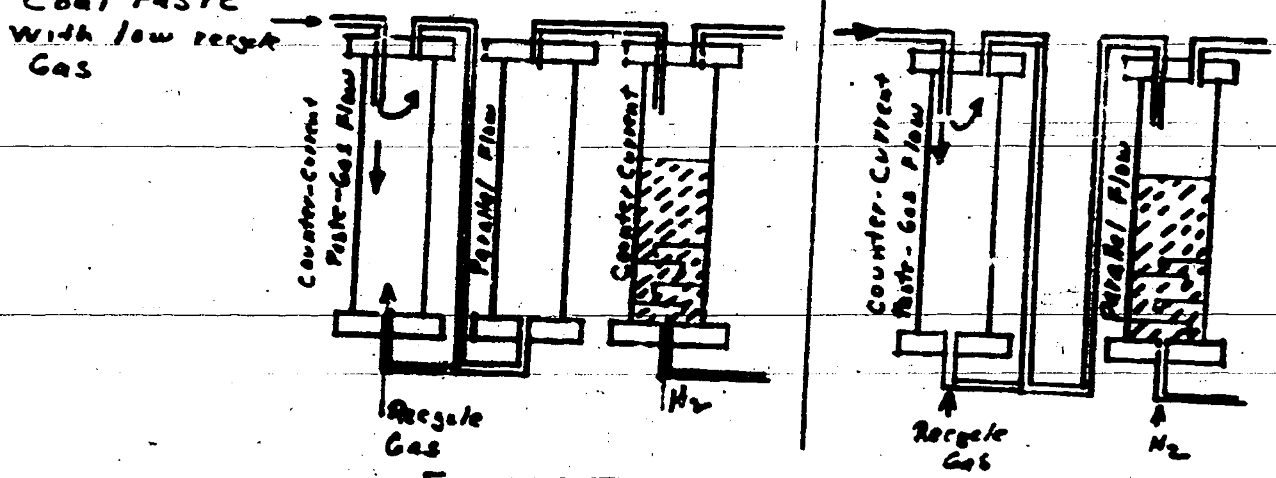
FIG. 18 — Two Types of Chambers



EXAMPLE I.

EXAMPLE II.

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II. HIGH PRESSURE HYDROGENATION. (Cont'd.)

FRESH GAS USED (Cont'd.)

Red earth based on dry lignite/water free	5.76	%
Sulfur - dry lignite/water free	0.129	%
Screen reject over 400 mesh	10.6	%
Screen reject over vibrating screen	0.6	kg/ton

COMPOSITION OF DILUENT OIL

Sump phase residue	34.2	%
Centrifuged oil	56.7	%
Outside oil	9.1	%
Boiling range-up to 340°C	10.6	%
Solids	4.0	%
Asphalt	8.85	%
Effluent (based on paste and seal oil)	51.0	%
Mud " " " " " "	33.8	%
Middle oil - up to 340°C in effluent	38.8	%
Middle oil - up to 340°C in mud	11.2	%
Solids in mud	18.5	%
Asphalts in mud oil	15.6	%

DISSOLVED GAS

In effluent	lean	74.9	cu.met/cu.met
	rich	14.2	
In mud		122.5	
In wash oil	lean	151.3	
	rich	46.9	

INTERMEDIATE EXPANSION PRESSURE

Effluent	38.	atm.
Wash oil	35.	atm.

HOURLY QUANTITIES

Coal paste	112.6	cu.met/hr
Cold oil and seal oil	8.8	cu.met/hr
Water injection	6.4	cu.met/hr
Effluent	65.5	

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II. HIGH PRESSURE HYDROGENATION. (Cont'd.)

HOURLY QUANTITIES (Cont'd.)

Mud		41.0	
Middle oil reformed		25.4	tons/hr
Fresh gas required		51,583.	cu.met/hr
Gas in effluent	lean	4,902.	" " "
	rich	929.	" " "
Wash gas	lean	7,851.	" " "
	rich	2,274.	" " "
Gas in mud		5,027.	
Wash oil		50.1	cu.met/hr

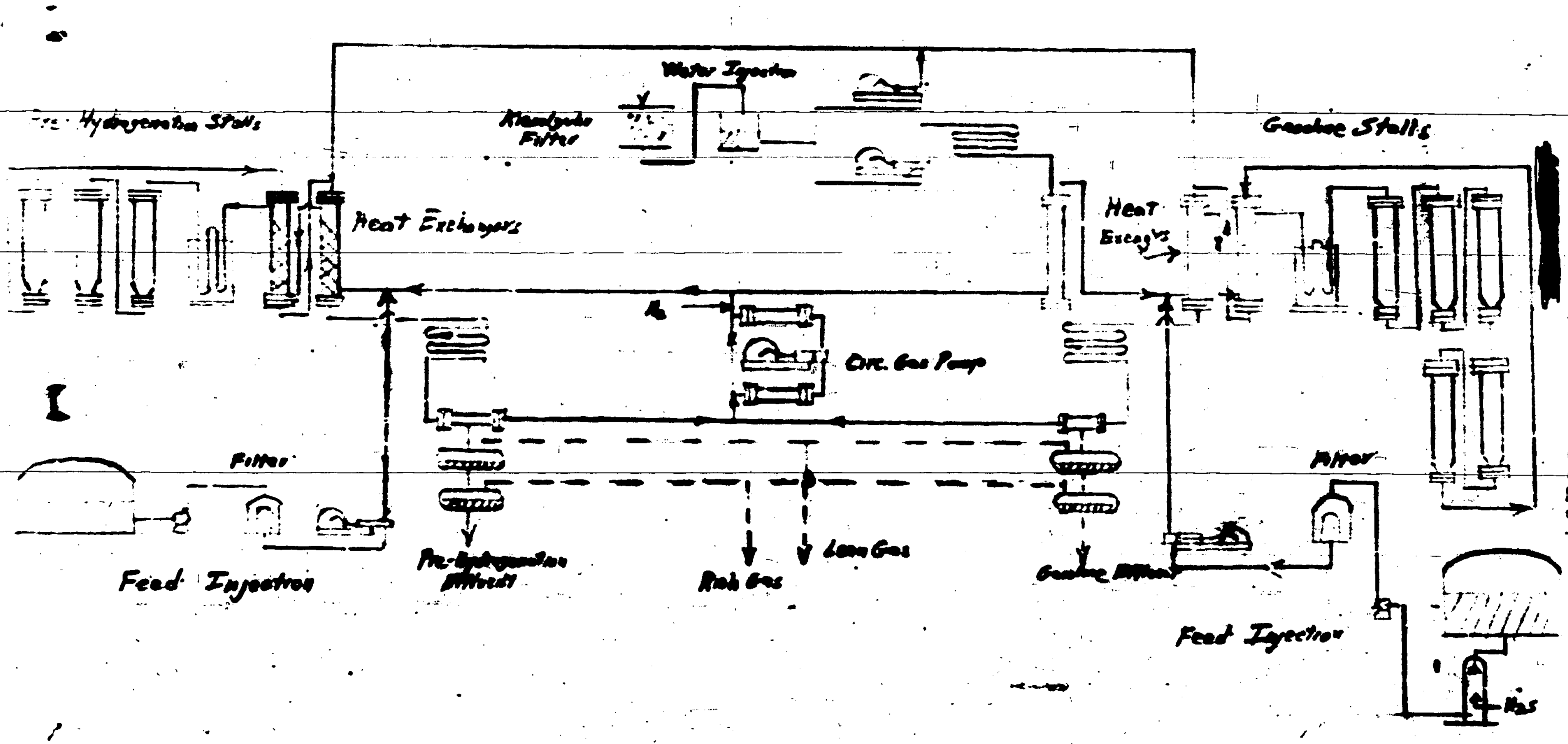
III. GAS PHASE HYDROGENATION.

(a) This unit runs at three hundred twenty-five atmospheres pressure. It consists of four (4) stalls, four (4) gas circulating pumps, six (6) feed pumps for middle oil, three (3) feed pumps for water injection, two (2) water wash towers and sulfurizing equipemnt for the prehydrogenation and gasoline stalls (Fig. 19).

(b) The stalls each have two (2) regenerators, six hundred (600) millimeters diameter, and catalyst chambers. The latter are one thousand (1,000) millimeters diameter, eighteen (18) meters long and have a catalyst volume of eight (8) cubic meters. Two of the stalls have electric preheaters and the other two gas-buring preheaters. The latter have one (1) oil burner and two (2) circulating blowers. At this time, two (2) stalls of three (3) chambers and one (1) stall of five (5) chambers are filled with the prehydrogenation catalyst 5058/7846 W. The fourth stall of five (5) chambers is filled with gasoline catalyst 6434. Each circulating pump handles seventy-five thousand (75,000) cubic meters/hour at a differential pressure of thirty-five (35) atmospheres. All middle oil injection pumps are enclosed in the stalls. In order to prevent the products of the prehydrogenation and gasoline stalls from mixing, all piping is equipped with double valves and intermediate expansion. The pump suction lines are fitted with porous filters. Three (3) of the six (6) feed pumps have variable speed motors. The feed pumps will handle twenty-five (25) cubic meters/hour and the condensate pumps six (6) cubic meters/hour. The condensate is filtered through kieselguhr.

Fig. 19

High Pressure Gas Phase



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III. GAS PHASE HYDROGENATION. (Cont'd.)

