

In search for relief we first considered conditions at Scholven, where pure bituminous coal products are processed. However, a comparison showed us that conditions at Leuna are much less favorable. The chlorine content here is seven times as high, and the $H_2S$ content at the inlet and outlet of the stalls is roughly ten times higher than in Scholven. Also, Scholven injects 800 liter/h of a 0.04 - 0.07% soda solution, while we must inject at least 1000 liter seven times as strong. Earlier local experiments had already indicated that the water of such solutions vaporizes and the resistance is increased by the deposition of salt.

Since this method could not be used for the elimination of corrosion and fouling, experiments were made to obtain a harmless segregation of the ammonium salt by a different connection, or operating method, of heat exchanger II. The following two different connections were made:

Contrary to normal operation, the gas and condensate did not run through the inside of the tubes, but around them on the outside, in one case from top to bottom, in another from bottom to top (See Fig. 4, T-128).

In the latter case it was intended to provide a liquid sump at the bottom, which would prevent all salt deposits.

In Stall 9, heat exchanger II was connected on the suction side to the space outside of the tubes and ran from top to bottom. After only one month's operation, the resistance suddenly rose from 1.5 to 8 atm., and remained at this height until it was shut down after 6½ months operation. A short circuit occurred through a hole in the upper tube-sheet. The dismantling and disassembly also showed very heavy fouling by the products of corrosion, FeS and ZnO, on the upper end, outside.

In Stall 10, heat exchanger II was connected the other way, from bottom to top, with a sump at the bottom. The resistance remained low, and the heat transmission dropped only from 250 to 175, which was still usable. The eddies in the sump had apparently prevented the salt deposits and consequent increased resistance. The stall had to be shut down because of a fire, when the exchanger offered a sorry sight on dismantling.

The lower part was badly fouled by products of corrosion, and the insulation was badly damaged. The binder (mortar) was washed out and the bricks themselves had been loosened and ground against each other.

Both findings, therefor, showed that any other method of operating the heat exchangers would lead to heavy damages due to corrosion.

Some dismantled normally operating standard connected heat exchangers showed that the clogged tubes were not uniformly distributed over the tube-sheet, indicating irregular water distribution. Experiments to find the best nozzle for uniform water distribution are described by Schwab (in T-130).

These improved nozzles were installed in four stalls, #9, 10, 13, and 16. Every new heat exchanger II was provided with a spray nozzle above the upper tube-sheet. In Stalls 10, 13 and 16, a trapped pipe was installed at the same time, just as in Scholven, which was intended to spray the lower tube-sheet in heat exchanger I. About 3500 liter/h of water was injected into each stall at these two points combined. The trapped pipe was omitted in Stall 9 for comparison.

At first these measures proved very successful. The resistances in heat exchanger II remained much longer near their original values. However, in Stall 16 it had risen so appreciably after seven months that an investigation seemed desirable. In this investigation, it was found that the point of water injection at the bottom of heat exchanger I was so badly corroded that a break in the connecting line could be expected with further operation. The water injections at this point in Stalls 10 and 13 were, therefore, immediately discontinued and the stalls prepared for examination shortly thereafter. Only Stall 9, into which no water had been injected, could continue operating. After almost two years of operation its resistance gradually rose but not as high as formerly. The heat transmission also dropped only a little.

The heat exchangers in Stalls 10, 13, and 16 showed the following condition:

The point of injection to the lower tube-sheet of heat exchanger I was badly corroded. Residual salts of the injected condensate water were also deposited here. Several Kg of $NH_4Cl$ deposits were found on the lower tube-sheet of heat exchanger I. The tube bundle itself was partly clogged.

Heat exchanger II was fouled very little. No salts were found on the tube sheets, at the most a little FeS.

It was, therefore, to be expected that, after eliminating the continuous water injection at the bottom of Heat Exchanger I and a further improvement in the spray nozzle on the upper tube-sheet of heat exchanger II, still less fouling and lower resistances would result, without heavy corrosion.

Such nozzles were, therefore, installed in Stalls 10, 13 and 16. Stall 13 was rebuilt for B-product after only five months of operation. However, heat exchanger II could be used without any change for the new experiment with 6434 catalyst.

In Stall 10, the resistance in heat exchanger II was uniformly low for almost eleven months. On dismantling, it was found that of 151 tubes, 84 were clogged.

In Stall 16, the resistance in heat exchanger II rose after eight months operation. On dismantling after 400 operating days, barely half the tubes were clogged, the upper tube-sheet showed a little slaty FeS deposit, while the lower was clean.

In the new 5058 Stall 11, in which a 600 mm dia. heat exchanger II was installed, showed a uniformly low resistance over an eleven-month operating period. The dismantling showed 129 of 241 tubes clogged up. The upper tube-sheet had a little FeS deposit, the lower some $NH_4Cl$.

## Conclusion:

The water injections with the 7 mm dia. Leuna spray nozzles (see T-130) considerably lengthened the operating period, because there was little fouling. A change in connections, or operating methods, or water injection between heat exchanger I and II, causes heavy corrosions in case of sump formation. The present construction and point of installation of the spray nozzle is not subject to these conditions.

(Signed) Hähnel

KCBraun/jw

10/15/46

TOM Reel 181
pps. 412-416

U. S. Bureau of Mines
Hydro. Demon. Plant Div.

T-132

# Erecting a Filter Station for Middle Oil

Böhlen, 12 December 1941

Some time ago a filter station for middle oil was erected on the east side of Building II, in order to prevent obstructions in the stalls, particularly deposits in the heat exchanger tubes.

The filters provided for the installation had ceramic inserts. The manufacturers assured us of their effectiveness, which was confirmed in a small scale experiment. However, in a large scale experiment these ceramic filter columns (Kerzen) proved entirely unsuitable after only a few hours. The pores of these filter inserts were so badly clogged that the suction pressure of the injection pumps dropped so low that the filter station had to be shut down.

The method originally provided for cleaning the filter columns by reversing the direction of flow from the inside to the outside, in this manner flushing out the deposits on the filtering surface, proved to be impractical. The reason for it was shown most clearly after dismantling a filter, in which the insert was damaged on the upper end. The visible cross-section was uniformly filled with deposits, so that a flushing out of these colloidal particles was no longer possible. The assumption that the deposits would stick only to the surface or would penetrate only very little proved to be erroneous. Although the filter manufacturer maintained that the heavy fouling of the filter columns was due to a wrongly selected pore size, we were still convinced that a ceramic filter is basically unsuitable for our purpose. We have, therefore, turned to our own design of the filter insert.

This filter insert construction has already proved satisfactory at Leuna. It consists primarily of a filter cloth in combination with a fine wire mesh screen. The basic body consists of a perforated plate cylinder, which is covered by a 60 mesh/cm$^2$ wire screen. The latter is then covered by the filter cloth proper, consisting of a canvas fabric.

The wire screen serves the purpose of preventing the filter cloth from being drawn into the holes in the plate by the oil stream and possibly torn on their sharp edges. Another wire screen of 400 mesh/cm$^2$ is then drawn over the filter cloth. The cloth, as well as the wire screens, consist of one piece wrapped around the cylinder, overlapping about 100 mm. The joints of the various layers are staggered. This insert was then inserted into the filter housing, which was otherwise unchanged.

It is intended to run only A-middle oil over these filters. The installation of eight filters is arranged in groups of four each, so that either group may be shut down for cleaning.

KCBraun/jw

10/15/46

Newman

T.O.M. REEL 129
Pps. 2-51

U. S. BUREAU OF MINES

T-133

HYDRO DEMON. PLANT DIV.

Leuna, July 7, 1942

## I. Reasons for Creating Special Accounting Stations in Hydrogenation.

In the early years of hydrogenation, the principal problem consisted in overcoming the great operation difficulties. Economic considerations had at first to be postponed, until some actual production had been started. However, shortly after the initial difficulties had been overcome, the economic study had to come to the fore in order to discover the different sources of losses and to find ways of increasing the yields. The accounting stations were arranged according to plans and the operating results were reported monthly as "Hilburg Reports" to produce a general picture of the stage of development. To be able to observe and regulate costs, their progress, and especially the cost of repairs, short time balances were calculated every 10 days, the so called "decade accounts"; an ideal account was set up to get data for the theoretical costs.

Such a carefully carried out supervision of operating costs brought the concern in direct contact with business accounting. It became soon clear that a close cooperation between production and accounting was required for a proper gasoline accounting. The production of intermediates (i.e. illuminating oil) at times reached large volume, and the purchase of tars and oils required accurate evaluation, which could only be furnished by the management.

When new hydrogenation plants were planned, the designing was turned over to Leuna. It became always necessary to convert the Leuna experiences to at times radically different conditions. We may use the filling of hydrogen requirements as an illustration because of the importance of it as a basic material, and of the demands made upon its degree of purity.

These problems of supervision of operating costs, of accounting, and the selection of proper design assumed in the course of time such a volume that the carrying out of the task required a special office.

## II. Accounting Tasks in Hydrogenation.

### 1. Supervision of Operating Costs.

When the study of economics of hydrogenation was begun, after the initial difficulties of operations were overcome, the production costs of gasoline were too high to be carried permanently.

The production costs were, therefore, studied from all angles; and not Leuna alone, but also the I.G. commission participated in this analysis. A properly functioning supervision of operating costs has not, however, proven to be a simple matter. One could readily see that the costs were too high, or that the level and compoenents of costs were changing with time; it was much more difficult to find the underlying reasons or the possible costs which could be reached within a reasonable time. Comparative figures were to be developed to permit a dependable supervision of operating costs and to properly evaluate them. It was further necessary to refine gasoline calculations to the point which would permit defining the principal reasons of the costs. An important requirement of accounting which would fulfill these requirements consists in an exact determination and distribution of the raw material and energy.

### a). Later development and systematic evaluation of the "Hilburg Reports".

An enormous amount of data has been collected by the operation's comptroller's office, using occasionally entirely novel methods at a great number of control stations. The selection of controlling stations is primarily based on the requirements of the operating department for the proper supervision of operations for accounting. However, all the control work is today of little worth if the large number of the currently obtained determinations are not evaluated systematically. The evaluation is much facilitated, and frequently made at all possible by proper classification of the results of determinations. For that reason, the collecting of the facts should not be over simplified, which is not always easy to avoid. Among the many peculiarities of hydrogenation are the great variety of raw products which may be worked in the same equipment, The many returns of products into the cycle and recirculations, and the method of presentation becomes very important. The following requirements must be met:

A. A visual presentation of the total field of Hydrogenation with all the returns of the product and the important recirculations.

B. The selection of characteristic factors.

A. When the manufacture consists of a number of consecutive steps, with the final product of each step used in the next step, the movement of the product may be readily seen by simply presenting the steps in their proper order. When, however, intermediates are introduced into the process or there is circulation, the visual presentation of the movement of the feed is made more difficult.

It is represented then in the familiar flow sheets, as has been done in a simplified form for the liquid phase on sheet 1. The advantage of this method of presentation consists in the clear picture of the progress of the feed. However, flow schemes have been found to be very laborious and tedious when used in practice to make calculations and other evaluations, where simple means of control are desired. The general presentation has therefore for several years been done in principle according to the scheme shown in sheet 2. Two vertical columns for intake and output are assigned to every operations; to the left of the columns is a column stating the raw materials (also intermediates from other concerns), to the right are columns devoted to production, losses, etc. The individual materials are added separately on different lines. Let us consider the intake and outlet columns of an operation; the consumption and production are set side by side, the sum of the intake and output must agree and give the thruput. When considering, however, the numbers along one line, we may see the movement of one product; the sum of the intakes must again equal the total outgo. A check is also provided for the total movement of the product: the total raw material input must equal the total production plus losses.

This method of presentation has been found very convenient and may be adjusted to the greatest variety of operating conditions. It has been accepted by most hydrogenation concerns, and therefore offers easy comparisons. We see here, that this purely formal presentation of operating results has a thoroughly practical significance.

B. While such a visible method of presentation of operating results as described above does furnish a basis for accounting and subsequent evaluation, it is not sufficient for an effective supervision of operating costs. I.e., were we to compare the consumption of hydrogen during different months of the year, we would find variations resulting from different levels of production, the nature of raw materials and intermediates, changes in stocks, etc., which are of such importance as to overshadow any improvements in methods which should have resulted in savings in hydrogen. It becomes therefore necessary to derive characteristic, specific factors from the "gross" figures of monthly production, a way which would largely eliminate the accidental effects. In general this can not be done by a simple division of the figures for the month by the production. An example for charateristic and non-characteristic factors is shown in sheet 3. The consumption of hydrogen per ton of final product, or the thruput thru a converter stall, is not characteristic for judging the vapor phase, because it depends very largely on the role played by 6434; on the other hand, the consumption of hydrogen in the 6434 step/te of gasoline, or the thruput thru the 6434 stall/te of 6434-L gasoline are characteristic. We shall return later to the selection of such factors.

Operations control calculate therefore monthly specific values for the different operations, making every effort that these values be characteristic in the above sense. This requirement can not always be entirely fulfilled. An assurance of having the specific values of the individual operations agree among themselves, is obtained by entering them into the so-called "1000 te scheme" similar to the monthly figures. The most important values are shown in curves which are discussed in detail in the monthly, "Hilburg Reports". The curves permit a ready recognition of changes.

The "1000 te scheme" mentioned is a product balance with a detailed subdivision of losses. The " elementary balances" afford a still further insight; in this case a balance sheet is made for the individual elements, C,H,O, N and S. A dependable production balance and good analytical results are important for a good elementary balance and are a prerequisite for setting it up, and the difference between the intake and output are a measure for it. Elementary balances are set up monthly for the liquid and the vapor phases (sheets 4 and 5 and the average balance for 1941). The principal values of the elementary balance are now represented in curves (sheet 6).

The results for the liquid phase were remarkably constant in 1941; for C the balance difference amounted to 5%, and 3% for hydrogen, and they were relatively high in comparison with the vapor phase - 0.4 for C and 2% for hydrogen. The reason for it must be found in systematic errors of measurement or analyses, because actually such losses could not exist undetected. The practical importance of the elementary balance is in the sharp control of measurements and analysis as well as in that it shows the reason for changes in yield and in hydrogen consumption (i.e. changes in the amount gasified); on the other hand when the accuracy is known, with which elementary balances can be set up, they can advantageously be used in design and accounting. It is frequently the only means to determine the hydrogen requirements of a new material. A graphic presentation is obtained by expressing the elementary balance in the form of flow sheets, and it gives information on the distribution of the elements between the final products and the intermediates.

### C). Checking

Several items of costs of hydrogenation products are combined in accounts, formerly made out monthly, now quarterly, which represent a number of operational factors. Their critical examination must therefore give information on the operational conditions at anytime and on their effect upon costs. The gasoline accounting is set up by the controller's office; operation departments informs it about operations in their reports, and these reports are brought in alignment with the above mentioned summarized report of the movement of the products. Gasoline accounts first furnish information on the production costs per te of finished products (motor gasoline, avaiation gasoline, diesel oil), classified according to the nature of costs and by the cost stations. This does not yet satisfy all requirements which may be demanded of cost accounting. Thus the costs of final products (motor gasoline, aviation gasoline, diesel oil and all the byproducts), and the production costs from the various raw materials (i.e. in addition to the cost of motor gasoline, also the costs of this product from coal, tars and oils) are as important as the blending costs of the finished product; in other words, a separation of costs according to raw materials and finished products is desirable. Finally, not only the finished products, but also intermediates must be properly evaluated; this is important in the evaluation of stocks for the yearly balance sheet and for insurance, to estimate the price for sales and for shipments to other concerns for credit. A correct cost assessment for the different finished and intermediate products in the different sections of the accounting, must also facilitate decisions about operational conditions, in particular the effect of the level of production upon costs; i.e. costs must be given as a function of the variably (operational effects). Fulfillment of this requirement will largely determine the possibility of making dependable predictions of costs. Because of the peculiarity of hydrogenation processes, these tasks, namely the

separation of costs into that of the raw and the finished materials,
correct evaluation of the intermediates,
numerical information on the relationship between costs and conditions of operation

can not be accomplished, by the methods commonly used in bookkeeping and accounting. Their solution is briefly indicated below.

## Separation of costs into raw and finished products; evaluation of the intermediates.

Sheet 9 shows schematically a greatly simplified accounting of coal middle oil in the form of a cost flow sheet, keeping only the essentials. For purpose of comparison, there is also given a flow sheet scheme of a simple step production with no returns into the process. The latter is very simple; starting with the costs of raw materials one gets, after the addition of operating costs (including additional materials, etc) of the operation A, the value of the intermediate product B which is placed into operation after addition to, or removal from, stock. The addition of costs of the different operations with consideration of changes in stock will give first the costs of the intermediate, and then that of the finished product. It must be observed in this connection, that changes in value are produced not only at the different cost stations, but also thru changes in available stocks, if the value of an intermediate is formed at any one station as a combination price of the amounts produced and the value of the stock in previous accounts; as a rule these two prices will differ somewhat from each other. Calculations must therefore be made step by step; should however fixed prices for stock be introduced, the cost of the finished product can be found directly by the addition of the costs of all operations and all changes of stock, which can be calculated in advance with fixed stock prices.

Gasoline accounting can not be directly made by this step process, because a return product, the pasting oil, of an at first unknown value, is produced in the first step when demands for pasting oil in the coal of the liquid phase is just covered, and an entirely arbitrary price can be attached to it, and debits and credits for the pasting oil (heavy oil) delivered and consumed are balanced. Such is no longer the case when a larger reserve stock of the pasting oil is obtained, or operations are conducted with an excess or deficiency of oil, as is actually the case in hydrogenation. The accounting can in this case be done as follows:

1. We find first with what proportion of the tar residue (in case of deficiency of heavy oil) the different cost stations are charged during the conversion into middle oil; these costs are set aside. (Isolation of tar constituent).

22. Computations are made with fixed stock prices. The total costs for coal liquifaction can then be found as such when referred to the amount of middle oil from coal (i.e. after subtraction of the middle oil from tar) we will get the production costs of coal middle oil.

3. The heavy oil (tar residue etc.) is so priced, that the middle oil obtained from it has the same production cost as other middle oil.

4. These values for the heavy oil are now introduced into the heavy oil computations, which then can be readily carried out. It must here be noticed that HOLD must also be evaluated "backwards", i.e. starting with the precooler and aftercooler oils. A check is obtained when the same average value is obtained towards the end.

The same process is carried out for the separation of finished products (motor gasoline, aviation gasoline, diesel oil). In actual calculations the relations are still more complicated, but the same means are always used:

1. Fixed stock prices (to permit calculating the price of the finished product).
2. Isolation of the return cycle.
3. Evaluation of intermediates from the value of the finished product (i.e. gasoline) produced from them.

It must be mentioned here that key factors for each calculation section as furnished by the operating department for use in the final calculations to permit "isolation: of return cycles and the combined operations on the product; from these are calculated the production costs of the finished product, the middle oil, heavy oil and waste oil. It enters into the step calculation with the heavy oil which is completely absorbed in operations. Step calculations must therefore result in the same price of middle oil and finished products as found previously. This acts as an accurate check on the accuracy of the key factors; extremely small errors will thereby be indicated.

An intimate numerical knowledge of operating conditions is a prerequisite for such calculations, and this knowledge is in part furnished by the Hilburg reports mentioned in Section A, and also from further study which will be discussed later.

The need of carrying out calculations with such refinements is also shown from purely economic considerations. It is, e.g. very important in the purchase of tars to know the permissible purchase price. Separation of costs is of further great importance for the finished products, because they may be handled in different ways contractually; aviation gasoline may be part of the contract, while motor gasoline and most of the diesel oil may, under the existing production set-up, be outside the contract. Inaccurate cost limits will result yearly in a difference of millions in cash receipts. (Guarantee contract is further discussed below).

Relationship between Costs and Volume of Production.