(c) The process, as mentioned, works in two (2) steps; the prehydrogenation of the sump-phase middle oil, and the gasoline production step. The former is accomplished by a simultaneous cracking and hydrogenating of the middle oil to a liquid suitable for the production of gasoline. The latter catalyst is more of a cracking catalyst, producing aromatics and iso-paraffins. The former catalysts are designated 5058 and 7846. Catalyst 5058 contains tungsten, an element difficult to obtain in Germany, so 7846 was developed as a substitute. The final catalyst is 6434. All chambers in one stall are connected in series. The operation and arrangement of the stalls is almost identical with the sump phase units.

(d) It must be emphasized that special precautions must be used with catalyst 6434, as it is extremely sensitive to alkaline nitrogen compounds as well as oxygen, both free and combined. Hence the prehydrogenation product must be well refined. Its phenol content can not exceed 0.03 percent and the alkaline nitrogen five (5) milligrams/liter. By water wash, the NH_3 content is reduced to from 0.02 to 0.03 grams/cubic meter. The catalyst must also have H_2S added, up to from 0.4 to 0.5 percent.

(e) The degree of refinement of this feed is measured by the difference in specific gravity between the feed and effluent streams of the stall. These should be from 0.10 to 0.11 entering the prehydrogenator, and 0.075 leaving.

(f) From these values, the catalyst temperatures are established. Using catalyst 5058 this should be 18.5 M.V. and 7846 one (1) M.V. higher. The 6434 catalyst chamber uses nineteen (19) to twenty-one (21) M.V. The increased value is due to slow loss of catalyst activity through refining requirements which the 6434 catalyst requires. The loss of activity in the prehydrogenation chamber took three (3) years to occur and in the 6434 chamber one and one-fourth (1¼) years. This may be considered a normal life.

(g) The A middle oil used in the gas phase consists of seventy-five (75) percent liquid from lignite and twenty-five (25) percent oil from the outside (tar, etc). The composition varies with the specifications of the oil from outside. It normally

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III. GAS PHASE HYDROGENATION. (g)(Cont'd.)

contains fifteen (15) percent phenols but has gone up as high as twenty (20) percent. The high phenol content, attained during the early days of operation, caused high heating of the chambers with resulting loss in production. Later, when the phenol content dropped, the original catalyst activity was restored and full capacity regained.

(h) In the beginning of 1943, a 6434 stall was built to produce aviation gasoline. This required increased purity from the prehydrogenation unit which in turn lowered the capacity of the same. The average capacity was 0.6 kilograms/liter catalyst space (going up at times to one (1) kilogram/liter.). The capacity of the 6434 stall was higher, and averaged 0.75 to 0.8 kilograms/liter (maximum 1.1 kilograms/liter of space).

OPERATING RESULTS - 1943

Stream efficiency	(actual operating hours) (possible " ")
Gasoline stalls	75.2
Middle oil stalls	51.8
Circulating pumps	53.2

	Catalyst		
No. of operating stalls (avg)	5058	2.08	
	6434	0.80	
Avg. reaction vol.	5058	37.4	cu.meters
	6434	12.4	" "
Avg. injection feed	5058	0.824	cu.met RV/H
	6434	1.120	" " " "
Avg. throughput	5058	0.764	tons/cu.met RV/H
	6434	1.070	" " " " "
Gasoline capacity (180°C end point)	5058	0.280	" " " " "
	6434	0.710	" " " " "

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III. GAS PHASE HYDROGENATION. (Cont'd.)

OPERATING RESULTS - 1943 (Cont'd.)

	Catalyst		
Fresh gas/injection feed	5058 6434	432.0 255.0	cu.met/ton " " "
Cooling gas/injection feed	5058 6434	700.0 262.5	" " " " " "
Circulating gas (stall inlet)	5058 6434	4325 1610	" " " " " "
H_2 in circulating gas (stall inlet)		83.9 %	@ 306.5 atm.
Gasoline (180 C end point) in A middle oil		22.8 %	
Phenols in A middle oil		15.4 %	
H_2S in injection feed	5058 6434	38.2 % 68.0 %	
Freed gas in effluent	5058 lean 5058 rich 6434 lean 6434 rich	24.9 11.5 58.2 29.3	cu.met/cu.met " " " " " " " " " " " "
Intermediate expansion pressure	5058 6434	28. 28	atm. "
Hourly rates - Middle oil injection	5058 6434	29.9 12.1	cu.met/hr " " "
Water injected (NH_3 wash water)	5058 + 6434	6.85	cu.met/hr
Fresh feed gas	5058 6434	12,340 3,670	" " " " " "
Effluent gas	5058 lean 5058 rich 6434 lean 6434 rich	818 377 1,660 750	" " " " " " " " " " " "

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III. GAS PHASE HYDROGENATION. (Cont'd.)

AVERAGE PROPERTIES OF ENTERING AND EFFLUENT PRODUCTS - 1943

PREHYDROGENATION

A Middle Oil

Sp. gravity	0.927	@ 20°C	(Aromatics 62.5 %
API (Phenol free prod)	4.0	?	(Olefines 17.2 %
Phenol content	15.4		(Naphthenes 9.2 %
Mat'l boiling up to 180°C	20.5		(Paraffines 11.4 %

5058 Effluent

Sp. gravity	0.825	@ 20°C	(Aromatics 15.0 %
API	52.0		(Olefines 2.0 %
Phenol content	0.03		(Naphthenes 29.4 %
Alkaline nitrogen in B middle oil	5	mg/liter	(
Gasoline content up to 180°C	38	%	(

Properties of the Gasoline - 180°C End Point

Sp. gravity	0. 765	@ 20°C	(Aromatics 8.4 %
API	43.4	?	(Olefines 1.9 %
Cut below 100°C	22.	%	(Naphthenes 30.4 %
Octane number (motor method)	60.5		(Paraffines 59.3 %

Samples taken after the 5058 stall had the following inspections:

Sp. gravity	0.825	@ 20°C
API	20.0	?
Phenol content	6.0	%
Gasoline up to 180°C	25.0	%

GASOLINE MANUFACTURE

Feed to 6434 Stall

Prehydrogenation middle oil	56.0	%
6434 recycled middle oil	44.	
Sp. gravity	0.824	@ 20°C

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III. GAS PHASE HYDROGENATION. (Cont'd.)

Feed to 6434 Stall (Cont'd.)

API	54.0	
Alkaline nitrogen	5.0	mg/liter
End point	328.	°C.

6434 Effluent

Sp. gravity	0.768 @ 20°C	(Aromatics 7.2 %
API	54.	(Olefines 2.6 %
Gasoline - 150°C end point	49.0 %	(Naphthenes 58.0 %
Gasoline - 180°C end point	68.0 %	(Paraffines 32.2 %

Gasoline properties - 150°C End Point

Sp. gravity	0.724 @ 20°C	(Aromatics 6.1 %
API	53.5	(Olefines 1.9 %
Gasoline - 100°C end point	49.0	(Naphthenes 43.5 %
Octane number (motor method)	73.3	(Paraffines 48.5 %

IV. CENTRIFUGING UNITS.

(a) The unit consists of thirty-six (36) continuously operating De Laval centrifuges, each handling two (2) cubic meters/hour throughput (Fig. 20).

(b) The mud in the coal stall effluent is separated in the centrifuging units into an oil free from solids, suitable for diluent oil, and a solid residue which is later coked in coke ovens.

(c) The mud is first de-sanded in a conical settling tank, forty (40) cubic meters capacity. The feed enters tangentally and passes down through a fine screen (0.8 millimeter mesh). The sand is removed through the bottom cone.

(d) The de-sanded product is pumped from a recirculating pipe system to the centrifuges. These rotate at three thousand two hundred (3,200) revolutions per minute and have a drum diameter of four hundred thirty (430) millimeters, and a factor:

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IV. CENTRIFUGING UNITS. (Cont'd.)

C = 2,500 kilograms. The vertical shaft carries on its upper end the so called plate block, consisting of two hundred twenty-five (225) superposed plates, two hundred eighty (280) millimeters in diameter and 0.5 millimeters apart. The plate block rotates in the drum which has a discharge orifice at the center made of Widia metal (tungsten carbide). Between the plate block and the drum is a latticed basket with Widia edges which scrapes off the residue from the drum sides. Through cyclic operation, a difference in speeds of fifteen (15) revolutions per minute is set up between the basket and the drum.

(e) The feed enters the centrifuge from the top through a throat to a measuring device and then through the hollow shaft. In the narrow space between the plates, the separation of oil and mud takes place. The oil flows upwards through holes in the plates near the shaft. The solids contained in the residue pass through orifices in the drum wall.

(f) The resistance offered by the basket has an important influence on good operation. This normally amounts to 1.5 kilograms but rises occasionally to from 3.0 to 3.5 kilograms. As a safety device, shear pins are installed. After numerous experiments, it was possible to arrange the motor circuit to cut out if the resistance on the basket became too great.

(g) Proper operation of the centrifuges depends on the following factors:

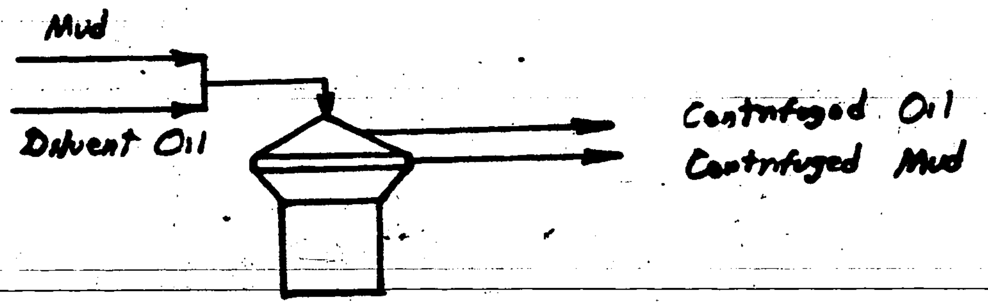
(1) Pressure in recirculating lines;
(2) Solid content;
(3) Temperature of feed (140°C.)

Hence the throat and orifice diameters in the centrifuge must be so chosen as to give the highest possible solid content in the residue and the lowest in the centrifuged oil.

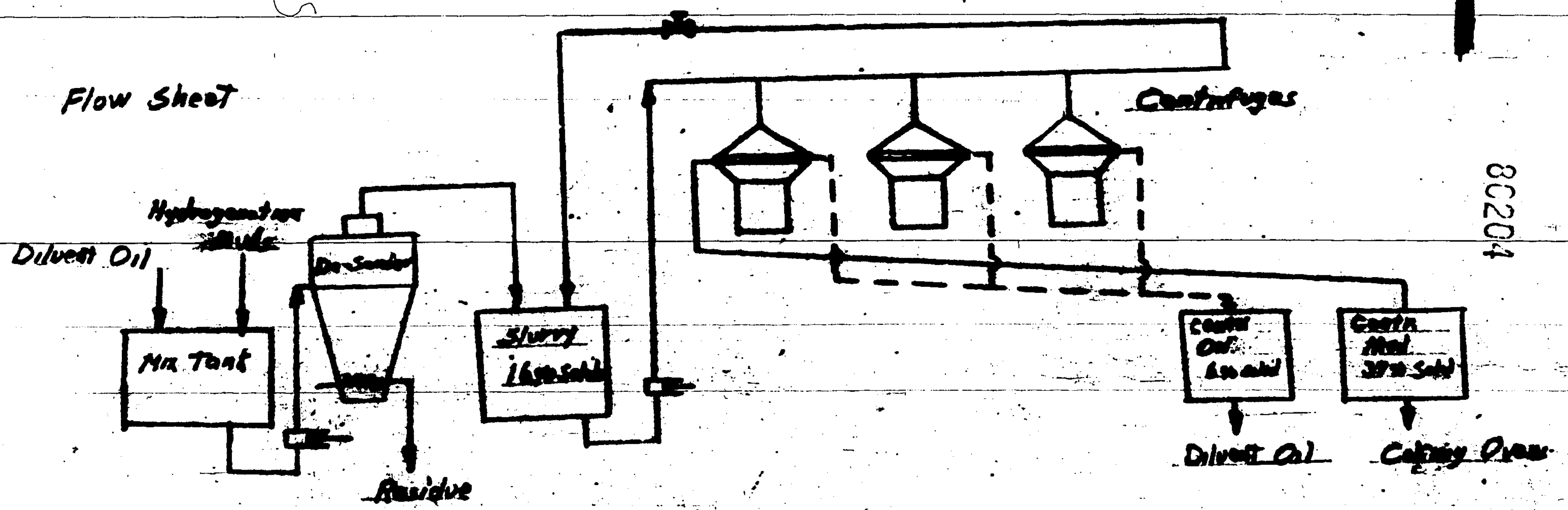
(h) The solids in the mud vary from eighteen (18) to twenty-two (22) percent and can be lowered to sixteen (16) percent by dilution with effluent from the coal stalls. By doing this, the coarse particles can be separated easier in the de-sanding step.

Fig. 20
Centrifuge Units

Principal



Flow Sheet



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IV. CENTRIFUGING UNITS. (Cont'd.)

(i) The capacity of the machine can be altered by varying the pressure in the feed pipe system. This pressure is normally maintained at one (1) atmosphere but can be raised to 1.2 atmospheres. A variation in feed rate is accomplished through changing the neck in the feed pipe. These run from 1.8 to 2.2 millimeters. By the above changes, the following operating results can be had:

Load on one centrifuge	3.2 tons/hr	100 %
Product: Centrifuged oil	2.2 tons/hr	69 %
Product: Residue	1.0 tons/hr	31 %
Solids in centrifuged oil		6 %
Solids in residue		39 %

By increasing the size of the residue exit orifice and keeping the same entrance throat size, the quantity of solids both in the residue and in the oil is lowered.

(j) Ash, Asphalt and Sand.

The solids is the mud contain from ninety (90) to ninety-two (92) percent coal ash. The ash content in the centrifuged oil is seventy-five (75) percent and in the residue ninety-five (95) percent. The asphalt content of the feed to the centrifuge unit is five (5) percent. The discharge from the de-sander contains twelve (12) percent which removes 0.75 of the total solids in the feed. The discharge is finally pumped to the residue stream.

(k) Operating Difficulties.

The highest allowable solid content in the residue is forty-two (42) percent. By further concentration the drum and basket become clogged with solids. It is impossible to operate the centrifuges without de-sanding. The biggest operating trouble was in starting up after a coal stall had been idle, as in stopping the nozzles would become clogged with material then in the unit. This was eliminated by thoroughly washing before the machines come to rest. The originally installed pneumatic valves for pressure control were replaced by hand operated ones as the former did not work well. This was due to the clogging up of instrument piping with the product.

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IV. CENTRIFUGING UNITS. (Cont'd.)

IMPORTANT OPERATING RESULTS

Stream efficiency	53.0 %
Avg. No. of units	19.1 %
Avg. capacity	2.86 tons/hr
Operating hours	166,906 hrs/month

FEED COMPOSITION

Mud	88.51 %
Diluent oil	11.49 %

SOLIDS IN:

Mud	18.5 %
Feed	16.4 %
Centrifuged oil	6.8 %
Residue	38.8 %

HOURLY QUANTITIES

Mud to centrifuges	48.3 tons/hr
Diluent oil	6.3 tons/hr
Total feed	54.6 tons/hr
Centrifuged oil	39.7 tons/hr
Residue	15.4 tons/hr

V. COKING UNITS.

(a) The muds from the centrifuging units are coked in an atmosphere of steam which allows for the recovery of seventy-five (75) percent of their oil content, which is split into two (2) fractions (Fig. 21). The coke oven gas either goes to the flare or is used as heating gas. The residue consisting of sixty-five (65) percent ash-containing solids and thirty-five (35) percent oil is discarded. The unit consists of:

(1) Six rotating furnaces;
(2) Six worm type furnaces.

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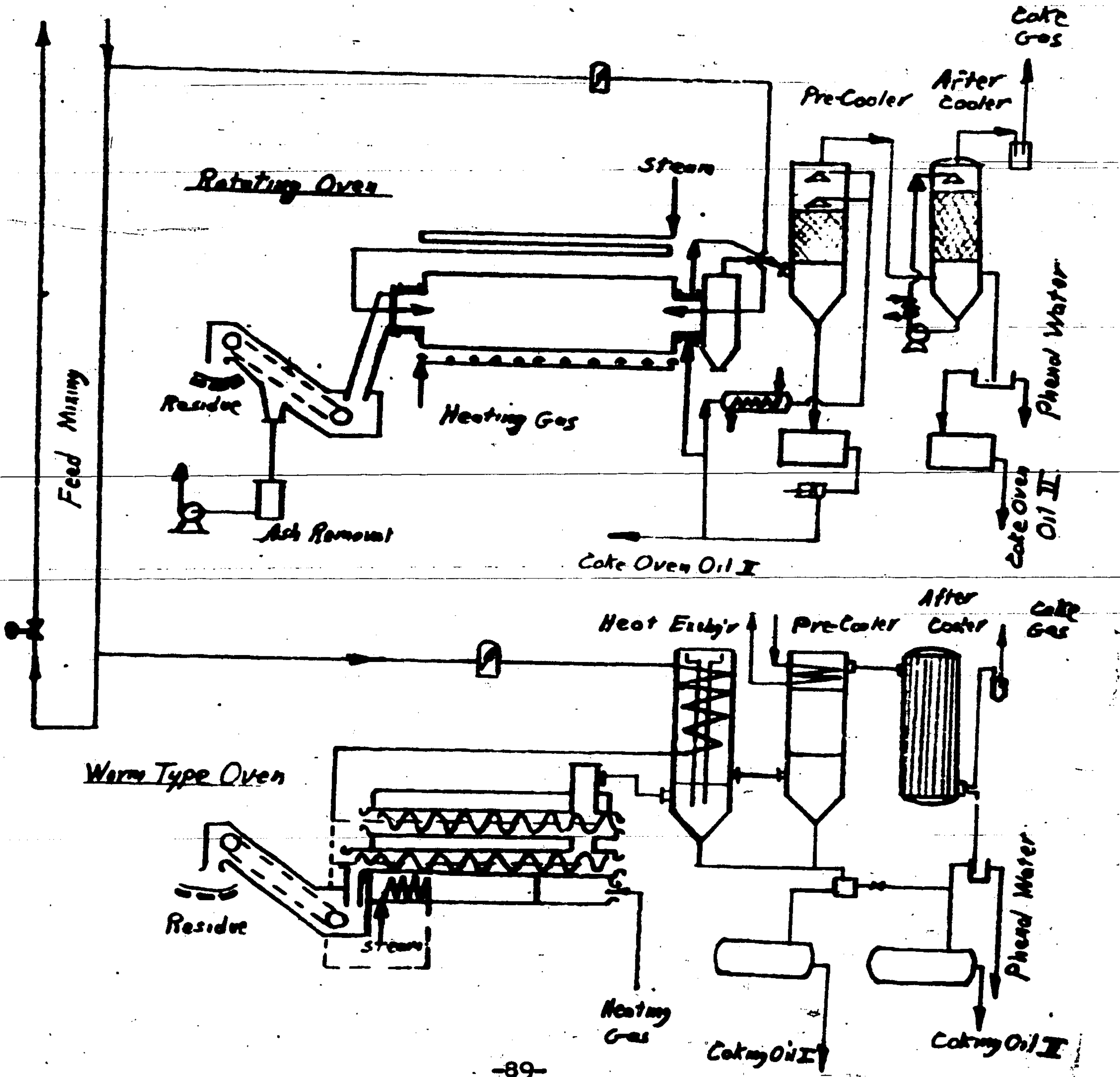
Fig. 51.