If the calculations are made as described, the effect of the various raw materials and finished products on the production costs can be usually found; however, the effect of the volume of production upon costs can not be calculated from it. To arrive at this, one should separate fixed costs from variable costs (app. 10). The "fixed costs" are costs in a given plant which are independent from the volume of production, (e.g. capital investment)"variables" are those dependent on it (e.g. consumption of raw materials). Fixed costs remain even with vanishing production, while the variable costs will drop then to zero. The study of costs during the last years has shown that the variable costs of hydrogenation plants are largely proportional to the level of production, unless affected by changes in operations and by improvements. When costs in each section of the accounting are plotted a straight line is produced, which intersects the ordinate at zero production, giving directly the fixed costs, while the slope of the line is a measure of the variable costs, or of the so-called "peak costs". If the costs are calculated per te of product, a curve is obtained which slopes downwards with increasing proportion; the curve is a hyperbola which approaches the peak costs assymptotically. It may be expressed by the formula

$$\text{Costs/te of product} = \text{peak costs} + \frac{\text{Fixed costs}}{\text{Volume of Production}}$$

$$K = K_c + \frac{K}{P}$$

Such a cost curve is shown on sheet 10 for total hydrogenation. For the sake of simplicity, all liquid and gaseous fuels are here combined. On emay see how well the treatment of costs during the preceding years can be expressed by a simple equation. A more detailed examination will permit dividing the peak costs among raw materials and finished products; we explain below how to find the fixed costs and the variable costs.

With a basis of accounting which contains a separation of production costs into fixed costs and variable costs, for raw materials and the finished products, one can safely make predictions about changes in costs which will result from modifications of the processes.

Consideration of peak costs has an other important purpose; peak costs in many cases are of even greater importance in judging the economics of production, than are total costs. This is primarily true when changes in production are made in a given plant without changes in the plant, i.e. without new investments; fixed charges are in such a case unchanged. We may define a peak production using the concept of peak charges as follows:

Profits = net proceeds - production costs

= net proceeds - peak charges - fixed charges

= peak profits - fixed charges

Whenever fixed charges remain unchanged in production changes, which actually is of frequent occurance, a change in the peak production produces a measuring stick for the economy of the change. This is explained with several examples (Sheet11).

The peak costs per te of motor gasoline from coal are about 147 RM per te of motor gasoline; from tar (with 15% light oil and a mixture price of 80 TM/te) about 151 RM; if the peak costs for fuel gas obtained at the same time be added, we arrive at peak costs of 167 and 163 RM/te motor gasoline. There is, accordingly, a peak gain of 180 RM per te of motor gasoline from tar and 199 RM per te motor gasoline from coal. With the price for tar of 80 RM/te, there is no economic incentive to increase the proportion of tar in hydrogenation when the latter can be done with hydrogenation of coal alone, with the production of the same amount of gasoline as given by tar. This is essentially the case if the vapor phase forms the bottle neck of the production. This may happen in the course of the present year. In the past, as well as in the near future if the works be considered as a whole, the total production is limited by the available hydrogen, especially by the size of the compressors. In this case, however, we are not dealing with the choice between 1 te of coal gasoline and 1 te tar gaoline, but, since the hydrogen consumption must remain unaltered, between 1 te coal gasoline and 2½ te tar gasoline. The peak gain for 2.5 te of tar gasoline amounts however to 450 RM, or considerably more than per ton of coal gasoline.

We may also use in the same way the peak gain in nitrogen as a standard for comparison. Should we select calcium ammonium nitrate as a profitable product, we will find it to be 230 RM/to N above the peak gain from coal gasoline. However, since the bottle neck for the whole production is formed by the compressor capcity, we may not compare 1 te nitrogen with 1 te gasoline, but the peak gains, which will result per 1000 $m^3$ make-up gas. This is the highest for tar gasoline with 184 RM, next comes coal gasoline with 81 RM, and nitrogen comes last with 59 RM. One may also ask the reverse question, what additional price may be paid for tar if the total economic gains should not be reduced. If the vapor phase forms the bottle neck, and should the production of coal gasoline be reduced, te per te, by the added tar, we will get in the first case (i.e. with no reduction of gains) 65 RM per te tar (with 15% light oil readily hydrogenating). Should there remain however sufficient available vapor phase capacity, and the gas compressors should form the bottle neck, 159 RM/te may be added if hydrogen be taken away from the coal, 176 RM/te when taken away from ammonia. We see, that the substitution of tar is not generally acceptable, but depends on the existing manufacturing conditions.

The above examples show that the economic evaluation of changes in production must take capacity limitations into consideration as well as the peak costs.

The separation of operating costs into fixed costs and variable costs is very important, and is made in all hydrogenation plants, with a breaking down of the costs in the usual way into the different components ( power, repairs, etc). Sheet 12 serves as an illustration of such cost accounting of the coal stall. The finding of these costs, discussed in greater detail below, is based essentially on a comparison of different production periods with a variable high thruput. Peak costs may not therefore in general be derived from the costs of one single operating period, but only from comparison of different accounting periods. In general, the fixed and variable costs of hydrogenation were redetermined at the different plants at the close of each accounting year, with an extensive use of reports for preceding years, and with a proper consideration of any changes to be expected that year. A valuable accounting basis is in this way obtained which could be used to advantage in economic computations. In addition means is also furnished for an effective supervision of operating costs, by considering them as "anticipated" or "theoretical" costs and comparing at all times the actual costs with them. This method of comparison offers the advantage of having the "theoretical" costs used as a standard not remain constant, but changing with the level of production. In this way, changes in costs caused by increasing production could be directly seen, eliminated in the comparison of costs, and only these changes taken into consideration which resulted from special causes. In practice, the comparison of costs is made by considering the theoretical costs according to the formula.

costs = peak costs x thruput / fixed costs
(during 1 quarter) (during 1 quarter) (during 1 quarter)

The difference from actual costs, in RM and in %, gives a measure for the change. This comparison can be very readily made for each location. Should one however wish to compare the different costs of hydrogenation with the theoretical costs, nearly 500 comparisons will have to be made during each accounting period (now 1 quarter). The amount of computation required will be almost prohibitive. In order never-the-less not to lose the advantages from this kind of cost computation, this whole comparative study is done fully automatically by the Hollerith division. Only the thruputs are reported quarterly. The thruput and the effective costs are punched on a perforated card for each item of costs, and these are already known to the accounting office; also the variable and the fixed theoretical costs. The latter are not as a rule changed during a current year, they have to be entered but once in one quarter by hand, and are transferred automatically during the 3 remaining quarters upon the perforated card. In general there are but two numbers to be punched to a card, and all the computations are carried out by machines. Moreover, the results are given in a visual form, and at the close of the year can be collected. The Hollerith division recalculates power at a constant price, which is necessary for the purpose of comparisons. Sheet 13 shows an excerpt from such Hollerith presentation. Sheet 14 shows the percent deviation between actual and theoretical costs for the total hydrogenation during 1941. The agreement between the actual and the theoretical costs will be seen to be very good.

The above method permits to find readily the stations in which changes occur in costs and determining their causes. It is occasionally desirable to carry out further the separation of costs to ascertain the causes of losses. This is in particular important, when dealing with new processes, still in the development stage, and when the whole production is divided among several departments. We show here by way of example the HD phenol oil report (Sheel 15 not reproduced). The theoretical computation was made here as well, and the theoretical costs compared with the actual costs. The differences were further subdivided (it was, e.g. determined to what extent the higher costs in the use of NaOH were to be attributed to higher consumption, and to what extent to the higher price of NaOH). Comparison of different quarters showed, how costs of extraction and distillation have been reduced, which is especially true of the costs of repairs. An increase in the capital costs in the first quarter of 1942 was made necessary by the increased valuation caused by taxation.

## 2. Precalculations.

The connection between precalculations and post auditing for the supervision of the operating costs of hydrogenation has been pointed out repeatedly. We shall show below that many decisions in the field of hydrogenation are based on precalculations best made from some station of operation. The evaluation of the raw materials of hydrogenation may be mentioned first. The gasoline accounting, as has been said previously, is designed to give separately the production costs of individual raw materials, and a precalculation offers no difficulties. Analyses will furnish information on the proportion of returns, middle oil and gasoline, of the solid content and of asphalt, and for more detailed information, the ultimate analysis and the basis for accounting will become available. The currently made balance of the elements furnishes the required experimental figures for the calculation of hydrogen consumption and the production of off-gas, calculations will lead to the costs of processing residues and middle oil, these calculations being carried out in sufficient detail for the purpose. It has already been mentioned that in such evaluation the load on hydrogenation must be carefully taken into account, and that in many cases the peak costs are obtained instead of the total bookkeeping production costs.

A large amount of calculation is necessary to determine the guarantee price; itssignificance for this purpose was one of the reasons to develop hydrogenation accounting. In the guarantee agreement made with the government in 1933 the Ammoniakwerk Merseburg has obligated itself to build the hydrogenation up to 300,000 to 350,000 te/yr of gasoline, while the government obligated itself to grant between July 1, 1934 and June 30, 1944, t i.e. for 10 years, a price depending on the production costs. The guaranteed price was to be established for 2 years ahead (yearly during the first 3 years of the contract) and was equal to the cost of production with 5% amortization; the technical advances reached in the meantime were to be taken in this way into consideration. The determination of the production costs were to be made in accordance with certain directives. Should the proceeds be below the guarantee price, the government was to reimburse the difference to the Ammoniakwerk; in the reverse case the Ammoniakwerk was to pay the difference back to the government. Examination of the records show that the Ammoniakwerk made a profit on gasoline of 5% within the terms of the contract, from which the corporation tax was to be deducted. Additional profits resulted from any lowering of costs during the contract period; they were to remain with the company only for the duration of the contract, but were to be adjusted with the new guarantee price. The latest guarantee period had been put into operation in 1942, and the guaranteed price, to be enforced for the balance of the life of the contract, will have to be determined in the near future. Any cost reductions made by the Ammoniakwerke will then remain with the company. We may mention in addition, as a favorable stipulation of the contract, that when production costs were determined the hydrogenation off-gas was charged only as fuel; gains in propane for domestic use and the power gas were to remain with the company. In the course of years additions have been repeatedly made to the contract, the first one being the manufacture of aviation gasoline. It has been agreed that the price of aviation gasoline was to be raised in proportion to the increased cost of its manufacture; the guarantee price was first fixed at 285.30 RM/te. This price was to be also the sales price to the "WIFE" which has since been retained. The remarkable result of this arrangement is that the net receipts for the motor gasoline are in a higher proportion of the total gasoline receipts than the net receipt for aviation gasoline. As long as aviation gasoline is computed within the framework of the contract, Leuna suffers no disadvantage; however, after the expiration of the contract, there may be some undesirable consequences, if the sales price for aviation gasoline may not be raised because of price limitations. In addition, the production of aviation gasoline was to be included into the total yearly production of 300,000 - 350,000 te/yr during the guarantee period, but the minimum total amount was to be reduced from 300,000 to 270,000, after 200,000 te/yr aviation gasoline has been produced. The minimum production was to be reduced less with a lower aviation gasoline production. These clauses of the contract soon became objects of voluminous explanations. The hydrogenation production had in the meantime gradually exceeded the anticipated maximum production of 350,000 te/yr. The contract guaranteed only 350,000 te/yr., and it was understood and acknowledged by the represenatatives of the government, that no differentials were to be deducted for the production exceeding 350,000 te/yr. It was also decided that the excess aviation gasoline production demanded from us would reduce the total output, including the amount not covered by the contract. In order to minimize this disadvantage, after aviation gasoline was alloted to the contracted amount, its price was determined by using a certain factor. Representatives of the state first suggested to revaluate it in the same proportion in which the minimum amount was reduced. With a production of 200,000 te/yr of aviation gasoline, the minimum amount was to be reduced by 30,000 te/yr, or by 0.15 te per te aviation gasoline; should the same proportion be used for the maximum production, the correction factor would be 1.15. Therefore, with a yearly production of 150,000 te motor gasoline and 200,000 te aviation gasoline, or a total production of 350,000 te/yr, the maximum of the contract would be just reached, and no amount will be left over for free sale, and no factor will be used. However, should aviation gasoline be computed using the 1.15 factor, we will get a total production of 150,000 / 1.15 X 200,000 = 380,000 te/yr, and therefore an amount of 30,000 te of excess production above the contract, for which the full proceeds were to be allowed to us. As a result of this offer of the 1.15 factor, it has been in general decided, that bottle necks in production may be shifted and that with the ever increasing hydrogenation production, the production of hydrogen always formed the important bottle-neck and the correction factor should correspond to the proportion of hydrogen for aviation and motor gasolines. This has finally been accepted, as well as the method of distribution of hydrogen between aviation and motor gasolines. A correction factor of 1.37 was thus created for aviation gasoline, which was reduced to 1.30 in 1941 because of the improvements introduced in the meantime. A voluminous numerical material was necessary to fix the correction factor at this level, and it has been thoroughly tested by cost investigators. The fiscal foundation of the correction factor is as follows: the first factor suggested, 1.15, would have produced in 1941 377,000 te not covered by the contract, while with the finally selected factor the amount was 532,000 te, or 155,000 te more, with an average difference between production price and guarantee price of 60. RM/te; this represents an actual increase of receipts of about 9,000,000 R.M. The hydrogen calculations must be made accurately; with a change of 0.01 in the correction factor, i.e. from 1.29 to 1.30, with an aviation gasoline production of 20,500 te/mo., or of 492,000 te in the 2 year guarantee period, there will be a 300,000 RM difference in receipts.

The government agreement has been subjected to a further modification in the Diesel oil agreement. The computation for Diesel oil was made similarly to aviation gasoline. The guaranteed price was reduced by the minimum production costs for Diesel oil and the adjustment factor for finding the amount of the oil not covered by the guarantee was 0.95. It was further decided, that the unguaranteed amount be first recalculated to motor gasoline, next to Diesel oil, and only after that to aviation gasoline. The lighter fractions in the Diesel oil, below 195°C are to be computed as motor gasoline. We may summarize by saying that the contract has necessitated great refinement of calculations and operational accounting.

In addition to the precalculations made necessary by the contract and the evaluation of the raw produce, a number of others have been made, primarily in connection with new projects, such as TTH and DHD. Solid basis is unavailable in most such cases, and only rough approximations of cost can be obtained; it is then frequently advantageous not to limit calculations to special cases but to examine the costs in relationship to the as yet unknown size of production. The results then do not consist of one single value, but in a number of curves. A general prict̄ure is then obtained in spite of the inaccurate basis, the principal factors affecting the costs have become known, and experiments may be carried out accordingly. Extended calculations in this way were carried out for the DHD process (V. decisions of 1/8/41 and 12/21/40).

## 3. Operational Relationships.

The significance of the different circuits and returns in hydrogenation have already been pointed out in discussing gasoline accounting. This brings about a much closer coupling of the various processes than in cases in which the different processes follow each other with no return connections by means of which earlier steps are affected by later steps. An understanding of the operational connection found is very important not only for the supervision of operation costs and for precalculations, but also for the actual operation and for designing. These connections must be understood not only qualitatively, but quantitatively as well. A few examples will show such relationships.

The partial pressure of hydrogen in circulation gas is an important factor in hydrogenation. Its magnitude depends largely on the nature of the raw products to be hydrogenated, on the condition of these raw products, on the catalyst and on the converter performance. A definite partial pressure of hydrogen can only be obtained in some definite ways. One may begin with the intention of running with the least permissible pressure. The compression and the paste pump costs will then be low, but the amounts of washing oil will be relatively large to produce sufficiently high partial pressure of hydrogen. This will result in the solution of fairly large amounts of hydrogen and their return into the cycle. If, on the other hand, the operations are carried out at high pressures the same hydrogen partial pressure is produced with a lower hydrogen content of the gas circuit, the costs of compression and pumps become higher; the costs of washing and of the dissolved hydrogen are lowered thereby. It is important to appreciate these relationship quantitatively for an economic appraisal; they are shown in sheet 16 (curve I). Starting with a partial pressure of hydrogen of 160 atm, the consumption of make-up gas, and the costs of make-up gas, washing oil and power for the paste presses are plotted against the operation pressure. We see that with an operating pressure of 180 atm, but little above the required partial pressure of hydrogen of 160 atm, the consumption of make-up hydrogen and its costs are very high. With increasing operating pressure they drop very rapidly, and then ever slower. The reason for it is that the increase in cost of power with increasing operating pressure is very low in comparison with the cost of the make-up gas, and it takes a long while until their effect becomes noticeable. The curve begins to rise very slowly only at 400 atm, producing a very slight minimum. The higher compression costs per $m^3$ of the make-up gas as well as the higher costs of pumping the washing oil found with higher operating pressure have been taken into consideration. Quite similar curves are also obtained for higher partial pressures of hydrogen. We may therefore draw the following conclusion: if some partial pressure is sufficient for some purpose, and increasing it results in no advantages, and when there is an opportunity to operate at much higher total pressure, it pays to take advantage of this fact. If, on the other hand, the available pressure is limited, it becomes interesting to find out how the consumption of make-up gas and of washing oil increase for a given total pressure but with an increasing hydrogen content in the circulating gas.

The costs of pumping the paste and compression per $m^3$ of the make-up gas remain the same, but the consumption of make-up gas and of washing oil increase very rapidly (Sheet 16, fig 2). 98% is the highest theoretically possible $H_2$ content (i.e with infinitely great amounts of washing oil) of the make-up gas. The curves for make-up gas and dissolved hydrogen are independent of the operating pressure, but not that for the washing oil. The costs of washing oil and its pumping are very low, and the curves for costs practically coincide (within the limits of accuracy of the drawing). Increasing the partial pressure above 70% becomes very expensive, (if the operating pressure remains the same), considerable other advantages must accrue to overcome these added costs. We may point out in this connection the effect of nitrogen. When the nitrogen content of the make-up gas is increased from 1.8 to 2.8%, or by 1%, the partial pressure of hydrogen in the gas circuit does drop, unless the partial pressure be maintained by increasing washing. However, more hydrogen will dissolve with increased washing, resulting in a 3% increase in the make-up gas, or 3 times greater than the increase in hydrogen (with 70% $H_2$ in the circulating gas) If however, the nitrogen content is increased by 1% with the same proportion of make-up gas, the hydrogenation production will be reduced by 3%, or by about 15,000 te/yr.

We may use for an other example the relationship between isobutane production and the production level. According to experience gained since the separation of butane was begun, the latter is mostly produced in the 6434 step, with but little of it produced in the liquid phase and the pre-hydrogenation. The production of 6434 gasoline depends today exclusively on the proportion of aviation gasoline required, because the rest of the production should contain a minimum of motor gasoline. To satisfy requirements, aviation gasoline must form at least 50% of the 6434 gasoline, while the balance may consist of prehydrogenation gasoline up to about 115° C. However, insufficient prehydrogenation gasoline may occasionally be produced in the course of operations for 1/2 of the required aviation gasoline. Conversely, with a greater total production and a relatively lower aviation gasoline proportion, not all the prehydrogenation gasoline may be used in aviation gasoline and Diesel oil, some motor gasoline will also be produced. The 6434 step requires additional hydrogen production and gasification, and efforts are made to reduce the 6434 gasoline. These relationships are shown in Sheet 17. They reveal the surprising fact, that with an increasing total production, the proportion of isobutane may increase as well as decrease, and that occasionally a higher proportion of aviation gasoline in the total production may result in the production of no more isobutane than in a lower aviation gasoline production with a lower general production.

## 4. Determining the Basis of Design.

Most accurate knowledge is necessary for the lay-out and selection of the individual processes in the design of hydrogenation plants. A detailed flow scheme is of prime importance, and it should contain information on the hydrogen consumption and the production of return gas, as well as power estimates. Different hydrogenation plants are but rarely planned for the same raw materials and finished products, which makes it impossible to devise any generally acceptable standard scheme, and special requirements must be met from time to time. The same reason makes it impossible to transfer directly, eg the Leuna figures to the projected Brabag works. Tar and coal are used together in Leuna at a pressure of 200 atm, while the Brabag works were designed for the hydrogenation of tar alone at a pressure of 300 atm. It was necessary here as well as in the accounting to derive the factors for tar from the experimental values for tar + coal in Leuna, and recalculate them to the Brabag conditions. After operations were started the recalculations were found to have been made most satisfactorily. Change to higher pressure results in changes in reaction, in the gas distribution and the hydrogen consumption; it permits in many cases the recompression of the exhaust gases, which results in a saving in hydrogen. This will be briefly shown below (Sheet 16).

The off-gases formed during hydrogenation are removed from the circuit in the catch pot. This produces a partial pressure of $H_2$ in the circuit which depends on its solubility in the catch pot product, the amount and composition of the gasification and from the composition of the make-up gas. When this partial pressure is too low, it may be increased by additional scrubbing. Should however the partial pressure produced in the catchpot be higher than necessary, it may be reduced by recompressing into the circuit the lean gas from the intermediate gas let-down. A change in the pressure during intermediate gas relief regulates the partial pressure of $H_2$. Computations made during the designing of the Bohlen plant showed that the recompression of the gas phase resulted in a saving of hydrogen amounting to about 60 $m^3$/te of motor gasoline. The cost of recompression is low, and the process was suggested and carried out. It has also been used since in other hydrogenation plants with the expected saving in hydrogen.

## 5. Discussions and Other Tasks

Representatives of the different hydrogenation works meet for conferences, as agreed upon. Ludwigshafen has organized these conferences, and regular meetings of representatives from local and foreign plants were held prior to the war. Ludwigshafen has sent regularly to IHEC even before the war a summary of results of operations in summarized monthly reports. At these meetings production figures, yields, etc. were discussed, and it has been frequently found, that the figures presented by the different participants were not comparable and had to be rearranged to comparable values. Such conditions are very unfavorable to helpful discussions. A convenient basis for comparison is produced by uniformity of operating reports in most hydrogenating works (Leuna, Brabag, Welheim, Pölitz, Wesseling, Brüx and Blechhammer). In some cases, such a comparison of results helped in clarifying problems; a systematic evaluation of the numerical material and a comparison between different hydrogenation works surely present, however, many as yet unutilized possibilities of obtaining useful information.

The range of activity of the accounting office requires it to collect most of the material on hydrogenation. It was natural therefore to impose upon it the additional managerial duties in which numerical data of hydrogenation had to be used, as in the development of questionnaires, in the dealings with government officials, and in similar tasks. The office was also entrusted with the preparation of contracts, since they are based on a large number of accounting results.

## III. Working Methods

The importance of selecting characteristic, specific factors of hydrogenation for accounting, designing and comparison of operations has been repeatedly stressed. It is, e.g. of far greater importance for a general impression to know the consumption of hydrogen per te of aviation gasoline from coal, or to motor gasoline from low temperature coking, than to know merely the amount of hydrogen required per te of the finished product Different raw materials are treated together, and these amounts could not therefore be obtained by direct measurements, and had to be found by special methods. These methods are briefly described below

### 1. Statistics

First to be mentioned is statistics and the large number of tests, which frequently give the desired results Statistics, in its simplest form, consists in presenting in the form of tables or graphically some values obtained during different time intervals. This is done in the many monthly reports. It has already been pointed out, that characteristic data can conveniently be selected for such a purpose and that accidental results must be excluded. It is however not always simple to determine directly whether some number is characteristic in this sense, and the decision must frequently be based on special tests. Nevertheless even this simple method brings occasionally valuable results. Sheet 19 shows the repair hours during hydrogenation. During the last 6 years they amounted to between 3.60 and 4.00 T RM/hr, and are therefore rather constant; this is important for estimates. The increase during the last years is to be attributed to the rise in expense (air protection measures). The repair hours prorated among the different operational groups show that low pressure, distillation and machine operations have very similar costs, while the repairs in the high pressure units are greater. This is not to be attributed merely to the higher costs of materials, but also to the large proportion of converter accounting stations with their higher expense

Variations in statistical presentation require us to find out their causes. A measure frequently used with success in finding causes in the simultaneous presentation of a number of possible values which may cause variations. The simultaneous presence of variations may be used to draw conclusions on the inter-dependence of these factors. (V. Sheet 3, effect of 6434 on the requirements of make-up gas), and on the thruput. This method can be made more sensitive by simple means and it will then give a useful method to express numerically the relationship. This will be shown on a simple example of hydrogen consumption/te motor gasoline from coal and from tar for the years 1933 to 1935 (Sheet 20).

Should we set down side by side the hydrogen consumption/te motor gasoline during successive months we will be able to observe a sharp increase during the years 1933 to 1935. Were we to write down in the same way the proportion of coal gasoline, we shall see that it has risen in the same way, from which we conclude on the close connection between the proportion of coal gasoline and hydrogen consumption. This connection is made, however, much clearer, by plotting the hydrogen consumption/te motor gasoline on the ordinate, and the proportion of liquid phase gasoline on the abscissa. We will see that the individual values are scattered around a streightline with but slight deviations. One could not, however, expect this to be any different when the hydrogen consumption by coal and by tar are already known, and we calculate from that the hydrogen consumption/te of motor gasoline for different proportions of coal, the points found should lie exactly on a straight line, which will give the hydrogen consumption/te motor gasoline from tar with 0% coal, and for the 100% of coal the hydrogen consumption/te motor gasoline from coal. In practice, the straight line giving the information for 0% and for 100% coal is as yet not known; it can however be very readily found by passing it "with the greatest accuracy" thru the points shown. The concept of "the greatest accuracy" may be further refined by having the sum of the deviations from the straight line less than in all others. We select for a number of reasons instead the sum of the simple deviations of points the squares of these deviations, and the straight line wanted is defined by the requirement, that the sum of the deviations of the squares, or the squares of the errors, be at a minimum. This method of calculation is therefore called the method of the least squares. Points which differ greatly from the expected are left out of consideration. The method is very old; it has been developed by Gauss, is very well developed and is used in many fields. Computations are mostly made arithmetically, instead of graphically; the graphic method is in most cases used only to illustrate the results. In the above computation, the consumption of hydrogen/te of motor gasoline from coal is found to be 3000 $m^3$, and from tars and oils - 1250 $m^3$. These values have been much bettered in the meantime.

The method of least squares is by no means limited to straight line relationship; it may also be used whenever a given quantity depends on more than one variable. If the number of variables is only two, the method can be shown in a space model.

The consumption of hydrogen in the vapor phase depends, e.g., on the proportion of 6434 gasoline, and it is also important whether the 6434 gasoline is motor or aviation gasoline. However, even in this case, should the consumption of hydrogen during prehydrogenation and the manufacture of 6434 motor and aviation gasolines be known, the total consumption could be plotted for different proportions of 6434 motor and aviation gasolines. The points must lie in one plane, in which the point 0% motor gasoline, 0% liquid phase gasoline will indicate the consumption by 5058 (per te of A middle oil), the point 100% motor gasoline, 0% liquid phase gasoline the consumption for 6434 motor gasoline, and the point 0% motor gasoline, 100% liq. phase gasoline the consumption for aviation gasoline (per te of gasoline). One may also proceed in the opposite direction, plot the plane "with the greatest precision" and obtain from it the values for specific consumption.

This method has been used successfully in many cases to find specific values which could not be found otherwise. In addition to hydrogen consumption, data have also been obtained in this way for the amounts of return gas from the several components, also the power consumption (in relation to thruput, in case of water and steam, occasionally also in relation to thruput and temperature), and finally the costs in relation to thruput, and thereby also the fixed costs and the peak costs, etc. Some 500 such "leveling" computations have so far been made. In particularly complicated cases, i.e involving the evaluation of thousands of points, much work has been taken over by the Hollerith section. These computations play also an important role in the distribution of costs between motor gasoline, aviation gasoline and diesel oil, and in finding the factors for recalculating. The values so obtained were admitted by the cost examiners.

The method of least squares offers us an other advantage. It furnishes, in the course of its application, ways of estimating the "probable errors". A scale of probable errors is also plotted on Sheet 20, and one may readily see that the scale of errors is the larger the further removed the extrapolation is from the points. This check of the results of calculation is of the utmost value. This fact has also been used in the setting of the contract price. The separated costs for motor gasoline, aviation gasoline and diesel oil carry certain errors, the magnitude of which (but not their nature, whether positive or negative) may be numerically evaluated. There exists therefore the possibility, that actual computations based on a different grouping of production would give higher values than obtained in precalculations and which were used in determining the contract price. The method of calculations discussed provides the basis for a numerical evaluations of errors and as a result the guaranteed prices were increased by a so-called risk addition.

During 1937 to 1941 this amounted to 0.70 RM/te; altho this amount was relatively small, it nevertheless added up to 1,000,000 RM difference in the receipts, which shows the value of refining the calculations.

The principle of least squares may be useful in other cases as well, whenever one has to correlate different values among themselves. Should, i.e. the C content been found in middle oil and in the catchpot of the prehydrogenation step, while statistical calculations give information on the yield, the C-gasification and C losses, these values must be correlated as follows:

C in middle oil = C in catchpot + C in gas + C losses

In general this will not be found to be the case; these values may be "best correlated" by introducing such changes in each one of them, that the sum of the squares of the changes would be a minimum. The balance of the elements in the prehydrogenation and 6434 was made in this way and has been found valuable in many instances.

## 2. Calculation of Interrelationships.

While there are many instances when the statistical method may be used, there are also many problems in which they are inapplicable, such as those where the number of operation stations to be evaluated is too small, or when they are located too closely to each other. It sometimes is possible to reach the objective in a different way as will be shown in an example.

When lubricating oil installations were required to increase their yield, the question arose, whether hydrogenation could produce more ethane. Increasing the pressure during the intermediate pressure relief was suggested as the simplest way. Gases dissolved in the catch pot and the scrubbing oil were not exhausted in one single step, but in several steps; in the first step (about 10 to 40 atm) the high-hydrogen gases will escape, while the high-hydrocarbon gases remain first in solution and escape only in later steps. Raising the pressure of the intermediate exhaust will reduce the amount of the lean gases and increase the amount of the rich gases. The rich gases are sent to the alkazid washing for the separation of the hydrocarbons, and the production of ethane increases with a higher proportion of rich gases. The utmost accuracy in figures was required for the quantitative relationship between the amount of rich gases and the ethane production from the intermediate gas exhaust. Operating conditions do not permit such determinations. Other investigations have shown, however, that Henry's law of absorption produced sufficiently accurate results for the circulation scrubbing with intermediate exhaust; sufficient analyses were also known which permitted the computation of the absorption coefficients. The computations proper are simple, but the large number of mutually interacting components (about 10 of them, without counting the olefines) required some special devices for rapid calculations. The computations were made in February 1940, but the intermediate pressure has been changed many times, and additional operational data could be used to check the calculations. Sheet 21 shows that computations and operational results are in good agreement.

Other computations of the relationship of gases in the circuit are in a similar state; the Henry law has been found to be frequently, but not generally, applicable. All these computations are characteristically made on a basis of physical or chemical laws and on the simplest possible working hypothesis, and computations permit drawing further conclusions from them. A closer connection with reality is obtained if the as yet unknown constants to be used in computations, are derived from operating conditions; we may say, that computations are standardized. In such calculations the operational results are to a large extent rationally extrapolated from the known natural laws.

There are very narrow limits for the calculation of operational relationships and no information can be obtained in this way on the course of a reaction; there are however many instances, where results can be obtained on the strength of some very simple regularities, which are of importance in operations, accounting and designing, and cannot be obtained in other ways.

### 3. Tying in Post Auditing with Pre-calculations

We will call attention in this connection to one point, which is worthy of being mentioned in spite of its being self evident, namely the close relationship between precalculations and post auditing. It has been pointed out during the discussion of post auditing, that it can be solved as completely as desired not only by using the usual methods of bookkeeping and cost analysis, but that mental processes and accounting methods would have to be applied which are characteristic for precalculation of costs. The reverse is also true. An accurate precalculation must use extensively the most recent results of post auditing, eliminating as far as possible all accidental results. The computations of estimated costs form the connecting link between the two. It was first set up for the supervision of operating costs, is based on the effective values of definite auditing sections, but with a consideration of the changes of costs with changes in thruput, as well as the effect of contemplated changes of operation; the estimated costs may also be used directly for precalculations. In this way, a close connection is obtained between pre-calculations and post auditing; nor is it immaterial that the supervision of operational costs and precalculations be carried out by the same office, so that there might exist a "personal factor."

## IV. Organization of Work and Results

A special office has been created in hydrogenation plants to solve the problems discussed above. There are other possibilities, when considered merely from the standpoint of organization; the work could be carried out by one central office or else distributed among different offices and then correlated. The close connection with operations necessary to perform the work was an argument against the first method, while the argument against the second was that the close connection existing between the different sections might escape detection if the work is divided among a number of stations. This was the reason for doing the auditing from one central office of the hydrogenation plant. A close connection with other branches (operation control, bookkeeping, etc) avoids unnecessary duplications.

A thorough study of the problem, development of standard forms and calculation methods for repetitious calculations, the use of calculating machines, and delegating particularly laborious numerical calculations to the Hollerith office has permitted to accomplish a volume of work which has certainly not decreased during the war with a personnel which has been reduced by 30%

In general, when the accounting work was being organized, the prime consideration was whether the services will pay and are therefore justified, than whether they are satisfactory. No economic computation could be presented to answer this question; the cost of operation of hydrogenation would have been brought down even without the existence of an accoutning office and the savings accomplished can not be credited to accounting. Nor can there any accounting be made of the work accomplished, as it were statistics of statistics. The setting of contract prices may be used as the only example of advantages derived from actual knowledge of costs. Thus, the increase in basic price by 3 RM/te in the 1938-39 contract was justified on the strength of the proposal of the cost investigators, and obscure cost connections could be quantitatively proven during the price negotiations. This increase in price affected 620,000 te negotiated for in the 1938-39 agreement. The already mentioned effect of the recalculation factors and the risk additions have only been determined on the strength of thorough examination of operational reports and cost relationship with an extensive use of special statistical methods.

## V. Subsequent Developments

An attempt has been made above to give a survey of the purpose of accounting in hydrogenation. A careful evaluation of the numerical data of hydrogenation has been necessary and will continue to be for an economic balance and for the development work. During the solution of various problems, questions of various kinds have been asked. A thorough examination of these questions has permitted a rapid solution of many problems which formerly required many days. These problems have today been solved to a certain extent, but the developments in these fields have not been concluded. Operations do not remain fixed, but keep presenting new problems; otherwise even such a highly developed process as the Leuna hydrogenation could consider efforts in cost reduction to be hopeless. Advances will be rarer and the strides will be shorter, but hard work will continue to result in improvements, and many small improvements will add up to a large advance. The smaller the improvement, the finer must be the scale with which cost accounting will recognize and measure it. A picture of "an ideal hydrogenation" may perhaps offer means to find systematically any chances for improvement. One might base it on the minimum power requirements on the strength of the modern technical improvements; costs of repairs could be estimated from the known maximum life of the different units; labor costs may be reduced by automatic operations. When such a thoroughly worked-out ideal is compared with actual conditions, differences will give information on operations the cost of which can be lowered. Theory will have to be increasingly applied in solving these problems when limits of its applicability are properly appreciated and it does not result in speculations alien to the process. Computations of kinetics of the reactions could hardly be envisioned in the nearest time. On the other hand, a combination of theory and experiments may bring possible success in pilot plant operations.

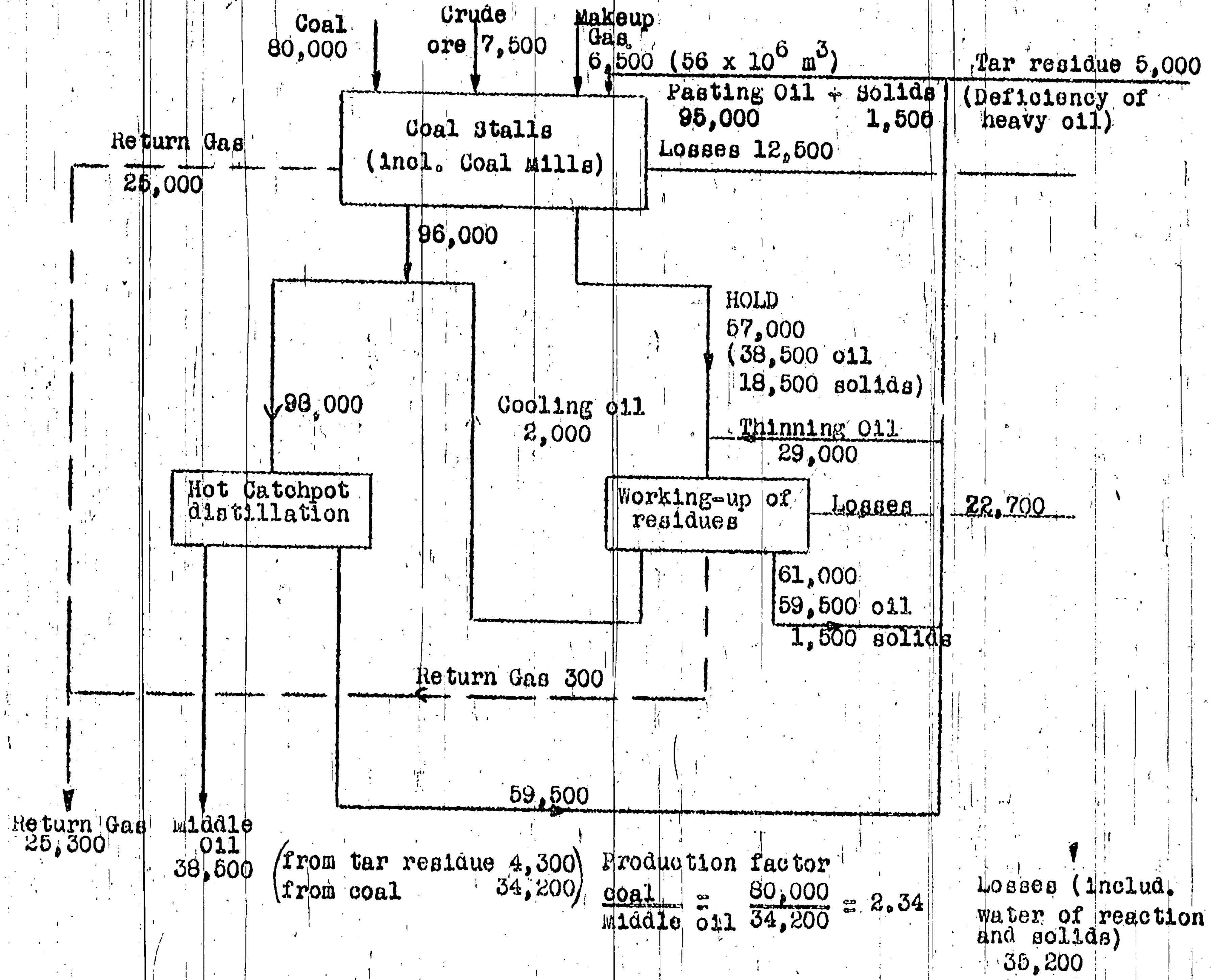
A greater amount of exchange of experience may in the future prove to pay. Several hydrogenation works have already consulted Leuna in designing the plants. Most hydrogenation works have contracts similar to Leuna, and similar accounting problems occur in them. Their uniform solution is of interest for all hydrogenation plants.

The predominating tasks of war economy and the shortage in personnel impose today great limitations on the solution of the above problems; work on them is nevertheless being carried out as much as possible.

(s) Pichler

Trlsd W. M. Sternberg

# Simplified Flow Sheet of the Liquid Phase



Appendix I.