Coking Ovens



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V. COKING UNITS. (Cont'd.)

(b) Rotating Furnace.

(1) The rotating oven consists of a horizontal, slightly inclined, drum eleven (11) meters long and 2.2 meters diameter. The inner lining of the drum has a worm welded to it of "guronite" (chrome content twenty-five (25) percent). The drum normally rotates nine (9) revolutions per minute but can be raised to eighteen (18) revolutions per minute. It is heated by twelve (12) gas burners. A second row of burners over the drum preheats the feed and produces superheated steam. The coking section of the drum, which is approximately three-fourths (3/4) of its length, has nine (9) tons of mill balls, of 1.8 kilograms weight each, while the rear section of the drum has twenty-four (24) mill balls, of ten (10) kilograms each.

(2) The feed after leaving the preheater passes through a feed orifice and is continuously fed to the forward part of the oven. The mill balls prevent the formation of coke on the hot sides of the drum and assist in heat transfer from the sides to the material. The product passes through the drum to the rear of the furnace, or exit chamber, where it is conveyed to a water washer by a worm. A scraper then feeds it to a loader which fills it into railway cars. Steam is injected through the whole length of travel. The released oil vapors leave the drum and enter a dust catcher. They are then condensed and separated in a system of towers and coolers.

(c) Worm Furnaces.

(1) The worm ovens consist of two stationary drums, one above the other, sixteen (16) meters long and one (1) meter in diameter. They are joined together at the front end by a connecting section. In both drums is a worm, each run by a motor, turning it one (1) revolution per minute. The upper worm is hollow and serves to feed material into the furnace. The material moves to the rear of the upper furnace and falls through the connecting section into the lower drum where it again is moved forward to the exit. From here it falls into a water bath and then is lifted by conveyor into railway cars.

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V. COKING UNITS. (c)(Cont'd.)

(2) The furnace is heated by a burner in the front section, under the lower drum. The heat is controlled by a heating gas regulating valve. The steam superheater tubes are in the rear sections of both the upper and lower furnaces. The oil vapors leave through a vertical pipe at the forward end of the upper drum. It gives up its heat to the incoming feed through a heat exchanger and is then condensed in two (2) stages by a precooler and an after-cooler, both water cooled. The former is a packed dephlegmator and the latter a tubular condenser. The condensate from the precooler and dust catcher is mixed to make coke oil I. Coke oil II comes from the after-cooler, and passes through a water separator. The gas is used either for heating or discarded.

(d) Operation.

(1) The operation of the coking units depends on the following factors:

((a)) Feed rate;
((b)) Furnace temperature;
((c)) Amount and temperature of injection steam;
((d)) Top temperatures of the coolers;
((e)) Furnace pressure.

(2) The two types of furnaces require different operation due to their design. The coked product from the rotating furnace easily goes to dust. In order to prevent stopping up the equipment, only small quantities of scrubber steam can be used, one hundred (100) kilograms/ton of feed as opposed to five hundred (500) kilograms/ton in the worm oven. To obtain the same coking effect the temperature in the former must be kept higher, namely at five hundred ninety (590) degrees centigrade at the exit while the worm oven is only kept at five hundred sixty (560) degrees centigrade. Higher temperatures tend to coke up the worms. The products are approximately the same, except that the rotating oven residue has more coke due to the higher temperature.

(3) The top temperatures of the pre- and after-coolers require careful attention if a good separation of water in

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V. COKING UNITS. (d)(Cont'd.)

coke oil II is to be had. The former runs around two hundred twenty (220) to two hundred forty (240) degrees centigrade and the latter one hundred ten (110) to one hundred thirty (130) degrees centigrade. The pressure in the furnace differs in both types, eighty (80) to one hundred twenty (120) millimeters for H_2O for the rotating oven and forty (40) to sixty (60) for the worm type oven.

(e) Operating difficulties.

(1) The rotating furnace started up without difficulty. Frequent stopping of operation due to air raids would often cause the tubes in the preheater to coke up, requiring the by-passing of the same. The resulting objections were eliminated by reducing the throughput fifteen (15) percent and raising the furnace temperature from five hundred seventy-five (575) to five hundred ninety (590) degrees centigrade. Further, a new type of preheater was considered which would work with the central burner and avoid the errors in the former type. The stopping up of steam superheater tubes, made of Sichromal, was frequent because the flow through three (3) parallel streams is difficult to regulate. By building a single stream superheater, much better operation resulted. The coking residue tends to become slimy due to pulverization by the mill balls and small remaining oil content. For this reason, conveyance by a rubber belt was impossible, and a slurry had to be used. The residue is passed over a grate by the water stream. The grate removes the coarse particles which can then be moved in the normal way. The remainder falls through the grate in fine particles and is sluiced with much water in a tank. It then is pumped through pipes to the ash dump where it is handled by cranes.

(2) The worm type furnaces started up without difficulty. Difficulties were met in the even distribution of heat over the drums. The heating up of a furnace required forty-eight (48) hours as opposed to the six (6) hours of the rotating type. By constructing baffles and by diminishing the size of the combustion chamber a small improvement was obtained. It was finally necessary to build circulating gas blowers as with the rotating ovens. The operating period

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V. COKING UNITS. (e)(Cont'd.)

of a furnace is fixed by the coking up time of the worms. This was seventeen (17) to twenty (20) days for the lower and one hundred (100) to one hundred twenty (120) days for the upper worms. An improvement was obtained by not shutting down during alerts and by constructing circulating gas blowers. The heat exchangers were also stopped up due to air raid alarms. For this reason a furnace without preheat was used. In this way the heavy oil condensed in the uncooled exchanger. By circulating coke oven oil I in the exchanger, the process was able to operate and resulted only in a slight loss of capacity and a ten (10) percent loss of possible heat recovered.

OPERATING RESULTS

	Rotating Furnace	Worm Furnace
Dist. of load	70.0 %	30.0 %
Capacity - ton/hr/furnace	3.2	2.0
Capacity oil - ton/hr/furnace	2.0	1.25
Coke oven oil I - ton/hr/furnace	1.4 - 70 %	0.75 - 60 %
Coke oven oil II - ton/hr/furnace	0.1 - 5 %	0.20 - 16 %
Oil recovery	75.0 %	76.0 %
Furnace temperature	590.0 °C	560.0 °C
Heat required/charge	350,000.0 kg cal /ton	350000.0 kg cal/ton
Steam required/charge	100.0 kg/ton	500.0 kg/ton
Solid content of coke oven feed	39.0 %	39.0 %
Asphalt content of oil in oven feed	13 - 15%	13 - 15%
Analysis of Residue:		
Gasoline soluble	2.0 %	20.0 %
Coke	33.0 %	16.0 %
Ash	65.0 %	64.0 %
Heating valve	3,300.0 kg cal	3,450.0 kg cal

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V. COKING UNITS. (Cont'd.)

TOTAL COKE UNIT

Feed	16.0 tons/hr
Coke oven oil I	5.69 tons/hr
Coke oven oil II	1.34
Coke oven gas	0.42
Oil less from injected oil	27.29 %

ROTATING OVEN

Stream efficiency	57.59 %
Total hours in operation	30,269.0
Avg. No. of operating furnaces	3.46
Avg. furnace load	3.26 tons/hr

Charge

Solids	39.54 %
Asphalt content in oil	24.2

Residue

Gasoline soluble	2.4 %
Ash	64.2 %
Heating valve	3,498.0 K cal/kg

Hourly Quantities

Feed	11.28 tons/hr
Coke oven oil I	4.03 tons/hr
Coke oven oil II	0.84 tons/hr
Gas	0.35 tons/hr
Outside oil injected and lost	28.5 %

WORM OVEN

Stream efficiency	34.2 %
Operating hours	17,973.0
Avg. No. of operating furnaces	2.05 %
Avg. furnace load	2.30 tons/hr

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V. COKING UNITS. (Cont'd.)

	Monthly Quantity
Oil lost by injecting outside oil	24.4 %
	Charge
Solids	34.49 %
Asphalt in oil	24.2 %
	Residue
Gasoline soluble	18.9 %
Ash	80.31 %
Heating	3,449.0 K cal/kg
	Hourly Quantities
Feed	4.72 tons/hr
Coke oven oil I	1.66 tons/hr
Coke oven oil II	0.50 tons/hr
Coke oven gas	0.07 tons/hr

(f) Production of Briquette Binder.

The large demand for briquette binder material for French hard coal led to experiments using the coke oven residue. In these, only a part of the light oil was removed at low temperature operation. As Fig. 22 indicates, the product from the oven enters a conical tank and is then circulated around by a pump through a cooler, or pumped directly to a tank car. The experiment was conducted under the following conditions.

	Feed	Product
Solid content	16.8 %	32.1 %
Ash content in solids	85.3 %	79.6 %
Asphalt in oil	26.3 %	41.0 %
Sp. gravity at 80°C	1.2 kg/liter	1.42 kg/liter
Penetration point (Krämer Sarnow)		74.5 °C

FIG. 2

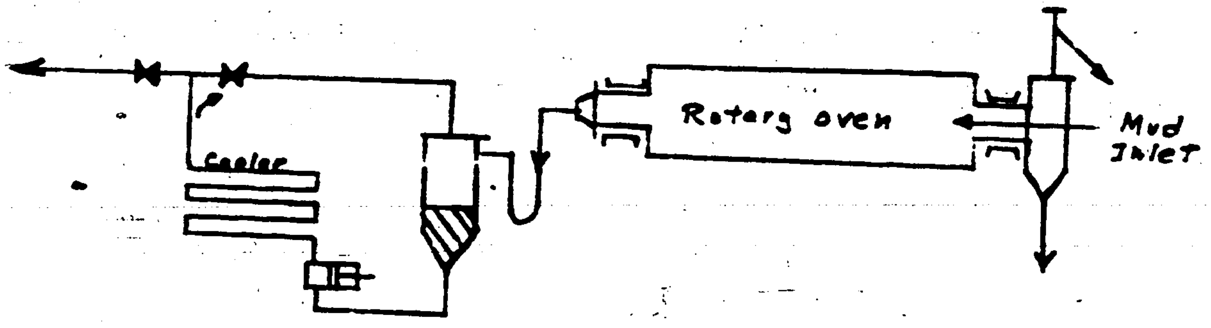
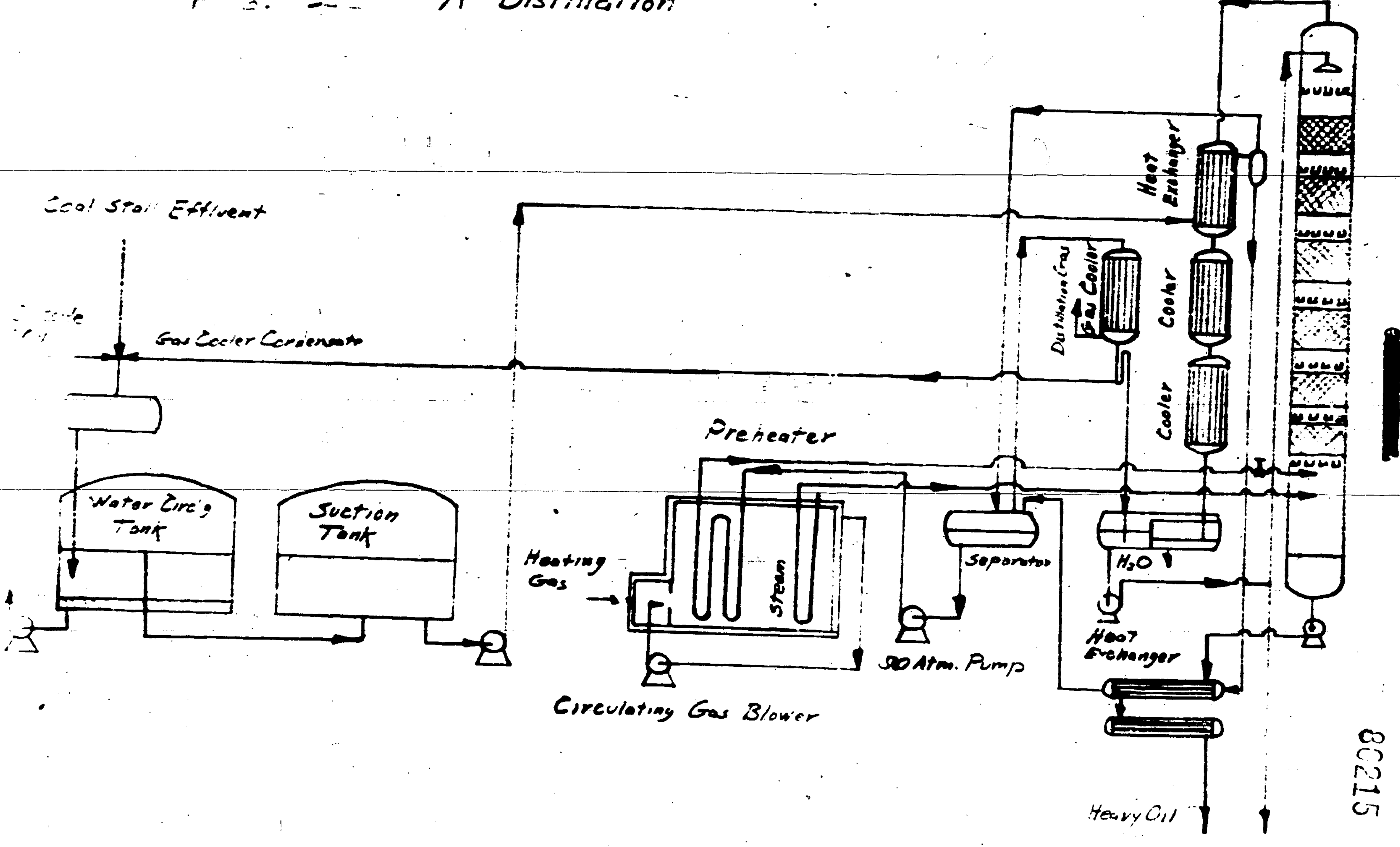


Fig. 22 A-Distillation



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V. COKING UNITS. (Cont'd.)

Capacity	3.6 tons/hr
Oil	3.0 tons/hr
Solid	0.6 tons/hr
Steam added	0.21 tons/hr
Furnace temperature	500.0 °C

YIELDS

Coke oven oil I + II	1.36 tons/hr
Residue	2.13
Oil	1.44
Solid	0.69

VI. DISTILLATION UNIT A.

(a) The A distillation unit consists of two (2) separate columns and equipment. In this unit the total coal hydrogenation product and outside oil for pasting are separated into the A-middle oil for the gas phase hydrogenation step and a heavy oil to be used again in the sump phase (Fig. 23). Both the product and pasting oil are mixed together, as only one storage tank exists for A distillation feed.

(b) The main tower is equipped with packed sections, four (4) meters apart. The feed is preheated under fifty (50) atmospheres pressure, thereby keeping it in liquid phase. This prevents erosion and clogging of the packing through too high vapor velocity. Two (2) pump stages are used. By the first the feed is pumped at atmospheric pressure over a heat exchanger into an intermediate storage tank, while the second pumps the feed through the pipe still into the tower. The gas resulting from this preheating is condensed and used as explained later. All pumps are centrifugal.

(c) The feed may not contain more than one (1) percent water, otherwise it will cause foaming with a resulting flooding of the tower. The water removal is accomplished by settling in two (2) storage tanks. In order to obtain a complete dehydration, sufficient gas condensate is added to the feed to keep its specific

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VI. DISTILLATION UNIT A. (Cont'd.)

gravity under 0.970 at fifty (50) degrees centigrade. This normally amounts to fifteen (15) percent of the feed.

not [illegible] ✓ (d) The middle oil for the gas phase must have an end point of three hundred fifty (350) degrees centigrade. This high boiling range material causes a heavy loading of the gas phase catalyst. Hence material boiling above three hundred fifty (350) degrees centigrade must be absolutely avoided. The distillation requirement therefore produces a gap between the end point (Engler) of the middle oil and the initial boiling point of the heavy pasting oil. This gap has to be paid for by burning extra heating gas in the preheater and using extra stripping steam in the base of the column. Hence the utility requirements, originally anticipated, are somewhat over the guaranteed figures.

(e) The unit started up without difficulty and has run well ever since. Water entrainment caused some trouble due to the emulsifying effect of hydrogenation mud and paste. This was remedied by improving the sump phase operation and by blending tower feed with outside pasting oil.

(f) The tower can be operated with good separation and ordinary utility requirements at between thirty (30) and one hundred fifty (150) percent of the guaranteed capacity figures.