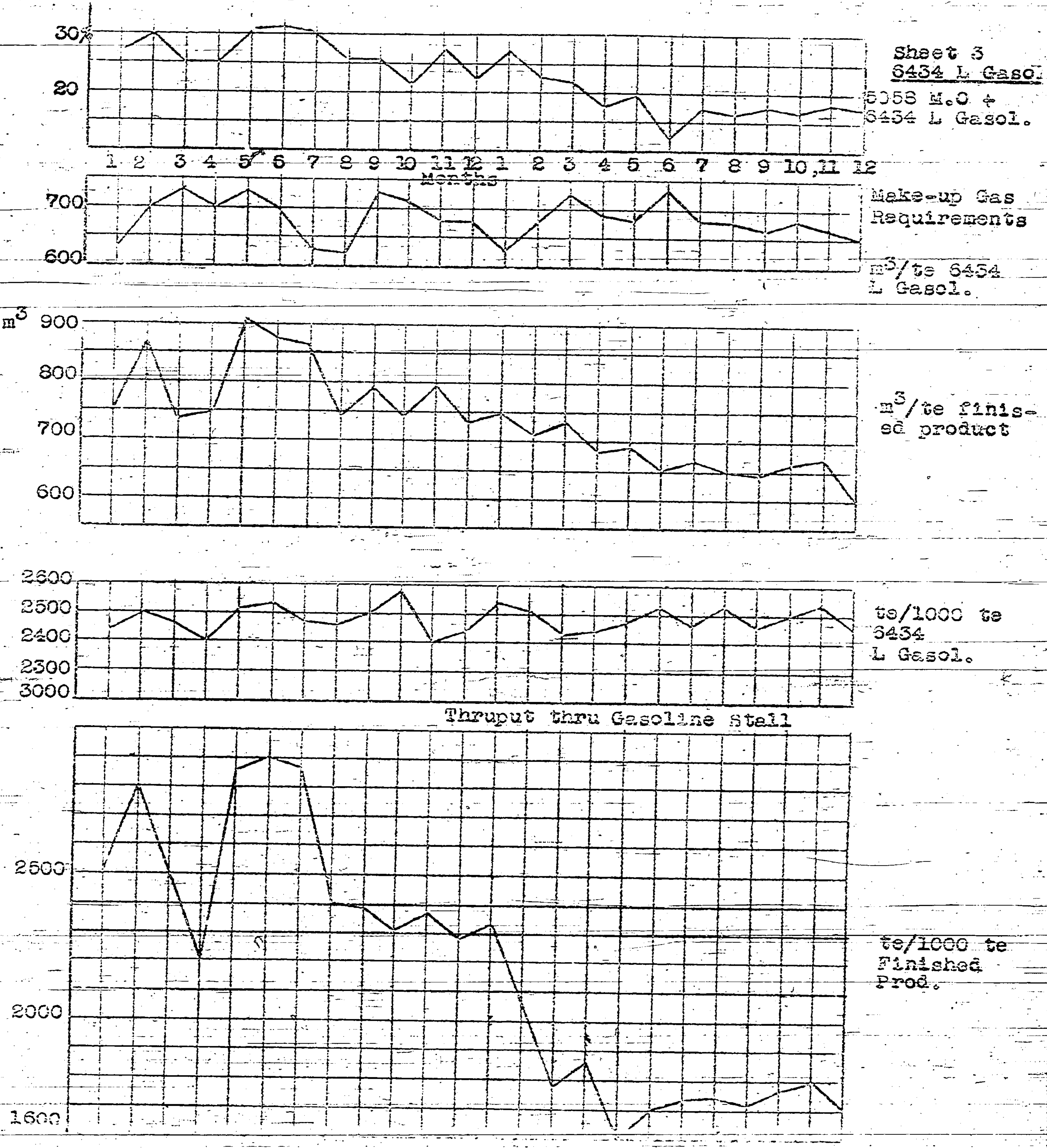
Sheet 2

T-133

## Simplified Scheme of Movement of Materials in the Liquid Phase

| | | Raw Material | Coal Stall Input | Coal Stall Output | Working up of residues Input | Working up of residues Output | Catch-Pot distillation Input | Catch-Pot distillation Output | Heavy Oil Movement Input | Heavy Oil Movement Output | Prod. | Hydrogen Off Gas | Losses |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Coal | te | 80,000 | 80,000 | | | | | | | | | | |
| Red Ore | te | 7,500 | 7,500 | | | | | | | | | | |
| Make-up Gas | te | 6,500 | 6,500 | | | | | | | | | | |
| 1000m$^3$ | | (56,000) | | | | | | | | | | | |
| Pasting Oil:oil | te | | 95,000 | | | | | | | 95,000 | | | |
| " Solids | te | | 1,500 | | | | | | | 1,500 | | | |
| Catchpot | te | | | 96,000 | | | 96,000 | | | | | | |
| HOLD:Oil | " | | | 38,500 | 38,500 | | | | | | | | |
| Solids | " | | | 18,500 | 18,500 | | | | | | | | |
| Thinning Oil | " | | | | 29,000 | | | | | 29,000 | | | |
| Cooling Oil | " | | | | | 2,000 | 2,000 | | | | | | |
| Heavy oil from residues: Oil | " | | | | | 59,500 | | | 59,500 | | | | |
| Solids | " | | | | | 1,500 | | | 1,500 | | | | |
| Dist. Middle Oil | " | | | | | | | 38,500 | | | 38,500 | | |
| Heavy Oil, dist. | " | | | | | | | 58,500 | 58,500 | | | | |
| Hydrog. Off gas | " | | | 25,000 | | 300 | | | | | | 25,300 | |
| Losses | | | | 12,500 | | 22,700 | | | | | | | 35,200 |
| Defic. Heavy Oil | " | 5,000 | | | | | | 5,000 | | | | | |
| | | 99,000 | 190,500 | 190,500 | 86,000 | 86,000 | 98,000 | 98,000 | 125,000 | 125,000 | | | |
| | | | | | | | | | | | 38,500 | 25,300 | 35,200 |
| | | | | | | | | | | | | 99,000 | |

## Samples of Characteristic Factors



## Elementary Balance for Coal Liquid Phase, 1941 Per te Dry Brown Coal

| | Total, te | C, te | H, te | O, te | N, te | S, te | Coal Remainder, te |
|---|---|---|---|---|---|---|---|
| Dry Brown Coal | 1000.00 | 619.12 | 48.05 | 181.93 | 5.81 | 53.72 | 91.36 |
| Catalyst | 89.48 | | | 61.53 | | | 27.95 |
| Make-up Gas: $H_2$ | 52.95 | | 52.95 | | | | |
| $N_2$ | 13.94 | | | | 13.94 | | |
| CO | 3.03 | 1.30 | | 1.73 | | | |
| $CO_2$ | 2.48 | 0.68 | | 1.80 | | | |
| $CH_4$ | 5.76 | 4.31 | 1.45 | | | | |
| Total | 78.16 | 6.29 | 54.40 | 3.53 | 13.94 | | |
| Total input | 1167.64 | 625.41 | 102.46 | 246.99 | 19.75 | 53.72 | 119.31 |
| Middle Oil | 417 17 | 353.58 | 44.24 | 14.84 | 1.68 | 2.43 | |
| Gasol (High & low Press) | 19.73 | 16.42 | 3.31 | | | | |
| Total Liq. Prod. | 436.90 | 370.40 | 47.51 | 14.84 | 1.68 | 2.43 | |
| Return Gas: $H_2$ | 7.29 | | 7.29 | | | | |
| $N_2$ | 13.14 | | | | 13.14 | | |
| CO | 3.03 | 1.30 | | 1.73 | | | |
| $CO_2$ | 2.48 | 0.68 | | 1.80 | | | |
| $CH_4$ | 5.76 | 4.31 | 1.45 | | | | |
| Prep. of Make-up gas | 31.70 | 6.29 | 8.74 | 3.53 | 13 14 | | |
| C Gasif. (no gasol) | 221.44 | 126.08 | 24.95 | 70.41 | | | |
| $H_2S$ | 34.66 | | 2.05 | | | 32.61 | |
| Total Return gas | 287.80 | 132.37 | 35.74 | 73.94 | 13.14 | 32.61 | |
| Sol. in HOLD Excl. Past. Oil) | 214.13 | 18.01 | 0.72 | 38.99 | 0.67 | 21.00 | 134.74 |
| Water of react.) found | 148.25 | | 16.59 | 131.66 | | | |
| from O bal. | 128.12 | | 14.33 | 113.79 | | | |
| found | 1.21 | | 0.07 | | | + 1.14 | |
| $H_2S$ in off-water from S bal. | 2.80 | | 0.17 | | | 2.63 | |
| found | 3.21 | | 0.57 | | 2.64 | | |
| $NH_3$ in off water from N bal. | 3.82 | | 0.68 | | 3.14 | | |
| Phenols | 2.18 | 1.67 | 0.14 | 0.37 | | | |
| $CO_2$ in off-water | 4.49 | 1.22 | | 3.27 | | | |
| Oil loss in residue utiliz. | 75.05 | 70.50 | 4.18 | 0.27 | 0.05 | 0.05 | |
| Total Miscell. | 427.32 | 91.40 | 20.16 | 158.21 | 4.13 | 18.68 | 134.74 |
| found | 5.58 | + 31.24 | 3.09 | 16.36 | 1.57 | - 3.51 | 12.93 |
| Balance diff. | + 15.62 | + 31.24 | - 0.99 | -- | 0.80 | -- | 12.93 |
| Total Output | 1167.64 | 625.41 | 102.45 | 246.99 | 19.75 | 53.72 | 119.31 |
| | 0.46 | 5.00 | 3.02 | 5.62 | 7.95 | 5.53 | 12.93 |
| Bal. Dif. as % of intake | 1.34 | 5.00 | 0.97 | -- | 4.05 | -- | 12.93 |
| C Gasif. as % C in dry brown coal | | 20.36 | | | | | |
| Distrib. of C Gasific. (no gasol) $CO_2$ | 10.24 | 4.39 | | 5.85 | | | |
| CO | 88.78 | 24.22 | | 64.56 | | | |
| $C_1$ | 31.92 | 23.89 | 8.03 | | | | |
| $C_2$ | 31.80 | 25.40 | 6.40 | | | | |
| $C_3$ | 36.41 | 29.75 | 6.66 | | | | |
| $C_4$ | 19.39 | 16.02 | 3.37 | | | | |
| $C_5$ | 2.90 | 2.41 | 0.49 | | | | |
| Total | 221.44 | 126.08 | 214.95 | 70.41 | | | |

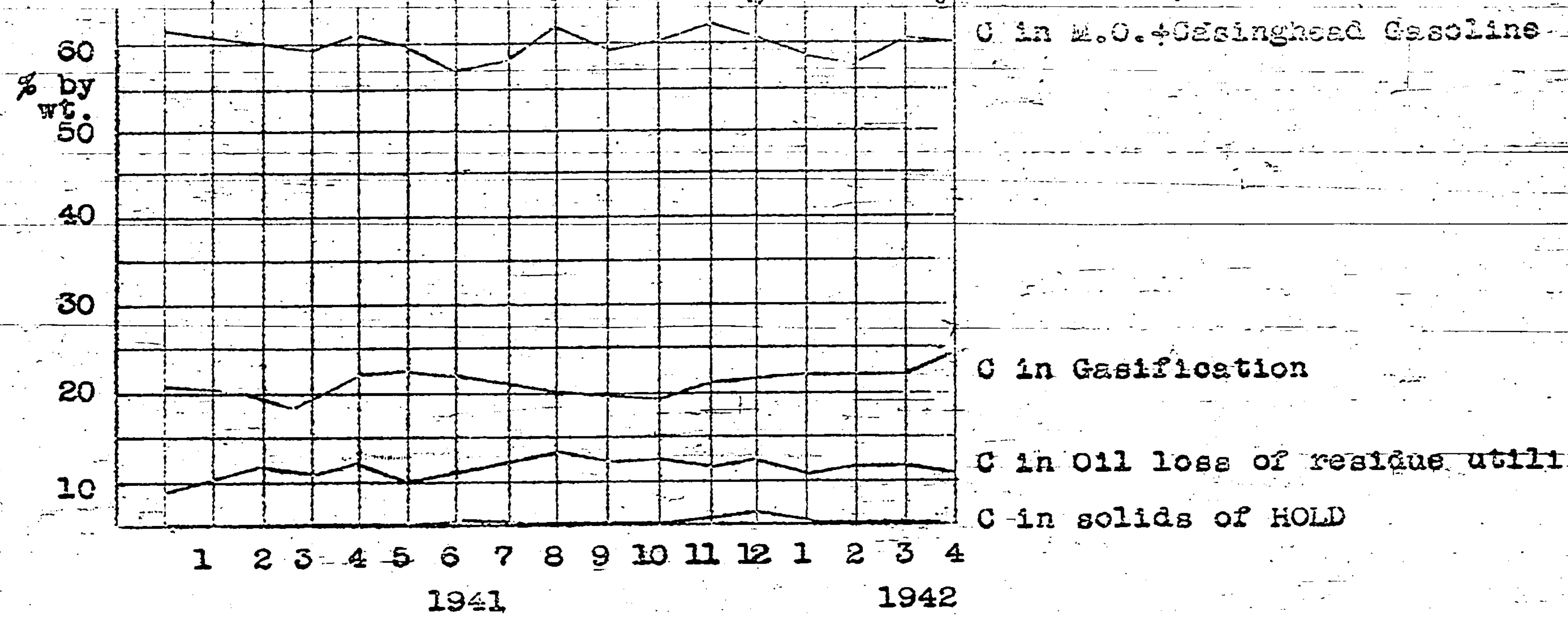
Sheet 5
Leuna, June 18, 1942

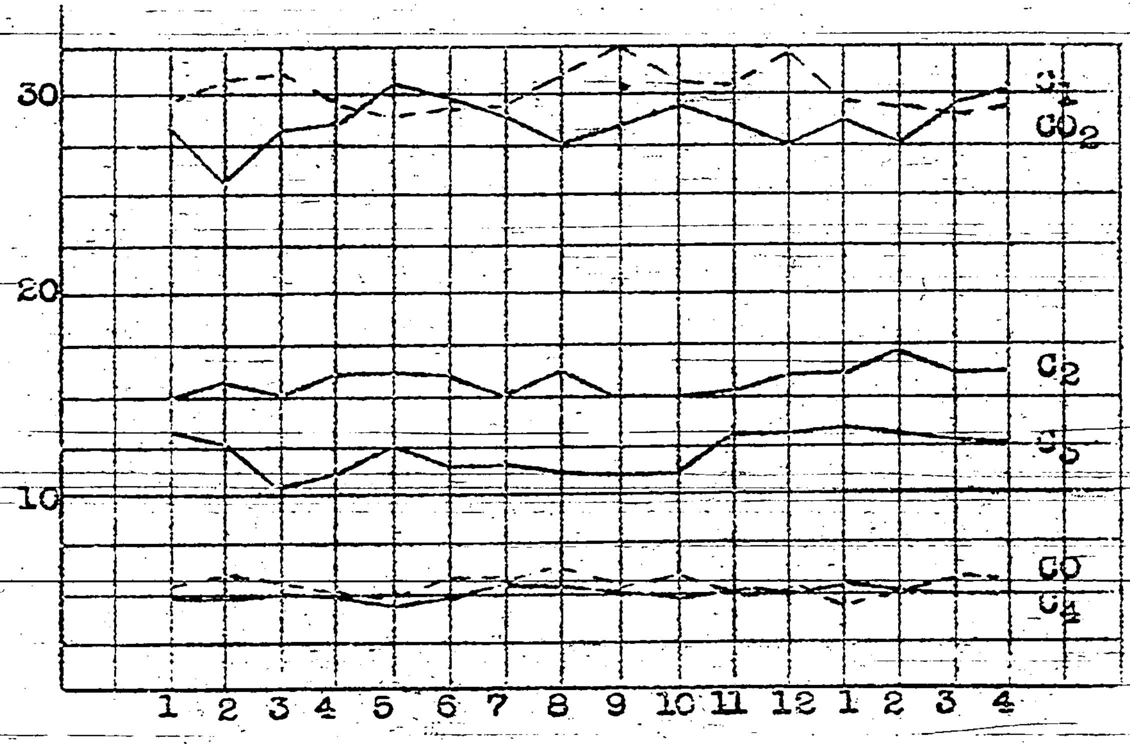
### Elementary Balance of Vapor Phase, 1941 /1000 te Finished Prod.

| | Total, te | C, te | H, te | O, te | N, te | S, te |
|---|---|---|---|---|---|---|
| Middle oil | 1102.98 | 935.88 | 116.92 | 39.26 | 4.52 | 6.40 |
| Gasol (casing head Gasol.) | 27.04 | 22.51 | 4.53 | | | |
| $H_2S$ | 3.36 | | 0.20 | | | 3.16 |
| Make-up gas: $H_2$ | 52.34 | | 52.34 | | | |
| $N_2$ | 13.70 | | | | 13.70 | |
| CO | 3.14 | 1.35 | | 1.79 | | |
| $CO_2$ | 2.61 | 0.71 | | 1.90 | | |
| $C_1$ | 5.62 | 4.21 | 1.41 | | | |
| Total | 77.41 | 6.27 | 53.75 | 3.69 | 13.70 | |
| Total intake | 1210.79 | 964.66 | 175.40 | 42.95 | 18.22 | 9.55 |
| Gasoline | 1000.00 | 858.32 | 139.46 | 0.94 | 11.14 | 0.14 |
| Return Gas: $H_2$ | 3.25 | | 3.25 | | | |
| $N_2$ | 11.84 | | | | 11.84 | |
| CO | 0.22 | 0.09 | | 0.13 | | |
| $CO_2$ | 0.92 | 0.25 | | 0.67 | | |
| $CH_4$ | 5.62 | 4.21 | 1.41 | | | |
| Proport. of Make-up Gas | 21.85 | 4.55 | 6.44 | 0.80 | 11.84 | |
| C gasificat. (Excl. Gasol) | 116.60 | 95.74 | 20.86 | | | |
| $H_2S$ | 2.44 | | 0.14 | | | 2.30 |
| Total Return gas | 140.89 | 100.29 | 25.66 | 0.80 | 11.84 | 2.30 |
| $H_2O$ of reaction | 45.13 | | 5.05 | 40.08 | | |
| Phenol (prod./in off-water) | 2.13 | 1.63 | 0.14 | 0.36 | | |
| $NH_3$ (in off-water) | 5.78 | | 1.03 | | 4.75 | |
| $H_2S$ " " " | 6.45 | | 0.38 | | | 6.07 |
| $CO_2$ " " " | 1.06 | 0.29 | | 0.77 | | |
| Total Miscell. | 60.55 | 1.92 | 6.60 | 41.21 | 4.75 | 6.07 |
| Differ. of Balance | 9.35 | 4.13 | 3.68 | -- | 0.49 | 1.05 |
| Total Output | 1210.75 | 964.66 | 175.40 | 42.95 | 18.22 | 9.56 |
| Differ. in Balance, % of intake | 0.76 | 0.43 | 2.10 | -- | 2.69 | 10.98 |
| C Gasific., % of C in M.O. | | 9.81 | | | | |
| Distrib. of C Gasif. (excl. of gasol) $C_1$ | 3.59 | 2.68 | 0.91 | | | |
| $C_2$ | 2.92 | 2.33 | 0.59 | | | |
| $C_3$ | 27.38 | 22.37 | 5.01 | | | |
| $C_4$ | 81.82 | 67.62 | 14.20 | | | |
| $C_5$ | 0.89 | 0.74 | 0.15 | | | |
| Total | 116.60 | 55.74 | 20.86 | | | |

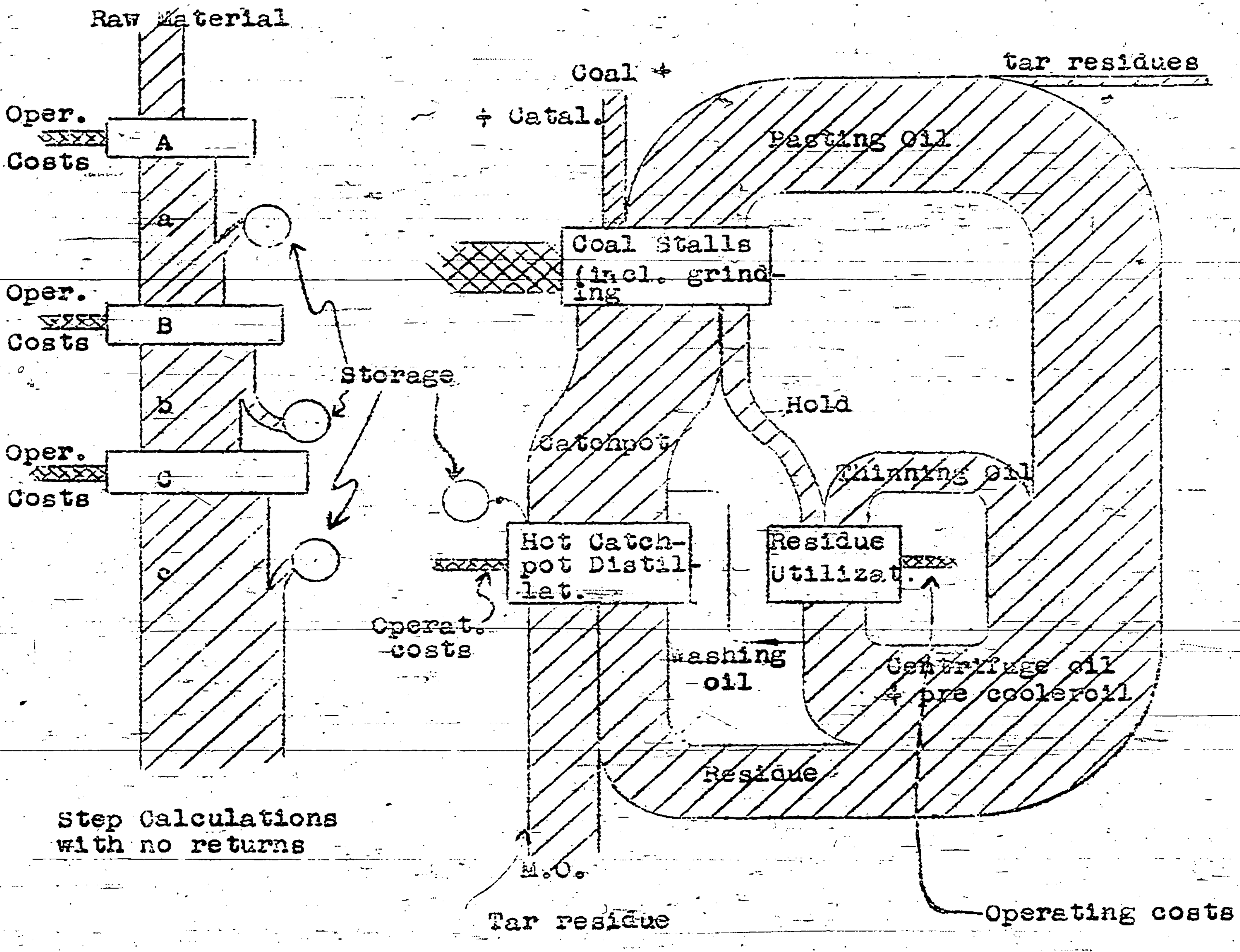
# Elementary Balance of Coal Liquid Phase

C balance (% C in dry brown coal).