OPERATING RESULTS

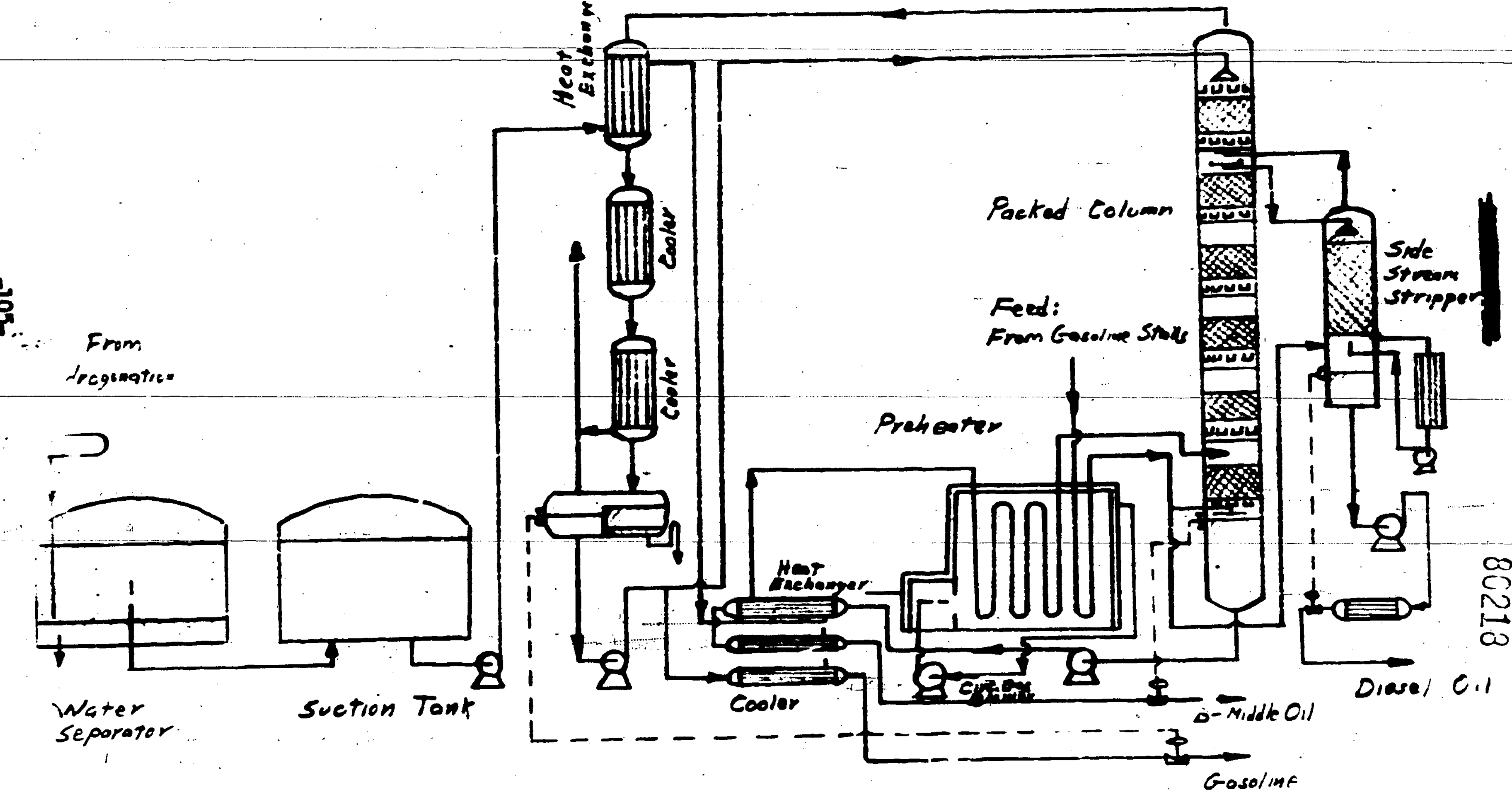
Avg. operating capacity	85.6	
"Number" of units used	1.715	
Avg. unit capacity (including circulation)	48.6	tons/hr

OPERATION WITHOUT GAS CONDENSATE

A-middle oil	40.05	%
Residue (bottoms)	59.32	%
Overhead gas K	0.58	%
Loss	0.05	%
Middle oil end point	342.0	°C
Residue - I.B.P.	349.0	°C
Gap	7.0	°C

Fig. ..

B-Distillation



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VI. DISTILLATION UNIT A. (Cont'd.)

OPERATION WITHOUT GAS CONDENSATE (Cont'd.)

Circulation quantity/total throughput	14.6	%
Distillation factor - without circ.	2.92	%
Distillation factor - with circ.	2.50	%

HOURLY QUANTITIES

Throughput (no recirculation)	71.3	tons/hr
A-middle oil	28.5	tons/hr
Residue	42.3	tons/hr
Tail gas	27.8	cu.met/hr
Gas condensate - returned	5.92	cu.met/hr

ENERGY REQUIREMENTS

Heating gas/ton throughput	0.125 mill kg. cal.
Steam/ton throughput	0.078 mill kg. cal.

VII. DISTILLATION UNIT B.

(a) In the B-distillation unit, the products from the gasoline stalls are separated. The apparatus greatly resembles that of the A-distillation. The tower packing is higher because a side stream stripper is connected to the column for removing intermediate products (Fig. 24).

(b) The products of prehydrogenation and the gasoline stalls are separated by distillation. To produce the normal products of aviation gasoline and diesel oil, the following conditions are used. The effluent from the prehydrogenation step is cut at one hundred twenty-five (125) to one hundred thirty (130) degrees centigrade. If a part of the distillation residue is to be sold as diesel fuel, an intermediate fraction of from one hundred thirty-five (135) to two hundred five (205) degrees is withdrawn. The part boiling above two hundred five (205) degrees is diesel oil. The intermediate cut plus some diesel oil is then fed to the gasoline stalls. In using the whole distillation residue from the gasoline stalls, the yields of intermediate product is assured. The gasoline stall effluent is separated into

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VII. DISTILLATION UNIT B. (b)(Cont'd.)

gasoline with an end point of one hundred fifty (150) degrees centigrade and a bottoms product which after mixing with the prehydrogenation residue is reused as feed to the gasoline stalls. The gasolines from both distillations are treated, and then blended with the condensed cut from C_4 unit followed by a caustic wash and stabilization.

OPERATING RESULTS

PREHYDROGENATION DISTILLATION - 5058

Stream efficiency	81.8	%
No. of operating units	0.83	
Avg. load/unit (including circulation)	37.3	tons/hr

Yields

Gasoline 5058	31.7	%
Heavy gasoline 5058	2.28	%
B-middle oil 5058	64.66	%
Distillation gas 5058	1.27	%
Losses	0.09	%
	100.00	

F.B.P. - gasoline	150°C
I.B.P. - heavy gasoline	136°C
F.B.P. - heavy gasoline	192°C
I.B.P. - B-middle oil 5058	155°C

Recycle product/total throughput	10.3
Distillations factor without recycle	3.26
Distillations factor with recycle	3.63

Hourly Quantities

Throughput without recycle	26.73	tons/hr
Gasoline 5058	8.21	tons/hr
Heavy gasoline	0.61	
B-middle oil 5058	17.55	
Distillation gas	180.0	cu.met/hr

[redacted]

VII. DISTILLATION UNIT B. (Cont'd.)

Utility Requirements

Heating gas/ton throughput	0.190 mill kg. cal.
Steam/ton throughput	0.139 ton

6434 - DISTILLATION

Stream efficiency	79.3 %
No. of operating units	0.55
Avg. load/unit (including circulating)	29.0 tons/hr

Yields

Gasoline 6434	48.08 %
B-middle oil 6434	49.57
Distillation gas 6434	2.35
Losses	0.00
F.B.P. gasoline	149°C
I.B.P. middle oil	152°C
Gap	3°C
Circulating product/total throughput	8.33 tons/hr
Distillation factor (throughput - distillation)	
With recycle	2.27
Without recycle	2.08

Hourly Quantities

Throughput without recycle	15.99 tons/hr
Gasoline 6434	7.69 tons/hr
B-middle oil 6434	7.92
Distillation gas	162.0 cu.met/hr

Utility Requirements

Heating gas/ton throughput	0.163 mill kg. cal.
Steam/ton throughput	0.038 ton

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VIII. ALKALINE WASH AND STABILIZATION.

(a) The crude gasoline is purified by an alkaline wash using dilute NaOH solution to remove H_2S and Phenolics. This is followed by treatment in the stabilizer to remove the light hydrocarbons and make the vapor pressure correct for a saleable product.

(b) Apparatus. (Fig. 25)

The alkaline wash precede the stabilizer in order to protect it from H_2S corrosion. A degasser may be installed ahead of the alkaline wash. The alkaline wash is done in two (2) stages. For washing entrained alkaline solution, a water wash is employed afterwards. The stabilizer is made with a round-based column, and is built for six (6) atmospheres working pressure. It operates fully automatic except for manual feed injection.