T-133
Sheet 9



Simplified Scheme for Hydrogenation Calculations (Liquid Phase)

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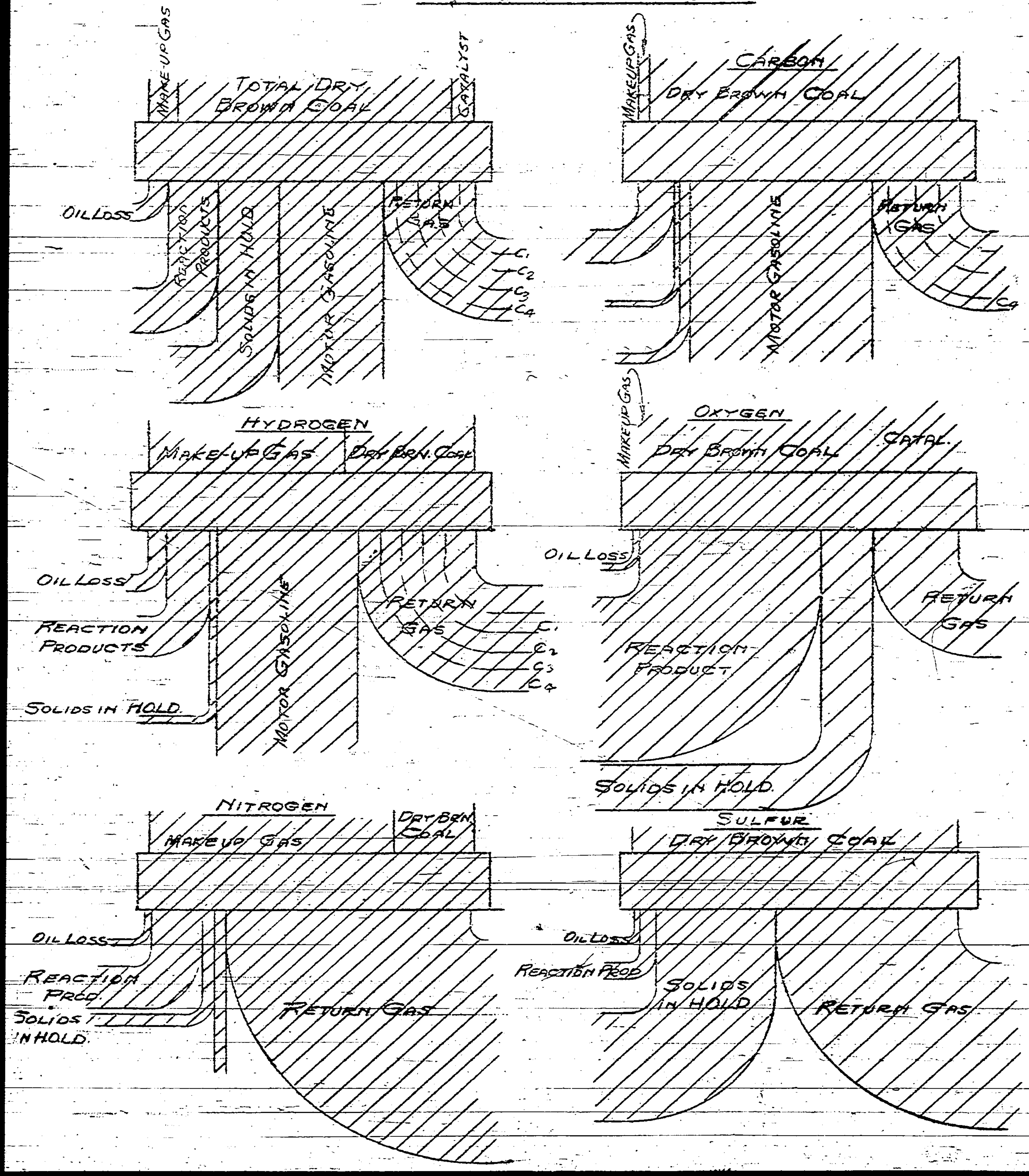
SHEET 6

# ELEMENTARY BALANCE



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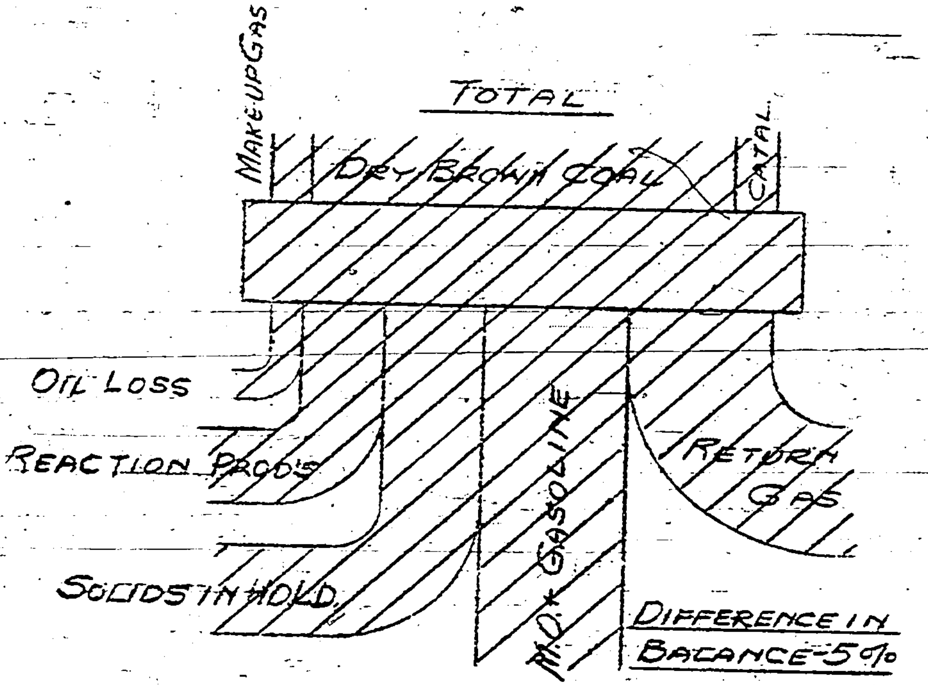
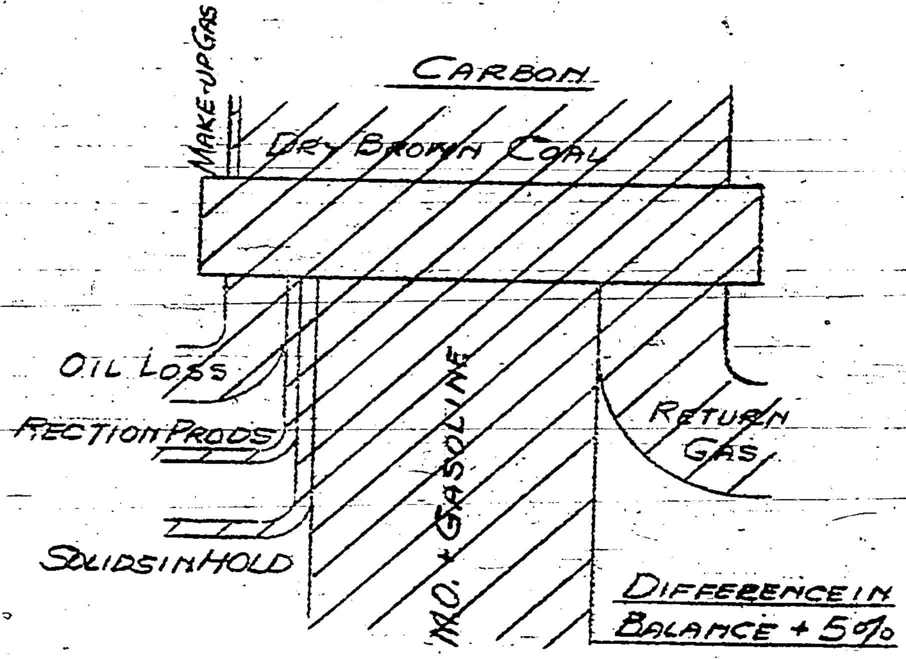
SHEET 7

# ELEMENTARY BALANCE COAL LIQUID PHASE. 1941

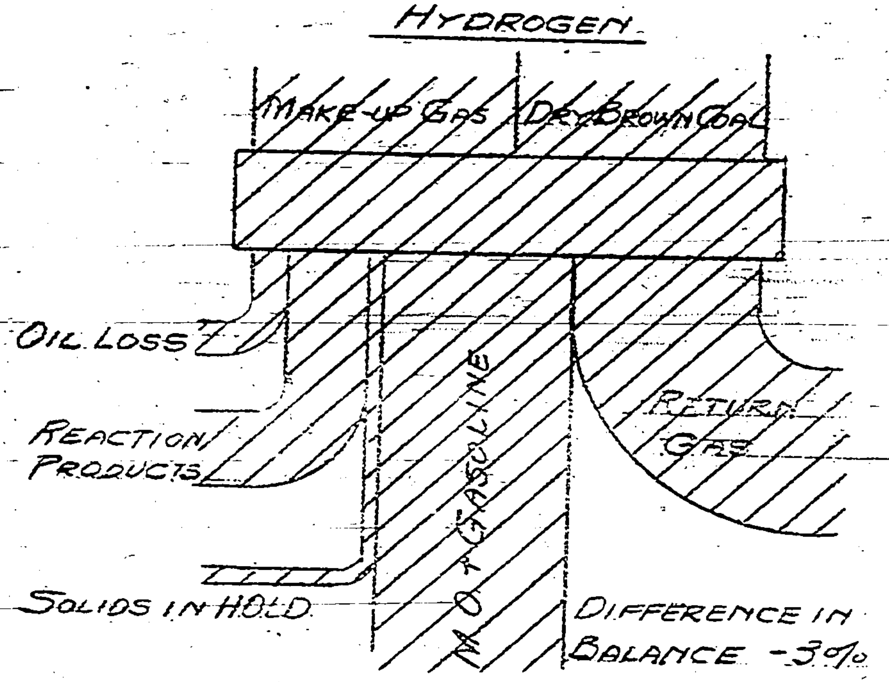
TOTAL



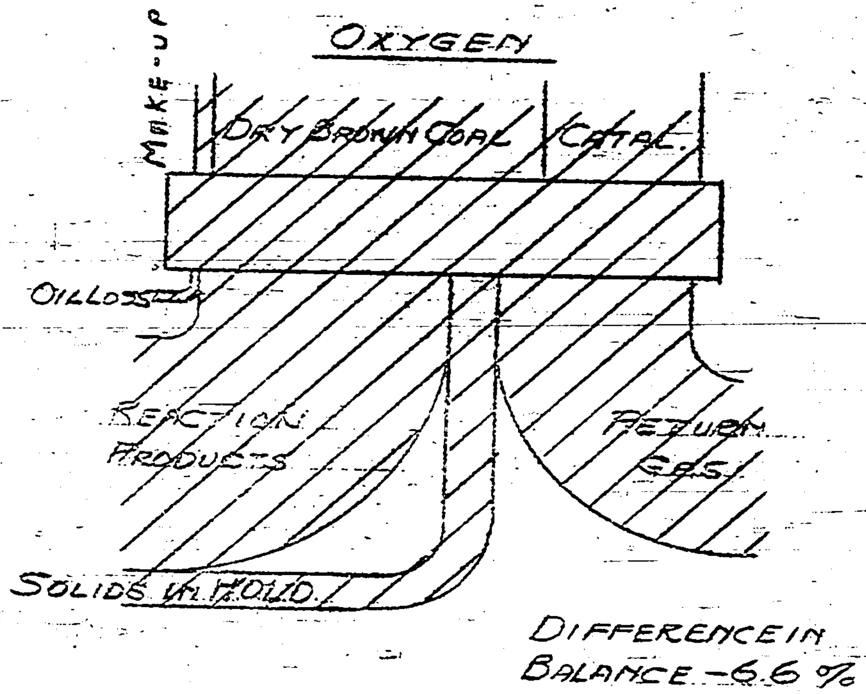
CARBON



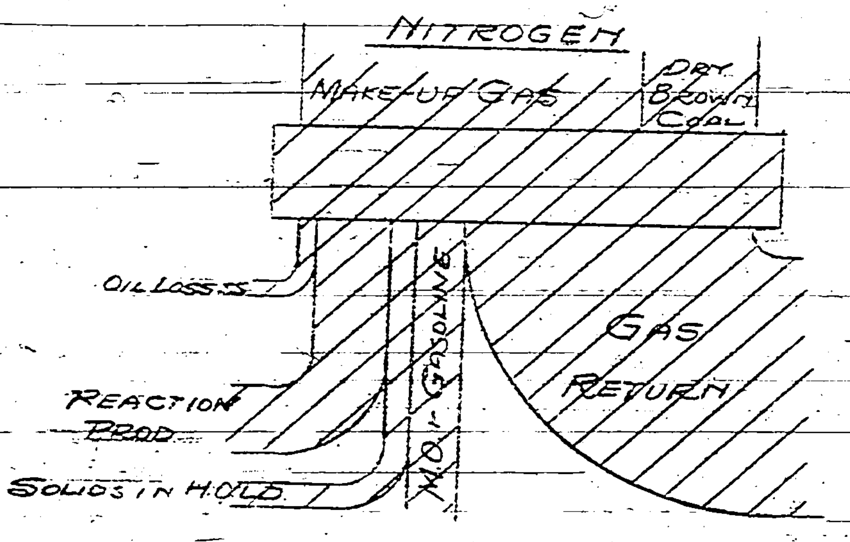
HYDROGEN



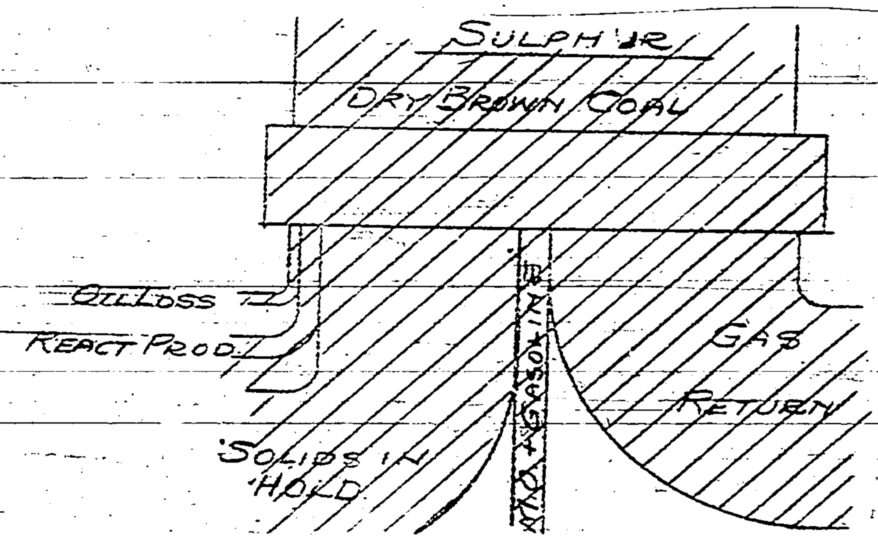
OXYGEN



NITROGEN

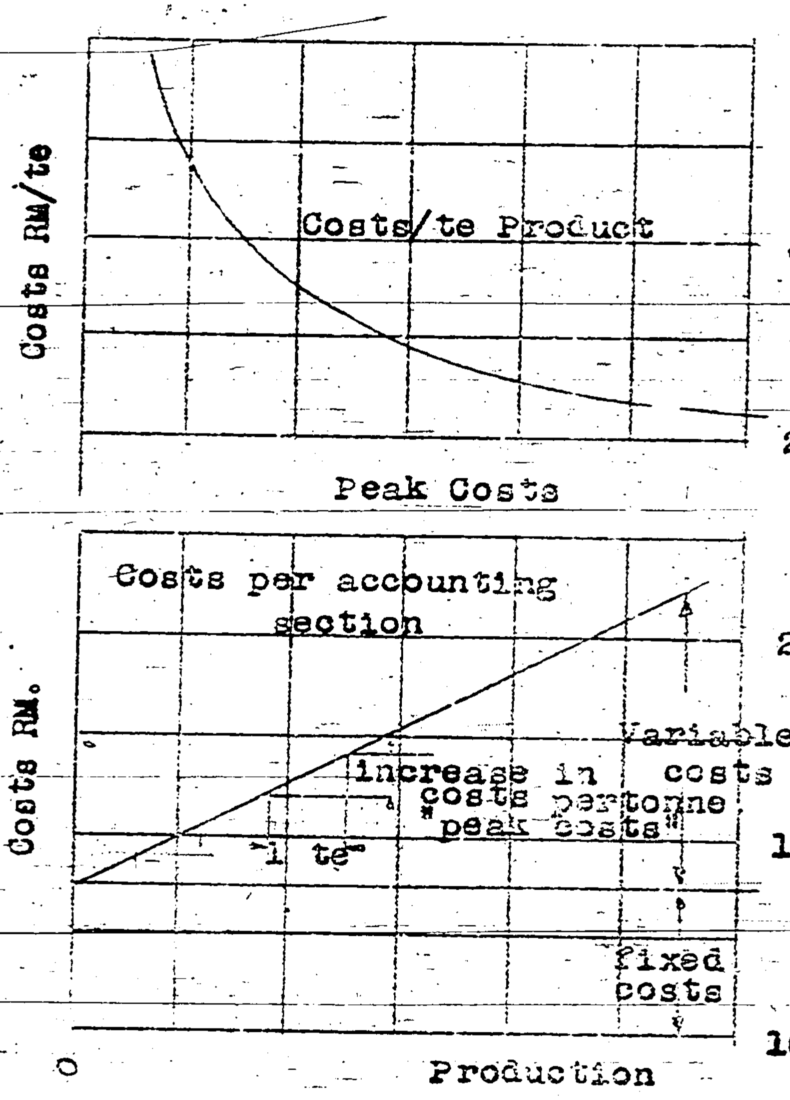


SULPHUR

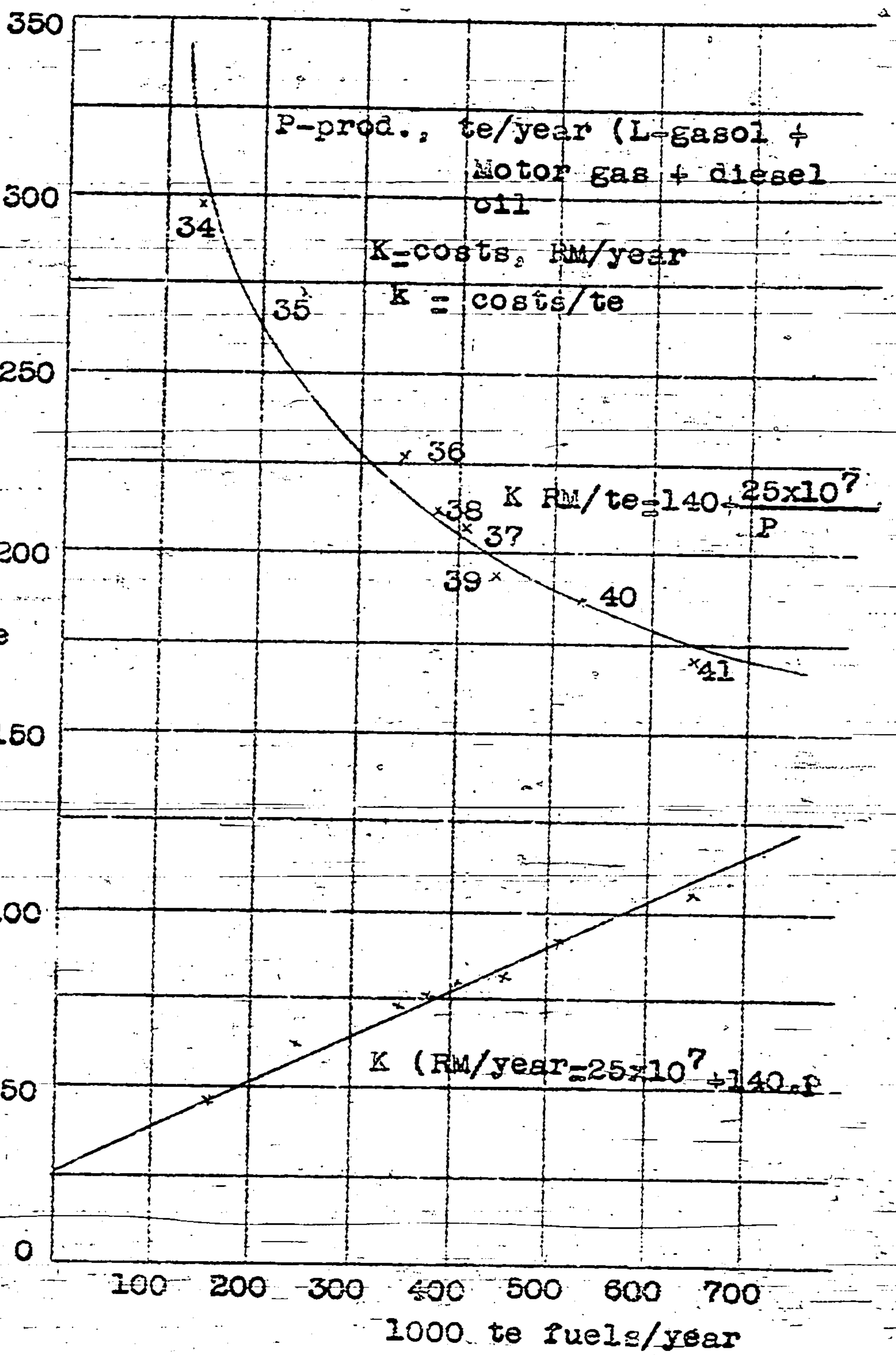


T-133

Sheet 10



Break-down of costs into fixed and variable costs.



## Comparison of Peak Productions of Different Materials

| | | Motor Gasoline from coal | Motor Gasoline from tar | Lime-Ammonium Nitrate (2) |
|---|---|---|---|---|
| Receipts, | RM/te | 310 | 310 | 430 |
| added, receipts from fuel gas | " " | 56 | 33 | -- |
| Total | " " | 366 | 343 | 430 |
| Peak Costs (1) | " " | 147 | 151 | 200 |
| added, for fuel gas | " " | 20 | 12 | -- |
| Total | | 167 | 163 | 200 |
| Peak Gain | | 199 | 180 | 230 |
| Required Make-up Gas | M $m^3$/te | 2440 | 980 | 3900 (3) |
| Peak gain, RM/1000 $m^3$ make-up gas | | 81 | 184 | 59 |

**Equivalent price for tar**

| | RM/te tar / L.O. |
|---|---|
| a). gain/te tar gasoline and per te coal gasol | 65 |
| b): " /1000 $m^3$ make up gas with tar and coal | 159 |
| c). " /1000 $m^3$ make-up gas for nitrogen and tar gasoline | 176 |

Remarks:

(1) The average price, instead of peak costs is given for hydrogen.

(2) Lime ammonium nitrate has been selected as standard, and variations in production are first placed against it.

(3) 3700 $m^3$/te N; 1.06 te N/te lime ammonium nitrate

Sheet 14
Leuna, June 14, 1942

## Differences (in percent) Between Actual and Estimated Costs
(+ = excess over estimate, - lower than estimate:)

### Total Hydrogenation 1941

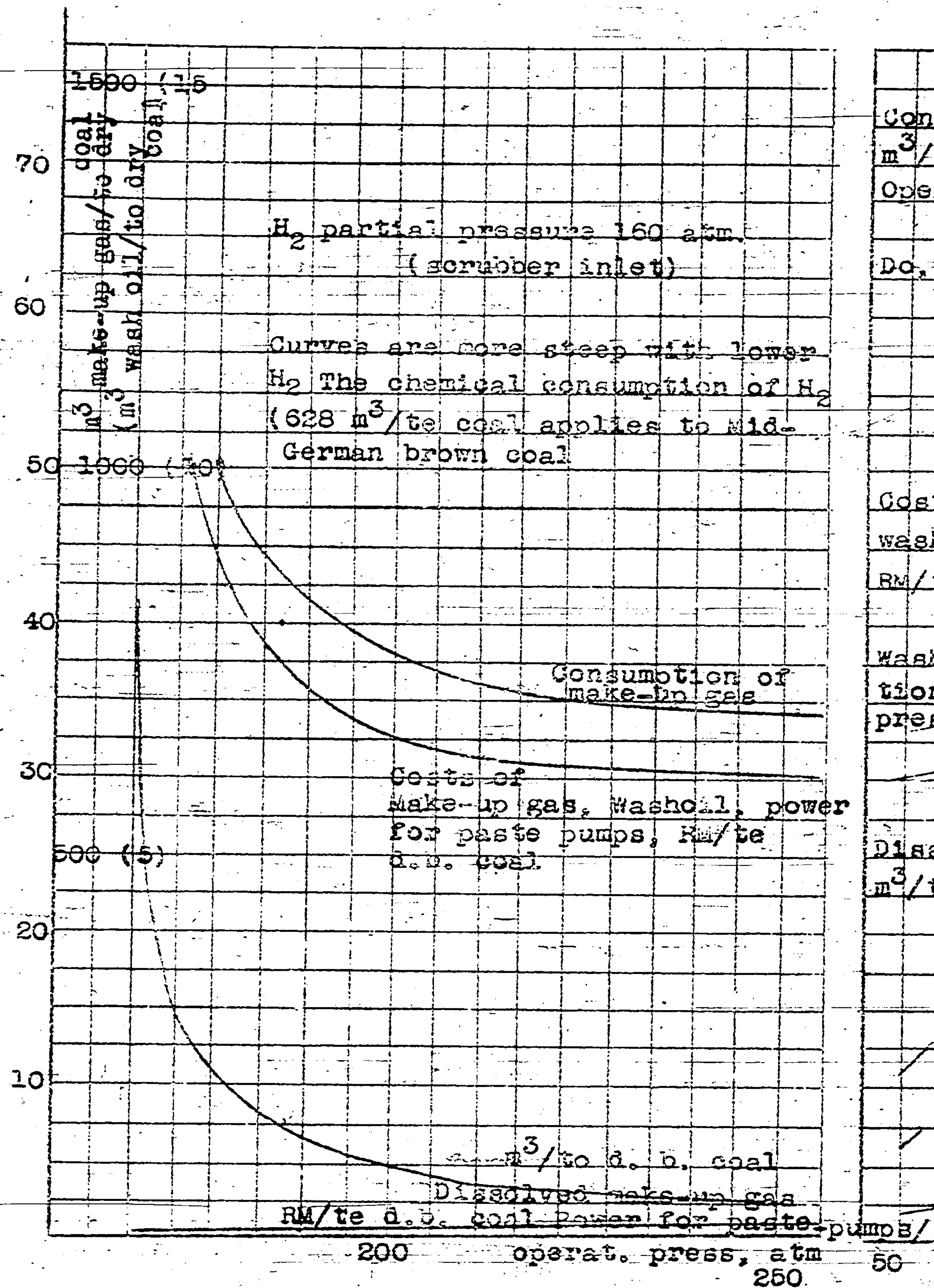
| | I | II | III | IV | Yearly |
|---|---|---|---|---|---|
| Personnel | - 0.88 | - 0.74 | - 4.49 | - 0.09 | - 1.57 |
| Power | + 4.99 | - 8.05 | - 4.23 | + 4.36 | - 0.85 |
| Repairs | + 1.03 | + 1.53 | - 6.36 | - 4.87 | - 2.29 |
| Raw Material | + 16.11 | + 11.56 | - 1.84 | + 8.73 | - 8.64 |
| Transportation | + 10.31 | - 2.86 | + 7.79 | +33.71 | + 12.63 |
| General Plant Exp. | - 13.16 | - 6.09 | - 9.87 | - 7.88 | - 9.21 |
| Interest on Capital | - 6.52 | - 4.56 | - 4.69 | - 1.55 | - 4.33 |
| Taxes | - 5.36 | + 20.10 | + 13.74 | +15.91 | + 11.23 |
| Miscellaneous Costs | + 12.91 | + 7.03 | + 4.59 | + 3.14 | + 6.93 |
| Credits | + 9.39 | - 1.60 | + 4.12 | + 3.25 | + 3.56 |
| | + 0.58 | - 2.83 | - 4.26 | + 0.72 | - 1.49 |
| Low pressure water | - 16.88 | + 2.90 | + 2.98 | -13.05 | - 4.48 |
| High " " | - 5.82 | + 11.91 | + 30.31 | - 4.62 | + 8.32 |
| High " steam | + 16.19 | - 6.40 | - 8.08 | + 3.50 | + 1.10 |
| Exhaust Steam | + 15.48 | - 2.87 | + 1.05 | +13.06 | + 6.67 |
| Low Pressure Steam | + 18.75 | - 14.80 | - 25.83 | +10.27 | - 2.33 |
| High Voltage Power | + 5.30 | - 3.33 | + 5.98 | +17.97 | + 6.64 |
| Low " " | - 1.57 | - 5.11 | - 5.67 | - 0.64 | - 3.34 |
| Fuel Gas | + 1.62 | - 8.86 | - 4.42 | + 1.33 | - 2.66 |
| Nitrogen, 6 atm | + 12.31 | + 3.70 | - 6.17 | +12.66 | + 5.62 |
| Carbon dioxide, 1/2 atm | + 12.13 | - 11.84 | - 6.17 | + 1.46 | - 1.31 |
| Compressed Air | + 5.56 | - 9.75 | - 16.20 | + 5.02 | - 4.14 |
| Raw Brown Coal | - 4.47 | - 0.65 | - 4.11 | - 7.99 | - 4.33 |

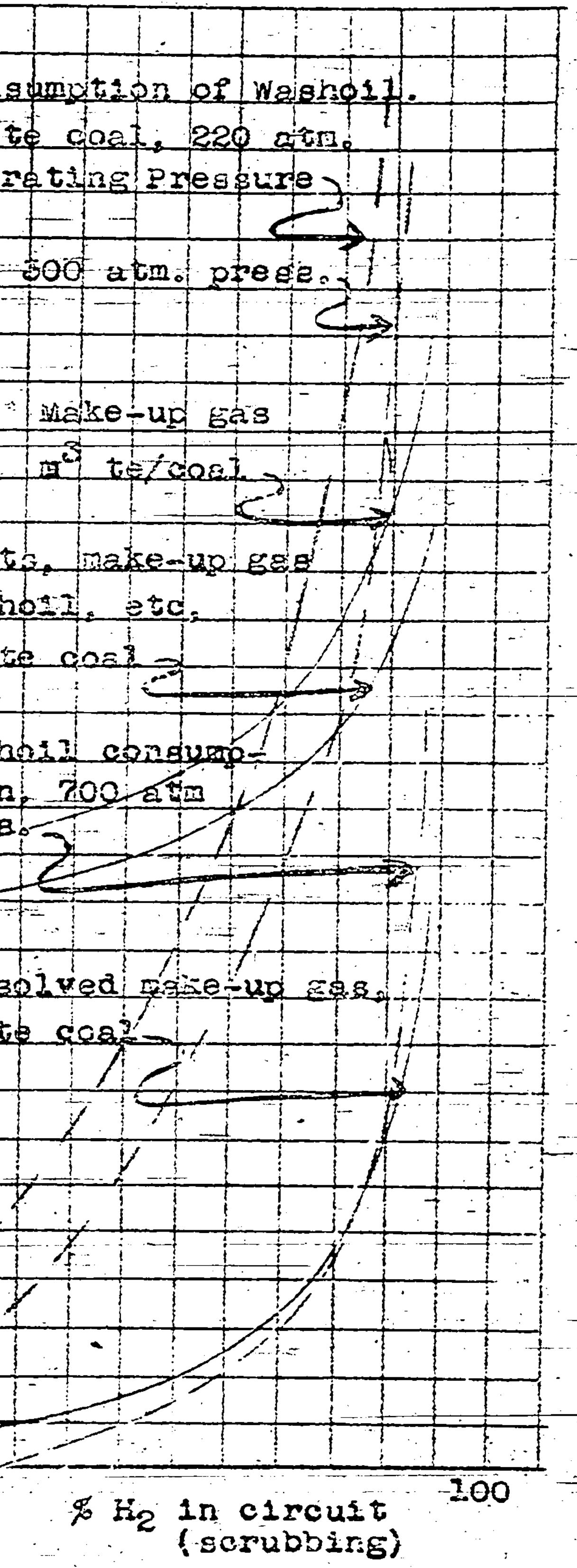
Sheet 15
Leuna, June 23, 1942

## Costs of Production per te HD phenol oil, in RM

| | I/41 | II/41 | III/41 | IV/41 | I/42 |
|---|---|---|---|---|---|
| Actual Production costs | 474.98 | 337.95 | 321.05 | 362.50 | 341.71 |
| Anticip.° " " | 242.07 | 242.07 | 242.07 | 242.07 | 242.07 |
| Difference | 232.91 | 95.88 | 78.98 | 120.43 | 99.64 |
| Distribution of Differences | | | | | |
| 1. Changes in stocks | -0.36 | +3.27 | -5.78 | -2.72 | +2.89 |
| 2. Price of NaOH | +17.02 | + 12.54 | +12.04 | +19.22 | +7.06 |
| 3. Carbonization losses | +14.85 | + 2.23 | +18.56 | +17.85 | +13.83 |
| 4. Operation costs of carboniz. | + 5.87 | + 5.81 | +12.49 | +13.37 | +20.07 |
| 5. NaOH consumption in extr. | +23.92 | + 11.56 | +16.34 | +28.48 | +16.82 |
| 6. Distillation losses | +25.02 | + 1.38 | + 3.05 | - 0.30 | + 9.49 |
| 7. Proportion of residue in dist. | + 2.48 | - 16.83 | -16.83 | -12.97 | -10.51 |
| 8. Reduct. of thruput dist. and extr. | +13.74 | + 20.79 | +12.28 | +24.40 | +22.15 |
| 9. Costs of operation, dist. & extr. | +70.37 | + 55.13 | +28.56 | +33.20 | +17.81 |
| (5+6+7+9). Total for dist. & extr. | (+121.91) | (+51.24) | (+29.39) | (+48.41) | (+33.61) |
| Total | +233.91 | +95.88 | +78.98 | +120.43 | +99.64 |
| Distribution of 9 | | | | | |
| Personnel | - 4.26 | + 3.04 | + 2.96 | + 1.51 | - 1.36 |
| Power | + 0.22 | - 6.22 | - 5.96 | + 0.40 | + 1.63 |
| Repairs | +72.89 | +55.70 | +28.09 | + 28.48 | + 8.52 |
| Raw Material | + 0.15 | - 0.28 | + 0.77 | + 0.56 | - 0.63 |
| Transportation | + 3.08 | + 1.23 | + 0.77 | + 1.79 | + 1.44 |
| General Plant expense | - 4.90 | - 0.83 | - 0.92 | - 1.50 | - 2.23 |
| Capital Investm. | - 0.19 | + 0.14 | + 0.39 | + 1.10 | + 8.12 |
| Taxes | + 1.79 | + 1.72 | + 1.49 | + 1.80 | + 1.12 |
| Miscellaneous | + 1.61 | + 0.63 | + 0.99 | + 0.96 | + 1.20 |
| | +70.37 | +55.13 | +28.58 | + 33.20 | +17.81 |

| ° Estimated costs | | per te HD oil | Price, RM/te | RM/te HD Oil |
|---|---|---|---|---|
| Raw materials: | A middle oil | 1.455 | 129.- | 187.64 |
| | NaOH(100%) | 0.436 | 83.83 | 38.58 |
| Credit: | Residue | 0.409 | 97.00 | 39.68 |
| Operating costs: | Extraction | | | 18.96 |
| | Carbonization | | | 10.03 |
| | Distillation | | | 28.54 |
| | Total | | | 242.07 |





Composition of make-up gas: 96.2% $H_2$,
1.6% $N_2$, 0.6% Co, 0.2% $CO_2$,
1.4% $CH_4$