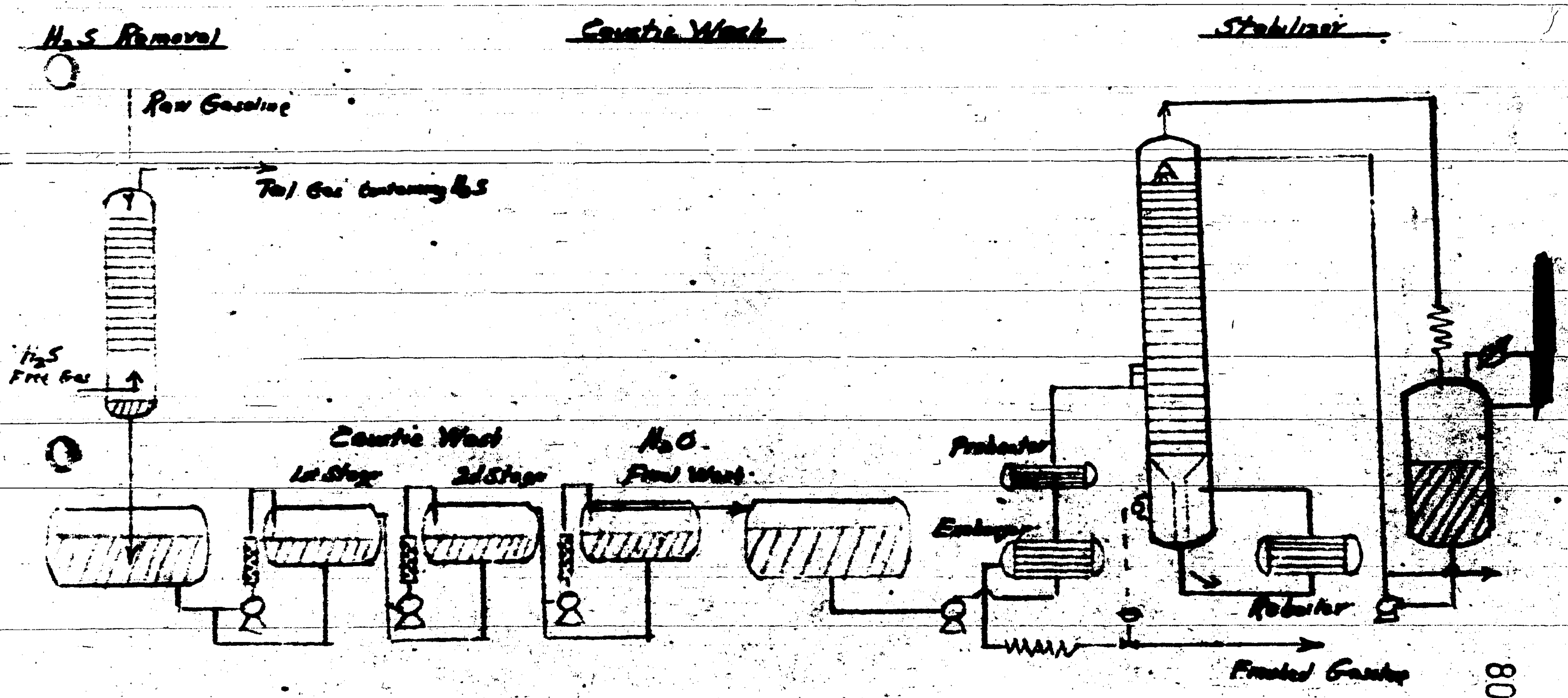
(c) Operation.

Since the crude gasoline contained only one hundred fifty (150) to two hundred (200) milligrams H_2S/liter, degassing was unnecessary. The gasoline was generally stabilized to have a vapor pressure of 0.5 atmospheres by the removal of dissolved C_1 to C_4. The resulting liquid heads product was vaporized and combined with the heads gas from the C_3 plant. With increased production the C_3-C_4 plant was not able to meet its guarantee, and the C_3 head product could not be used as mentioned. Consequently the reflux to the stabilizer had to be increased which was able to maintain the purity specifications for marketable C_3 gas. Thus the C_3 plant was kept supplied. The fraction of the total C_3 production resulting from C_3 heads gas amounted to about thirty (30) percent.

OPERATING CONDITIONS

Gasoline	21.5	ton/hr
Vapor pressure at entrance of stabilizer	0.95	atm.
Vapor pressure at exit of stabilizer	0.48	atm.
Liquid top product	1.1	ton/hr

Fig. 25


H2S Removal
Caustic Wash
Stabilizer
Raw Gasoline
Tail Gas containing H2S
H2S Free Gas
Caustic Wash
1st Stage
2d Stage
H2O
Final Wash
Preheater
Exchanger
Reboiler
Finished Gasoline

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[redacted]

VIII. ALKALINE WASH AND STABILIZATION. (Cont'd.)

OPERATING CONDITIONS (Cont'd.)

Reflux ratio	1 - 8
Operating pressure	5 - 7 atm.
Head temperature	45 - 55°
Boiler temperature	150 - 165°
18 atm. steam consumption	0.18 ton/ton inlet against 0.15 ton/ton when based on outlet top C_3gas

ANALYSIS OF LIQUID TOP PRODUCTS

	Mol %
C_2	nil
C_3	10.
iC_4	45.
nC_4	45.
C_5	nil

ANALYSIS OF HEAD GASES

	Mol %
C_1	2.0
C_2	8.0
C_3	28.0
iC_4	28.0
nC_4	25.0
C_5	8.0

IX. HYGAS PROCESSING.

(a) The outlet gases from the hydrogenation are freed from NH_3, CO_2 and H_2S in the Hygas unit. The gases rich in hydrocarbons are processed for gasoline, and the lean gas is sent to the cracking plant and the utility mains. The apparatus consists of an alkazid unit for removal of H_2S or $H_2S + CO_2$, an oil absorption unit for removing higher hydrocarbons, an organic sulfur converter, a NaOH absorber for final removal of H_2S and CO_2, and a gasoline plant for liquifaction and fractionation of the liquid products.

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IX. HYGAS PROCESSING. (Cont'd.)

(b) The outlet gases from the hydrogenation consist of:

(1) Flashed gas from the coal and gasoline chamber effluent product;
(2) Flashed gas from the recycled gas wash;
(3) Flashed gas from the mud of the coal stalls;
(4) Outlet gas from the coal and gasoline stripper distillation;
(5) Outlet gas from the stabilizer;
(6) Low temperature coke oven gas from the residue desulfurization.

(c) The flash from the liquid product is reprocessed; the sludge removal gas and the low temperature coke oven gas are sent to the utility mains or used directly for fuel.

(d) The liquid product and the absorption oil from the high pressure process are degassified by a multi-stage pressure breakdown, and then separated into rich and lean fractions. The individual steps are:

(1) Flashing to 30 - 40 atmospheres: coal and gasoline and washed gas;
(2) Flashing to about 0.1 atmospheres: coal and gasoline and washed lean gas;
(3) Heating at atmospheric pressure in the stripper: A and B distillation gas;
(4) Heating under pressure in the stabilizer: Stabilizer gas.

Ammonia is removed from the lean gas by a water wash, H_2S is removed with alkazid, and the gas is sent to the cracking plant or to fuel.

(e) The gasoline rich gas is freed from sulfur with alkazid caustic and further purified together with the pure coal rich gas. The mixture of the two gases treated with NaOH for removal of residual CO_2 and H_2S, and then largely liquified as mixed rich gas in the gasoline plant. The residue gas from the gasoline is sent to the cracking unit.

[redacted]

IX. HYGAS PROCESSING. (Cont'd.)

(f) Ammonia Absorption.

Rich and lean gas must be practically free of ammonia, or else ammonium bicarbonate is formed in the presence of CO_2 and water, which plugs the lines. The outlet power gas can contain only traces of ammonia. The ammonia absorption results partially from condensation in the gas lines and partially from complete washing with process water, where the water is circulated to a predetermined concentration of NH_3. By adding fresh water and drawing off used water the NH_3 in the cycle is kept low. Condensate or process water previously freed from calcium must be used.

(g) Lean Gas.

In the lines so much condensation from the purified lean gas occurs in the absence of an absorber (up to five (5) m^3/hour), that the original NH_3 content of about eight hundred (800) milligrams/m^3 is reduced to about thirty (30) milligrams/m^3. The removal of H_2S follows by means of a wash with D, K caustic (principally dimethyl and amino proprionic acid) at fifteen (15) atmospheres pressure. The H_2S content of the new gas is about ten (10) grams/liter and of the pure gas about one hundred (100) milligrams/m^3. The purified gas is sent to the cracking unit. A part of the lean gas is bled off before the alkazid wash and sent to fuel.

(h) Coal Stall Rich Gas.

The coal rich gas consists of the gases from the coal stripper, the absorption oil, and the A-distillation rich gas. The coal stripping rich gas is reduced in NH_3 content from forty (40) grams/m^3 to thirty (30) milligrams/m^3 by washing with process water in two thorough steps. The absorption oil rich gas is similarly treated and the NH_3 reduced from two hundred (200) milligrams/m^3 to forty (40) milligrams/m^3. After the NH_3 absorption these two (2) gases are combined with the NH_3 free A-distillation gas and the mixture purified. The coal stall rich gas passes through a three thousand (3,000) m^3 gasometer and is compressed in one stage to five (5) atmospheres. The condensation from the compressed cooled gas is added to the raw gasoline. The compressed gas is carefully washed twice with alkazid caustic (principally ethyl amino proprionic acid) in order to remove

[redacted]

CO_2 and H_2S. The raw gas contains about forty (40) grams/m^3 H_2S and about two hundred eighty (280) grams/m^3 CO_2 which are reduced to about two hundred (200) milligrams/m^3 and one (1) gram/m^3 respectively. The gas is finally given a wash with middle oil or diesel oil to remove heavy hydrocarbons so that they will not cake in the sulfur conversion over iron oxide catalyst at three hundred (300) to four hundred (400) degrees centigrade. Oil absorption and organic sulfur conversion which also operates at five (5) atmospheres have been shown to be unnecessary. After the organic sulfur purification the gas is reduced to 0.3 atmospheres and after purification of the gasoline rich gas is sent to the NaOH absorber.

(i) Gasoline Stall Rich Gas.

The gasoline rich gas consists of the flash from the liquid product of the primary hydrogenation, the gasoline chamber, and the B-distillation gas. The stabilizer gas is pure and is sent directly to the inlet of the power gas unit. The flash gas from the primary hydrogenation contains about thirty (30) grams/m^3 of NH_3 and must be processed in a packed absorber with process water to reduce this content to about thirty (30) milligrams/m^3. The gas from the gasoline chamber is ammonia free. The two gases from the B-distillation gas are washed with water after the NH_3 removal. The gasoline rich gas passes through a two thousand (2,000) m^3 gasometer and finally after compression to 0.4 atmospheres by a turbo-blower goes to an alkazid wash. The condensate from the compression is added to the raw gasoline in a bell-bottomed absorber; the H_2S is removed with alkazid Dik-caustic. The H_2S is reduced from about forty (40) grams/m^3 to about three hundred (300) milligrams/m^3. The gasoline rich gas and coal rich gas are then purified together in an NaOH absorber, removing the last traces of H_2S and CO_2, after which it is sent to the power gas plant. The H_2S content of the mixed rich gas is 0.0 milligrams/m^3.