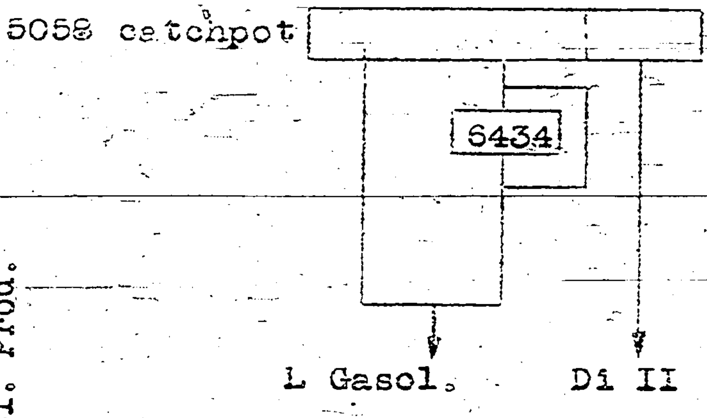
Fig. I

Fig. 2

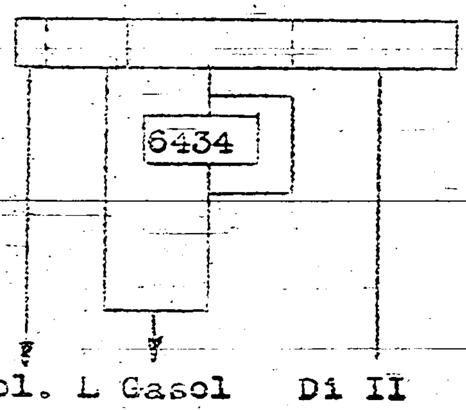
T-133

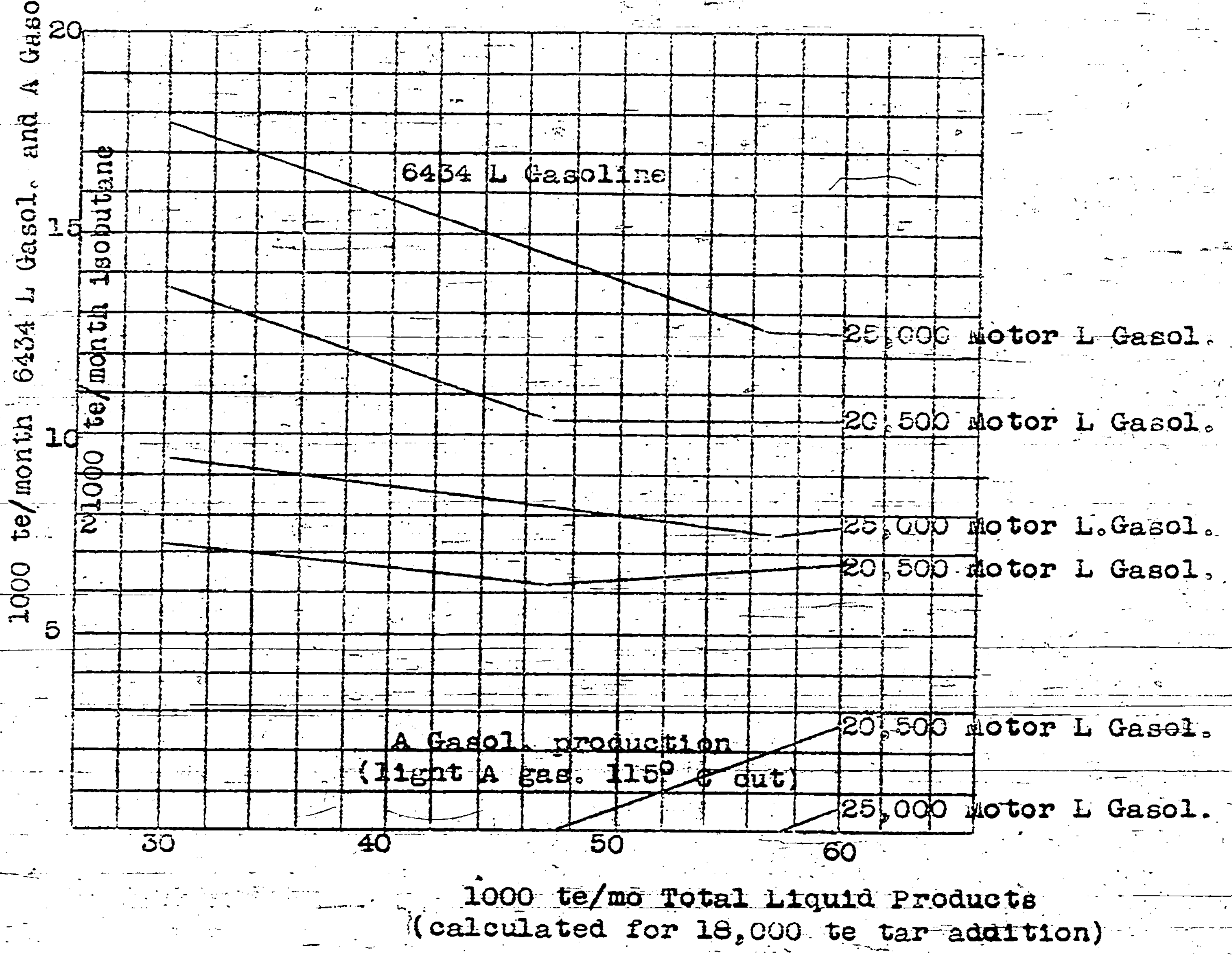
Sheet 17

Deficiency in 5058 L Gasol.

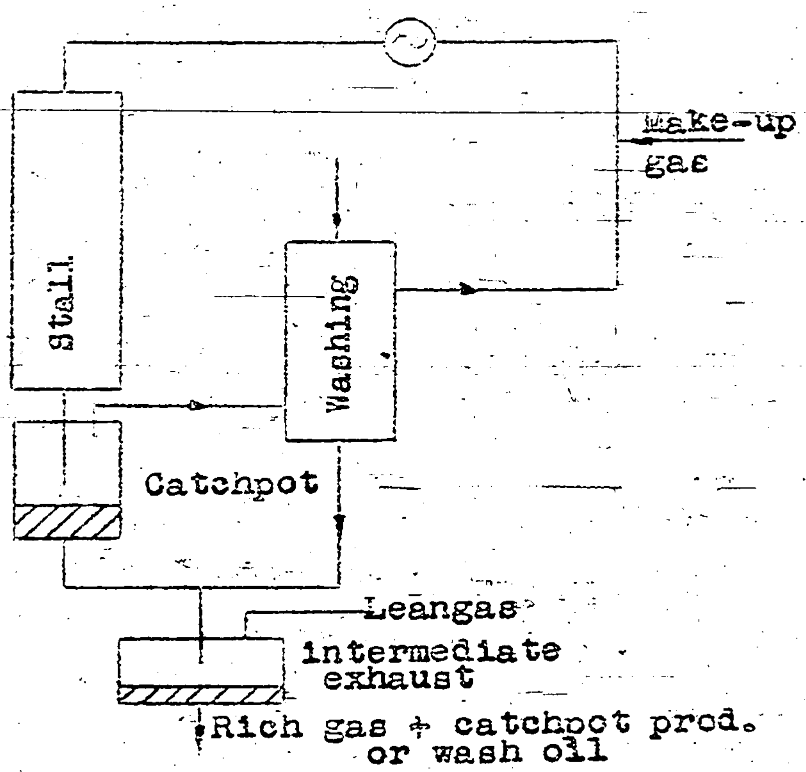


Excess in 5058 L Gasoline

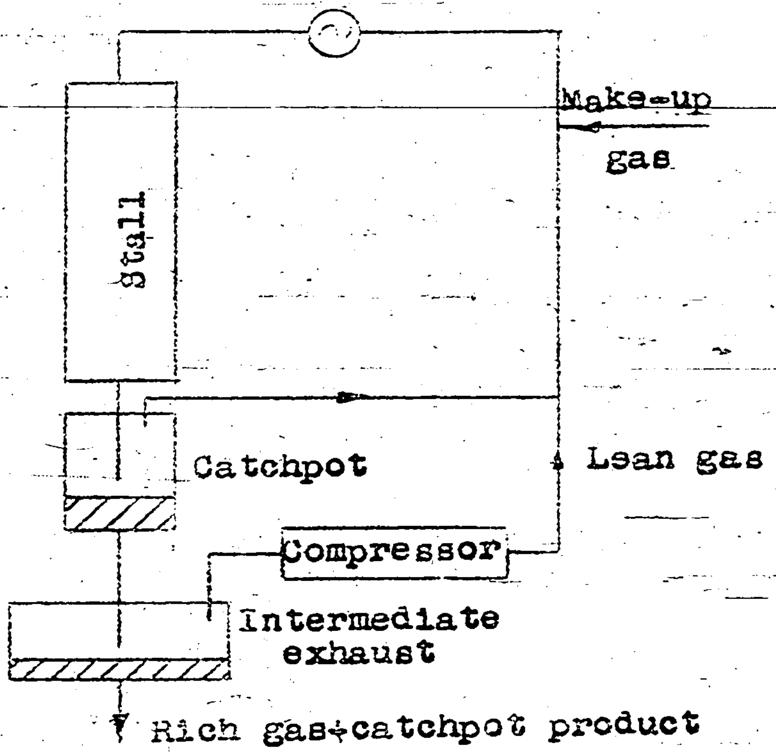


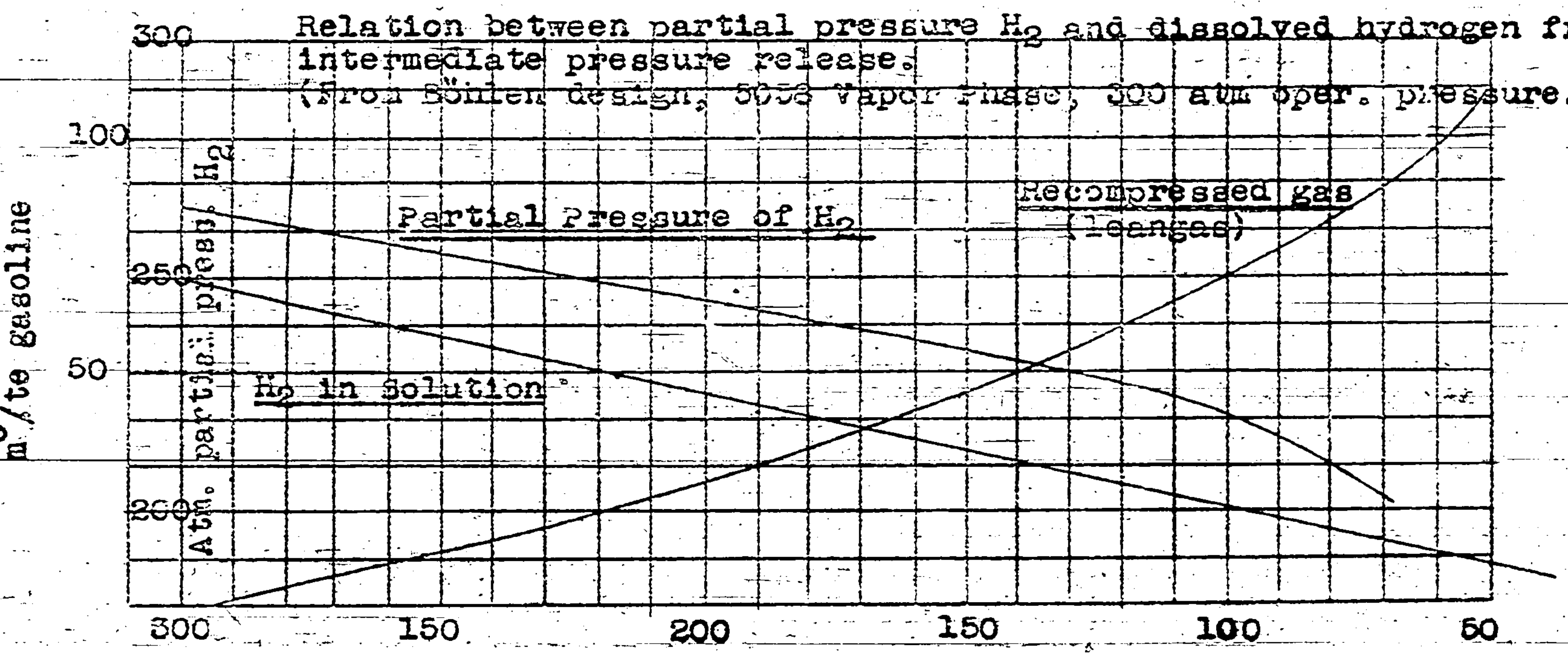


I. Partial pressure insufficient with solubility in catchpot. Raised by washing.



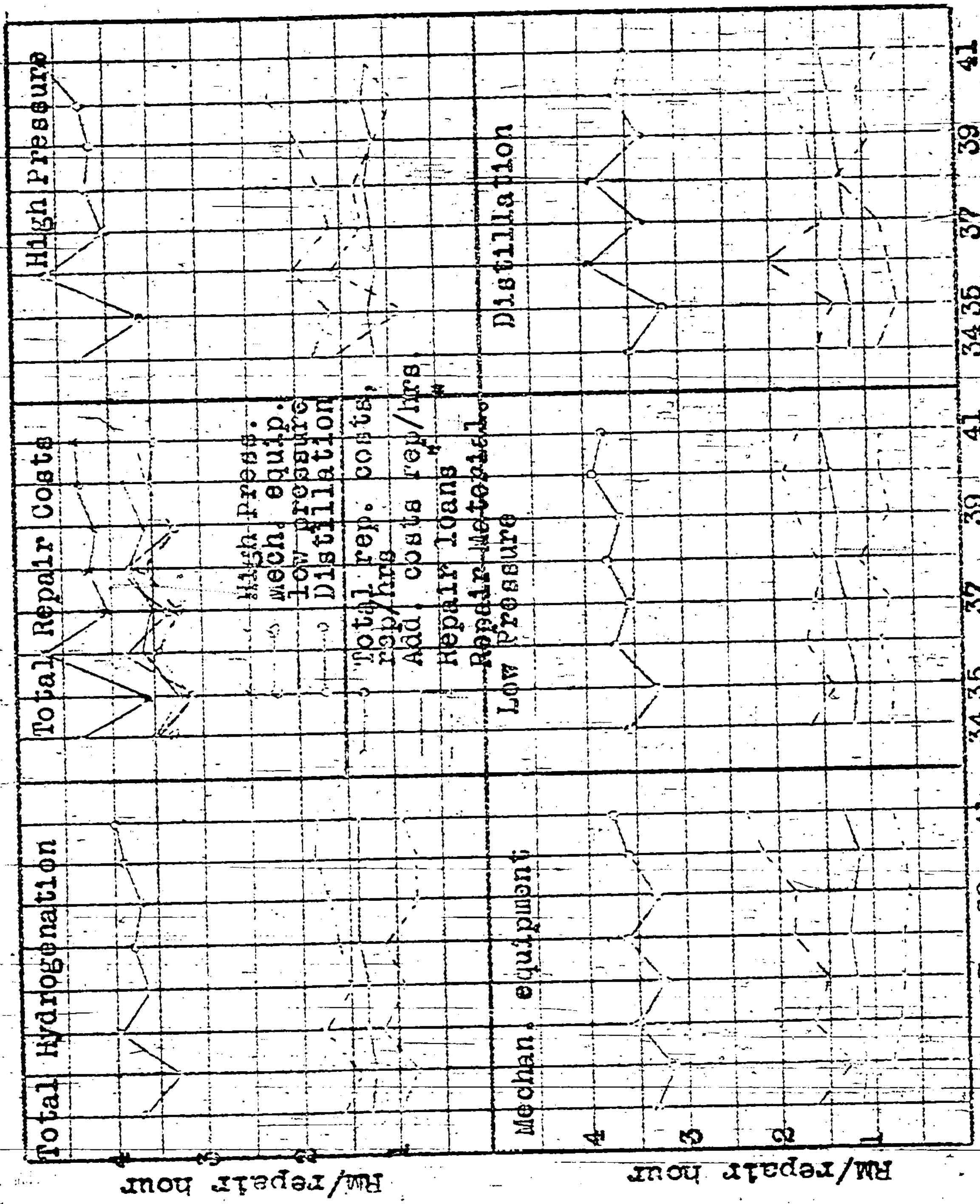
II. Partial pressure too high with solubility in catchpot. Lowered by return compression.





Relation between partial pressure $H_2$ and dissolved hydrogen from intermediate pressure release.
(From Böhlen design, 5058 Vapor Phase, 300 atm oper. pressure.)

T-133
Sheet 19



T.O.M. Reel 163
Frame 227

U. S. Bureau of Mines
Hydro. Demon. Plant Div.

T-134
10/20/1942

## Calorific Efficiency of Coal Hydrogenation

We have calculated as follows the efficiencies in our report on the calorific efficiency of coal hydrogenation:

$\eta$ of $H_2$ production 26%
$\eta$ of hydrogenation 49%
$\eta$ of (hydrogenation, incl $H_2$ prod.) 27.2%

It is explained below why $\eta$ (hydrogenation + $H_2$ production) is almost equal to that of the lower efficiency, although the ratio

$$\frac{\text{Coal for } H_2 \text{ production}}{\text{Coal for } H_2 + \text{energy}}$$

does not cause one to expect the lower efficiency

$\eta$ of hydrogenation proper 49% means:

converted energy (hydrogen + energy coal) $= 18\times10^6\times0.49 = 9\times10^6$
converted energy of hydrogen, purchased $7\times10^6\times0.49 = 3.5\times10^6$

Total $25\times10^6\times0.49 = 12.5\times10^6$

It is here entirely possible, and does not affect computations, that the efficiency of one or the other component differ more or less from 49%. The average efficiency (Mischwirkungsgrad) for all cases is 49%.

However, when hydrogen is not bought, but produced,

($\eta H_2 = 100$) then $\eta H_2 = 26\%$

The total efficiency then becomes

converted energy (hydrogenation + coal for power.) $18\times10^6\times0.49 =$ $9\times10^6$
converted energy (hydrogen produced) $26\times10^6\times0.49\times0.26 = 3.5\times10^6$

Total 40 x 272 $= 12\times10^6$

The efficiency of hydrogen production and combination is not therefore 26%;
this value refers only to the $H_2$ production; but 13%.

This lower value explains the drop of hydrogenation efficiency to 27.2%

Trld. - W. M. Sternberg

Signed: Schappert

# General Operating Instructions for Hydrogenation Plants and Special Instructions for High Pressure.

Hydrierwerke Pölitz A.G. - June 1940

TOM Reel 78
Bag 4
Target 30/4.13
Pp. 170-192
Trld. KCBraun

INDEX

## 1. GENERAL

a). Each operating disturbance, even at night, must be immediately reported to the foreman or superintendent and by the latter to the works manager or his deputy, if need be.

Should the shift boss notice any irregularity in or outside of the building, which should be corrected as soon as possible, he must record this in the operating report book and underscore it in red.

All changes or set-ups made on machines or apparatus during any shift must be entered by the shift boss in the operating report book, indicating the time and reason for same.

b). When the electric light fails, plant lights are to be used. Such flash lights must be available in every building in sufficient numbers and kept locked up. They must be regularly charged, whether in use or not and may be used only in case of emergency.

c). In case of leaks in gas or product lines in closed rooms, ventilation must be provided by opening windows, doors and vent-dampers.

d). Working with fires, welding, riveting, placing salamanders or lighting matches, is permitted only on written permission of the works manager or his deputy. Besides, a minimum distance of five meters from pipe bridges or phenol troughs must be held. Special instructions by the management, such as supervision of the work by firemen, screening off equipment against flying sparks, etc., must be strictly followed.

e). Only prescribed materials kept in stock must be used for cleaning (Neradol, P3). Inflammable liquids may be used only with the permission of the works manager. Vessels containing gasoline or light oils in buildings must always be covered.

f). In case of fire, the fire department and the works manager must be immediately notified. All employees must be instructed in the use of fire fighting equipment and its location. In case of fire in a building with elevated containers, such as paste press buildings, the bottom outlet valves of the tanks must be closed immediately. In case of fire in dangerous proximity of such buildings the window slides before the blinds, where provided, must be closed and the water sprinkling system at oil containers, where provided, must be turned on.

The following general rules must be observed in every fire:

1. Don't get excited.
2. Employees must remain at their post unless prevented by the fire.
3. Employees trained as emergency firemen must help the fire department only when directed.
4. Spectators at a fire only hinder the firemen and endanger themselves and their place of work.
5. Special instructions, where necessary, may be issued by the department foreman or works manager.

## 2. ORDER AND CLEANLINESS

a). Persons with open wounds on their hands are not permitted to make analyses or work with acids, alkalies, mercury, and other solid or fluid poisonous chemicals.

The use of chemicals intended for analyses for other purposes is prohibited.

Mercury supplies must always be kept locked up. Spilled mercury must be immediately collected and thoroughly cleaned up.

b). Only closets especially provided for them may be used to store food in the plant.

No clothing, portfolios, etc. may be hung up at the place of work.

c). Any oil from a leaky vessel, etc., must be immediately removed because of the fire hazard.

d). Where oil, etc. from a leaky vessel or line is flowing on the ground, it must be immediately removed and a container provided to catch the leaking fluid in order to prevent contamination of the ground water.

e). Fluids containing oil may not be diverted to the fresh water canal. Such fluids may only be collected in containers provided for them or diverted to the phenol-water canal. Cleaning or repairing oily equipment may not be done near the fresh water canal. The plant engineer will be responsible for this. If any one of the group of trouble shooters should report a waste water pollution, the operating department must immediately determine where and why oil gets into the waste water and initiate counter-measures. A complete report of the trouble and the counter measures must be made in the operating report book.

Every act, which may possibly cause the pollution of the waste water, must be reported in detail to the sanitary division so that unnecessary search may be avoided.

f). Filling in of the catalyst must be done in the presence of the foreman or his assistant. (Compare safety regulations). The catalyst must be stored in a well locked room. If catalyst has to be stored in an open space, the barrels must be lead sealed, as well as the barrels used for shipping it.

## 3. WORKING TOOLS

The working tools are the property of the plant and are entrusted to the care of every employee; their mis-use will be punished.

Drawing raw materials from stores as well as their dispensing at the warehouse is done by specifically designated persons.

## 4. PROTECTION AND SAFETY DEVICES

a). Each shift boss or someone specifically designated by him for the purpose, shall patrol the vicinity of the buildings under his jurisdiction at least once during the shift to see that all gutters, pits, pipe channels, platforms, ladders, etc. are in order and safe against accidents. If not, he must immediately see that they are properly protected. The patrolling of buildings and their vicinity must in all cases be done at the shift change, when the off-going shift boss must call the oncoming shift boss' attention to special conditions, repairs, new operation changes, etc.

The shift bosses are responsible for the enforcement of all safety measures at repairs within their department, such as closing off repair areas, covering up pits, etc., so that everything humanly possible is done to prevent accidents.

b). Books must be kept on the testing of weighted safety valves. The safety valves on the high pressure liquid pumps must be tested at every major repair, but at least every six months. A special report book must be kept for this test, for which the plant engineer is responsible.

c). All safety and alarm devices must be tested at least once a week by the shift boss or his assistant. Books must be kept.

If an alarm signal can not be tested within the prescribed time because of important operation changes, this must be reported in the operating report book and the test must be made as soon as possible.

Damages to alarm devices must be immediately reported to the department head and in the operating report book as well.

d). Before every repair on lines or vessels these must be flushed with nitrogen and tested for inflammable contents. Flanges may be opened only if the contents are less than 5% inflammable.

e). Before every flushing or compression of lines or vessels the nitrogen must be tested for its purity. It is prohibited to use nitrogen containing over 5% inflammables or over 1% oxygen for compression. After compression or flushing the intermediate pressure release in the nitrogen line must again be opened.

f). Plants in which gases dangerous to health may occur must be provided with proper gas protection devices. The fire department is responsible for the maintenance of gas protection devices.

g). All foremen and key men, and for each key man at least one deputy, must be instructed in the use of gas protection devices. The plant fire department is responsible for this task.

The foremen must see that when a man familiar with the use of these devices leaves the department another man is instructed in their use.

h). When filling or emptying dusty materials a respirator must be worn, when fresh air devices, for example, at the filling of converters with catalyst, are not required. Filling the converters with catalyst may be done only in the presence of an authorized employee, foreman or assistant.

i). The siphons and safety traps in the gas lines must be inspected and tested at each shift by the shift boss or his assistant.

Siphons, in which the gas has run through, must be immediately shut off against the gas line, filled with water and then reopened to the gas line.

j). When steam cleaning polluted or clogged lines, care must be taken that no one is hurt by the escaping steam. This may be done by shutting off the danger zone, connecting a piece of pipe that will deflect the escaping steam in a safe direction, screening off with baffle plates, etc.

Where flanges must be taken off a line, which is not definitely known to be empty, the workmen are required to wear leather gloves, suits and safety helmets.

k). Coal bunkers and bunkers for crude catalyst must always be under $CO_2$ or $N_2$ pressure. The oxygen content of the protective gas must not exceed 10% and must be tested once in every shift.

1). It is prohibited to apply any special signs or numbers on any machine, apparatus, or pipe line, etc. without authorization by the management, in order to avoid any mix-up or misunderstanding.

5. REPAIRS

a). Before every repair on an electric motor or the driven machine, the departmental shift boss must personally assure himself that:

1. On high tension motors the starter is locked.
2. On low tension motors the fuses are removed, and that in both cases the prescribed warning sign:

"Do not switch, danger" is attached to the starting switch or fuse box.

Not until then may repairs begin.

The locks and warning signs may not be removed, and the fuses may not be replaced, until repairs are completed. Repairs are considered completed only after the repair boss has reported this to the shift boss. From this point on the repair boss is responsible for his men not working on the machine again.

If a trial run of the motor is necessary before repairs are completed the responsible shift boss must assure himself that all coupling bolts between motor and machine are removed or that on belt drives the belts are properly taken off before he removes the lock on the switch or replaces the fuses. These bolts must be locked up and the electrical repair boss or his assistant is responsible for the safe procedure of the trial run. After the trial run the shift boss must immediately apply the original safety measures. Until this is done the electrical repair boss or his assistant are responsible.

b). The operating foremen are generally prohibited to enter the electrical substations, except:

1. In case of an accident in the sub-station,
2. To disconnect the oil switch in case of electrical control failure.

Switching with a switch bar is prohibited.

c). Before a stall is turned over to the mechanics by the operating department, the electric valves in the service aisle must be disconnected and locked and provided with a warning sign

"Do not switch".

Before working on the transformers or in the compartments of the sub-station, the electrical department must secure them against unintentional operation.

d). Before opening a gas line containing inflammable gases, it must be shut off against the gas pressure, the pressure released and, if possible, blinded off. See also (e) for high pressure lines.

The line in question must then be flushed out with $N_2$, $CO_2$ or steam. Not until then may the line be opened. (Compare article 4, "d" and "e").

If it is not possible to insert a blind disk in a fuel gas line between the repair point and a gate valve the line must be protected against the gas by putting the gate in question under water. To assure tightness of the gate under water the line to be repaired is pressure relieved and the relief gate is then closed again. If no rise in pressure occurs, the gate under water is tight. During the repair period the water overflow at the gate must be watched by a man specifically assigned to this task.

Wherever possible, a second gate valve behind the shut-off gate valve proper must be closed and a vent must be opened between them.

e). When working on high pressure lines, such as inserting blind disks, orifice plates, seals, etc., the repair point in question must be shut off on both sides by closing valves or gates so that between the repair point and all lines under pressure or parts of equipment at least one gate or two valves are closed. The piece of pipe between the two valves must be relieved of pressure. If, for operating purposes, this piece of pipe should be put under pressure before repairs are completed, the repair point must first be blinded off.

Closing one valve is sufficient only on lines having a diameter to 16 mm @ 300 atm. pressure, at higher pressure only on lines to 10 mm diameter.

When removing a piece from a high pressure line, or an orifice plate, the openings against the lines under pressure must be blinded off if the repairs should take more than an hour. Exceptions can be made only on lines below 10 mm diameter.

Only the works manager has authority to permit departures from these regulations.

f). Before starting work on a steam line the adjacent valves must be carefully closed, the lines blinded off and a sign

"Do not open"

attached to the valves. On short repairs or on small lines the blind disks may be omitted.

g). Apparatus under pressure, which is to be opened, must first be pressure relieved by the shift boss and, if necessary, flushed out with $CO_2$ or $N_2$. All connecting lines, through which gas could enter, must be blinded off before beginning work on them. Only after these safety measures have been taken may the shift boss turn over the apparatus to the repair boss. If an apparatus can not be relieved of pressure because of clogging the works management must be notified before starting the repair work.

Special care must be taken in opening lines or apparatus, which may possibly still contain some product. Particular attention must also be paid to the danger of hot fluids flowing from clogged lines or apparatus during repair work.

h). When apparatus or vessels are put into service they must first be freed of all gases by protracted ventilation, by blowing out with air, by artificial ventilation, or by filling with water. Then the operating foreman or his assistant must personally assure himself of the constitution of the air inside of the vessels and determine if the place of work is free of health endangering gases and if all safety measures have been taken, such as inserting a blind disk in each line connected to the apparatus or taking out a connecting piece between a line and a vessel.

The closing of valves, cocks or gates alone is not enough.

i). Before putting into service any high or low pressure inflammable gas line all parts into which air might have entered must be flushed with $N_2$ or $CO_2$ and blown out into the open.

The flushing must be controlled by gas analyses.

j). Newly mounted high pressure apparatus must be tested to the working pressure with nitrogen before being put into service. High pressure apparatus, which have been emptied and opened for major repairs must, in general, also be tested to the working pressure with nitrogen. Exceptions may be authorized only by the works manager (Compare Chapter 4, "d" and "e").

k). Before starting up or compressing a converter, analyses must be made after the flushing to see that the converter is free of oxygen. Such analyses must also be made on all other apparatus after flushing.

l). Before a converter stall is compressed all openings must be closed, the stall must be locked, and its condition indicated by a warning sign. No work may be done in the stall during compression. Only the operating foreman or master mechanic are permitted entry into the stall during compression for a short time for determining leaks. As long as either of these men is in the stall the pressure valves must be kept closed.

Whether any work may be done in the stall after the operating pressure has been reached in the compression operation and after a pressure drop has been noticed depends on the combined prescription of the plant manager and plant engineer.

m). Tightening bolts on a high pressure line under pressure is prohibited. Exceptions are subject to the permission of the works manager or plant engineer. Entering a stall under hydrogen pressure is permitted only the operating foreman, and only for a short time, for the purpose of maintaining regular operations and avoiding dangers due to leaks.

n). Raising high pressure lines under pressure with a crane is strictly prohibited.

o). Before lifting thermo-housings, cold gas pipes, converter covers, etc. the nuts may never be entirely removed until the thermo-housings or covers have been loosened.

p). For wedging apart the flanges of the 120 or 200 mm lines, the wedge device provided for this purpose must be used.

q). Only high pressure valve parts and pipes with control and test stamps may be installed.

r). It is prohibited to use two wrenches together for tightening bolts. The bolts must be tightened gradually and across from each other successively.

Bolt threads may be cleared only with a cutting nut. Never use a die stock. Each bolt must be inspected to see that no nut is loose.

s). Work on elevated pipe lines, on which there is no scaffolding and from which there is danger of falling due to slipping or becoming unconscious from escaping gases, etc., may be done only with safety belts.

t). Frozen high pressure lines must not be thawed out under any circumstances; they must be dismantled.

u). When repairing lines containing alkalies, acids, ammonia water, etc., special care must be exercised because of the danger of the discharge of caustic fluids, even when there is apparently no danger.

The lines must be carefully relieved of pressure, completely emptied, and blinded off.

When loosening flange connections on such lines, closed and absolutely tight safety goggles or, in special cases, face masks, must be worn without exception. The same applies to all work on machines or apparatus containing caustic fluids.

## 6. CRANES, ELEVATORS AND HOISTS

a). Differential hoist blocks, winches and other hoisting tools may be issued only by the store keeper or his assistant. The plant safety engineer is responsible for the working order and inspection of such equipment. The lending of hoisting apparatus between plants is, therefore, prohibited.

b). All rope slings must be inspected every Saturday by the crane foreman.

Ropes not meeting specifications or which are badly worn must not be used.

c). Elevators may be operated only by the elevator operators. Their instructions must be strictly followed.

Careful attention must be paid to proper servicing and maintenance of door closures. All irregularities in their mechanism must be reported immediately.

## 7. SERVICING OF MACHINES AND APPARATUS

a). Gas preheaters may be lighted only by the foremen. Before lighting by a torch the foreman must assure himself, by analysis or proper observation of the CO and $O_2$ measuring instruments, that no inflammable gases or enough oxygen to burn is present.

When a gas preheater is put into service the combustion chamber and smoke flue must first be flushed by starting the blowers or, if the preheater is still hot, by opening the chimney cap. The torch is then lit and the slide gate in the fuel gas flue is pulled. Immediately after pulling the slide gate the fuel gas flue must be flushed with nitrogen and the preheater is lit by opening the gas valves. When starting the blowers, the gas check damper, the suction damper and the chimney cap must be closely throttled.

In shutting off a gas preheater the gas valves on each side of the intermediate expansion (Zwischenentspannung) must be closed and the intermediate expansion opened.

If work is to be done on the preheater, the $CO_2$ must be replaced by air.

b). Starting tar pumps, paste presses, compressors or gas circulating pumps may only be done by the foremen or key men. These are responsible for safe operation. Special instructions must be observed.

c). The machine maintenance men are strictly prohibited from cleaning the handles of inlet valves or other moving parts on any machine in operation.

## 8. FROST PROTECTION

a). If there is danger that persons may be hurt by falling icicles from pipe bridges, roofs, etc., the endangered places must be closed off and warning signs must be erected. Larger ice formations must be removed as soon as possible with proper precautions.

b). The siphons provided for the draining of gas lines, water pots, etc., must be prevented from freezing by heating with steam. Frozen siphons must be immediately thawed out with hot water.

Care must be taken that the water in the traps is not discharged when turning on the steam.

Traps which can not be heated must not be filled with water but with an anti-freeze solution.

c). During the frost season, safety disks (bursting disks) must be strewn with salt at regular intervals.

d). During the frost season, machines, coolers, lines and vessels must be drained immediately after shut down. Steam or water inlets must be blinded off or disconnected wherever possible. Steam and water lines must be blown out with air. On the safety traps of heated oil tanks and gasometers the water must be drained and replaced with glycol or oil with a low pour point. Vessels containing water, such as let-down coolers, must be emptied when out of service.

On gasometers with water shut-off the water temperature must be kept above the freezing point by steam during the frost season.

e). All heating lines must be disconnected or blinded off from the steam or condensate mains after the steam has been shut off.

f). During the frost season, all ratchet valves and the by-passes of gas inlet valves to the stalls must be heated and insulated.

g). In case of frost, care must be taken that all gates and valves, above which water may collect because of their low position, remain open and that all water pockets in the lines, as well as all catch pots are drained every two hours.

All outlets on water and steam lines not in operation must be heated and insulated up to the valves or blind covers. Small size steam lines must also be insulated.

Every freezing of a line, including small manometer lines, etc., must be reported to the plant manager by the foremen and, in case the disturbance is not immediately relieved, it must be entered in the operating report book.

h). Where there is a second water connection, besides the normal, which is not protected against frost, this must be put in service or emptied in case of frost danger.

This must be reported to the water supply division.

## 9. TRAFFIC ON RAILS AND ROADS

a). When emptying tank cars, they must be protected against accidental collision or runaway, as follows:

1. The brakes must be tight.
2. A double derail must be placed about two to three car lengths on each side of the car.

3. Alongside of each of these derails a stop sign must be placed.

4. All these precautions must be applied before the car is connected to the line and must not be removed until after the car has been disconnected.

b). Road blocks must be erected at the entrance to the blocked road.

c). All road blocks must be reported to the fire department.

10. **ACCIDENTS**

a). Every department must have at least two persons in each shift who have been instructed in binding wounds. Whenever one of them leaves the department, he must be replaced immediately.

b). All accidents must be reported to the safety engineer, whose office must bear a special sign to this effect.

Newman

T.O.M. Reel 5
Pgs. 594-604

U. S. Bureau of Mines

Hydro. Demon. Plant Div.

T-137
KCBraun/mem
10/28/46

# Abstract of Report on High Pressure Vessels for Hydrogenation

By A. F. Maier (See also T-93, T-96, T-98 & T-99)

Technische Mitteilungen Krupp, Dec. 1941.

(<u>Note</u>: Much of the author's subject matter is covered in T-93, T-96, T-98 and T-99, or is common knowledge to American engineers in related fields, and only matter~~s~~ directly bearing on hydrogenation is, therefore, reproduced here.)

## Construction Materials.

As in all chemical plant equipment, strength and corrosion resistance are of great importance in the construction materials for hydrogenation. Apart from the production of gasoline from natural gas, the most important processes for liquid fuel production are:-

1.) ~~By-products coke plants.~~

2.) Combining hydrogen and carbon by:

   a)- direct hydrogenation of coal as used by I.G. Farbenindustrie, and

   b)- gasoline synthesis from CO and $H_2$ by the Fischer-Tropsch process.

3.) The cracking of petroleum, by the Dubbs or other American processes.

The processes in 1.) take place at temperatures between 500 and 800° C. Pressures above atmospheric do not occur, which simplifies construction materials.

In the Fischer-Tropsch process, 2b), also, operating at pressures to 20 atm. and temperatures around 200° C, plain carbon steel suffices for the equipment.

But the I.G. Farbenindustrie process, 2a), operating at pressures between 300 and 700 atm. and temperatures from 400 to 520° C, requires the highest quality construction materials. Atomic hydrogen, whose destructive effect on metals is well known, enters the walls of vessels and pipe lines and causes decarbonization where the steels have not been made resistant by suitable alloys, particularly chromium, (chromium carbides). The degree of attack is dependent upon pressure, temperature, stress, composition and structure of the steel. Only a few examples of resistance limits will be discussed here.

A 100 hour test on 2 plain SM-steels, containing 0.11 and 0.24% C, showed that such steels are hydrogen resistant at most up to 300°C.

Fig. 2. shows the influence of chromium content on hydrogen resistance. The steels also contain about 0.3% Mo. The left half of the diagram shows the limits at which the first signs of attack of the structure appear, the right half those at which rim-decarbonization is already present. The fields to the left of the curves may be considered safe.

It may be noted that a chromium content of only 1% increases its hydrogen resistance temperature by about 200° C.

A comparative test of a plain carbon steel and one containing 6% Cr and 0.5% Mo showed that the plain steel lost all but 1mKg/cm$^2$ of its original notched-bar impact strength of 38 mKg/cm$^2$ in the treatment with hydrogen at 400° C, and all of its original elongation of 25%, while the Cr-Mo steel looses none of its properties, even at 600° C.

Besides hydrogen, $H_2S$ and CO are, at times, produced in the I.G. - process, and the steels must also resist attacks by these gases. While the Cr-steels are fairly $H_2S$ resistant, copper linings have proved satisfactory against CO.

The cracking processes in 3.) take place at temperatures of 520 to 580° C and pressures of 25 to 70 atm. The first requirement of their construction materials is resistance against $H_2S$ as well as against scaling. Chromium alloyed steel is, therefore, properly used, whose resistance may be increased by the addition of silica. Aluminum alloyed steels may also be used for the splitting tubes, directly exposed to the fuel gases, because aluminum increases the resistance to scaling.

Fig. 4. shows the relation between temperature and strength of steels. The curves indicate the yield points and creep strength, the 2 most important properties for design, of steels containing 6%, 3% and 0.8% Cr, and of a soft carbon steel, at various temperatures. At temperatures above 350° C calculations must be based on

the creep strength, since it drops faster than the yield point. It may be noted that above 500° C the strength of these steels is sharply reduced and wall thicknesses must be correspondingly increased.

## Seamless Forged High-Pressure Jackets.

The forms and dimensions determined by the designer vary greatly and are dependent upon the purpose for which the apparatus is used. Certain principal dimensions have, however, been found practical because of limitations in fabrication. Inside diameters have an upper limit of about 1500 mm at working pressures of 300 atm, and 700 to 1000 mm at pressures to 1000 atm. The maximum lengths are limited, in general, to 15 to 18 meters by the weight of the ingot, if the wall thicknesses are based on the strength of the material in question. If the required weights are above forging limits or the wall thickness is so great that it can not be heat treated to the core with absolute reliability, recourse may be had to shrunk jackets of 2 or more parts. This will permit a more economical use of the material due to the initial tension, which the outer layers exert on the inner sleeves, so that a multi-part wall may be thinner than one made of one piece. The lengths may also be subdivided into 2 or more parts, in which case flange and bolt or butt welded connections are usually provided.

## Closures for High Pressure Vessels.

Fig. 12 shows perhaps the best known form of closure for pressures of somewhat over 200 atm. It was developed in England for the Bergius coal hydrogenation process. The vessel openings are restricted at the ends, so that inserts larger than the end openings can only be installed if the heads are forged seperately and attached to the body of the vessel by a detachable connection. This consists of a 3-part clamp ring with conical bearing surfaces enclosing a U-shaped steel sealing ring with convex bent shanks. This construction requires extreme precision work, fitting or retouching the ring is possible only to a very limited extent. The same type of seal may also be used for the cover closure and for pipe connections. Fig. 12 further shows a conical bearing surface in the bolted cover.

A somewhat simpler construction is shown in Fig. 18. The longitudinal forces are here also taken by bolts, which also provide the initial tension of the heavy seal ring provided with 2 wedgeshaped surfaces. To prevent overloading the ring, which would cause inward deformation, that is a decrease in the diameter, a limited play is provided in the cover groove. The operating pressure bears on the entire inside surface of the sealing ring and automatically regulates the pressure on the conical sealing surfaces.

## Welded High Pressure Vessels

Thick-walled welded high pressure vessels of alloy steel have been made possible by advances in electric arc welding and the development of high strength electrodes. A flawless weld is comparatively simple with soft steels. Alloy steels, however, are much more sensitive and require well trained and experienced welders. Testing the welds without destroying them, by X-rays, mesothorium rays, or the magnetic powder process, has greatly increased the safety of thick-walled welded vessels.