(j) Alkazid Plant. (Fig. 26)

The so-called alkazid caustic has the property of almost completely absorbing H_2S or $H_2S + CO_2$ at twenty (20) degrees to forty (40) degrees centigrade, and of releasing it at about

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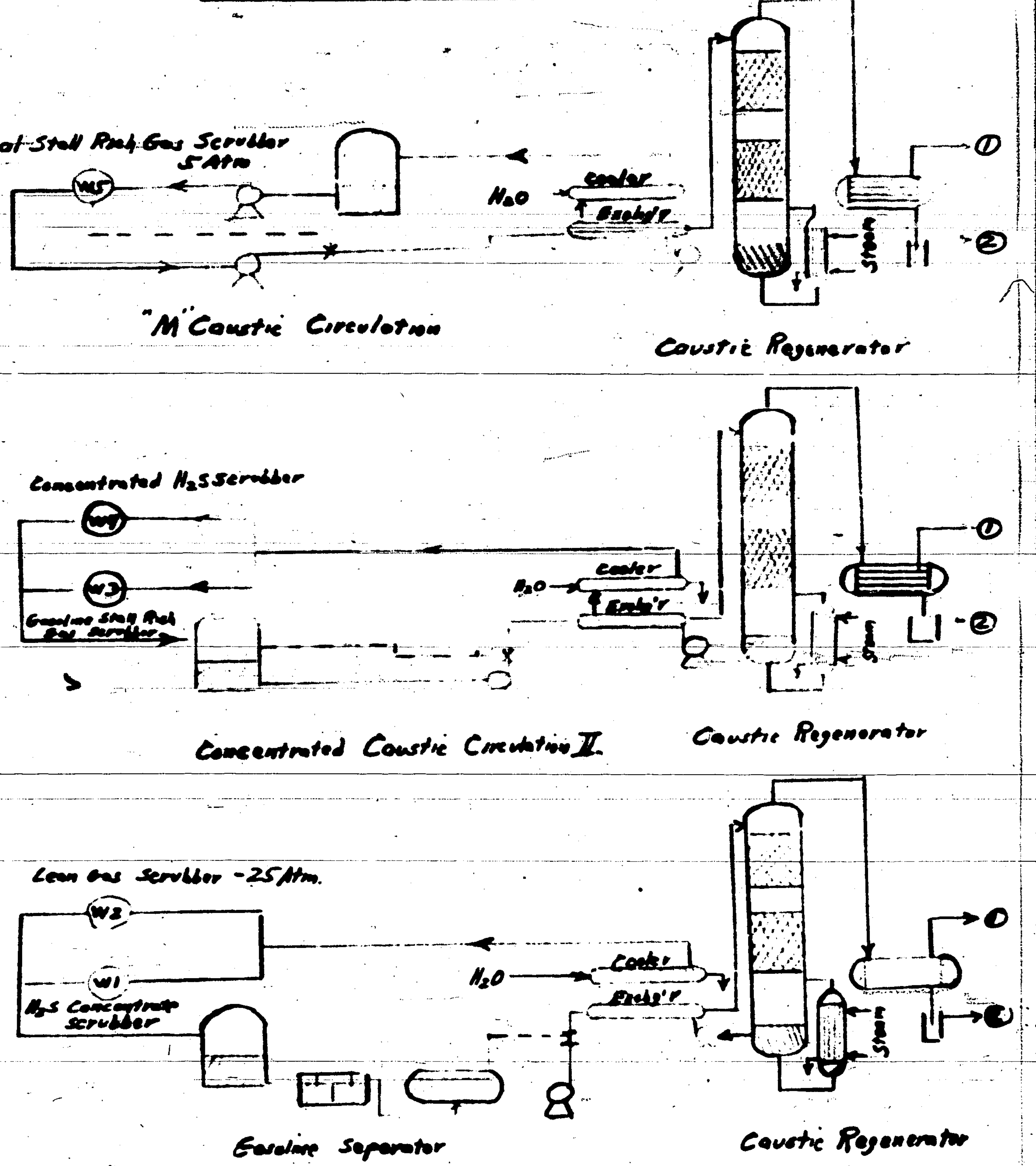
FIG. 26

Flow Sheet of Alkozid Unit



① = Gas containing H_2S
② = Condensate " "

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one hundred degrees centigrade. The apparatus consists of an absorber, a regenerating column, coolers, heat exchangers and pumps. The lean gas, the gas from outlet water recovery, and the gasoline-rich gas are washed in two (2) bell-bottom absorbers with D.K.-caustic (principally dimethyl amino acetic acid) the co-rich gas with M-caustic (principally methyl amino propri-onic acid) in two (2) packed columns. The saturated caustic goes to intermediate storage in the Dik-caustic system and from there is pumped through a heat exchanger counter current to the hot regenerated caustic from the regenerator column. In the lean gas washing system there is a gasoline separator between the heat exchanger and the tank to remove condensate up to seventy (70) degrees centigrade. The column is filled with rings and the kettle is fed with direct and indirect steam. The steam outlet connection leads to the side of the circulating kettle, which contains the tube bundle for indirect heating. The division between direct and indirect steam is determined by the specific gravity of the caustics, which must be controlled to prevent corrosion. After degasification to an economic degree, where the gas is cooled in a water cooler attached to the column, the hot caustic is pumped from the kettle through a heat exchanger counter current to the cold saturated caustic, through a water cooler, back to the absorber. For the twenty-five (25) atmosphere absorber there is a booster pump between the cooler and the absorber. In the coal rich gas system there is an intermediate storage tank for saturated caustic like the one for regenerated caustic after the cooler. From this tank the caustic is pumped to the five (5) atmosphere absorber.

(k) Production of High Purity Hydrogen Sulfide.

The gas from the stripper column of the lean gas absorber system contains about fifty (50) percent H_2S and fifty (50) percent CO_2, which results from the large CO_2 excess in the lean gas and which will be absorbed in caustic. The gas will be washed once with DiK-caustic in a bell-bottomed absorber to concentrate the H_2S. The saturated caustic from this wash will be regenerated together with the CO_2 free saturated caustic from the gasoline rich gas absorption. The stripper gas from this caustic cycle contains about ninety (90) percent H_2S. The stripper gas from the coal rich gas M-caustic contains about ten (10) percent H_2S

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IX. HYGAS PROCESSING. (k)(Cont'd.)

and ninety (90) percent CO_2. The ratio of H_2S and CO_2 approximately corresponds to that of the lean gas and therefore will be concentrated in a washer, and the caustic will be regenerated with the caustic from the lean gas system. In this concentrating washer the exit gas from enriching washer (20% H_2S), the outlet gas from the waste water recovery (5-8% H_2S), and the outlet gas from the middle oil desulfurization unit (10% H_2S) are washed for the production of high purity H_2S.

(l) Report of Operation of the Alkazid Unit.

The alkazid unit was put into operation in June 1943. No basic difficulties have been experienced. Wet aluminum corrosion occurred only on heating tubes of a column, and appears as pitting. Iron corrosion occurred to a greater extent on the water side of numerous coolers. Strong benzin condensation in the lean gas washer caused considerable trouble by pump abrasion and by carry over in the caustic to the intermediate storage and the columns. A benzin separator remedied this in normal operation. By degassing the caustic in the columns, a small but continual caustic loss occurred. A lower caustic inlet temperature and a layer of tower packing above the inlet corrected this condition. Increased oxygen content reduced the effectiveness of the M-caustic, and regeneration with potash made no improvement. The efficiency of the caustic cooler and H_2S condensers was often impaired by water side fouling.

(m) Power Gas Plant.

The power gas plant serves to condense the liquifiable gases and fractionates them into C_3, C_4 and gasoline fractions. The gas mixture containing about fifteen (15) percent CH_4, fifteen (15) percent C_2, H6, twenty-four (24) percent C_3H_8, twenty-eight (28) percent C_4H_{10}, nine (9) percent C_5 and heavier and ten (10) percent residue gas (H_2O, CO, N_2) is compressed to twenty-five (25) atmospheres in a two stage machine, and the entrained lube oil is then removed with an oil wash. The oil wash consists of a small packed absorber over which liquid product is trickled. The lube oil is knocked down to the kettle. The gas from the oil wash is cooled to about sixty (60) degrees with water. Gas and condensate together are sprayed into column 1. In column 1 the

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IX. HYGAS PROCESSING. (m)(Cont'd.)

residue gas, CH_4, C_2, H_6, C_3H_8 goes overhead and the C_4 and heavier fraction is taken from the kettle. The kettle product is fed to column 3 through a heat exchanger, where C_4H_{10} is removed overhead and the remainder from the kettle. This column operates at seven (7) atmospheres, and the pressure is controlled by the water flow to the C_4H_{10} condenser. Part of the condensate is used to reflux column 3 and part is removed as product through a cooler and a displacement meter to intermediate storage. The kettle product is passed through a cooler, a displacement meter, and is added to raw gasoline. The heads from column 1 are partially condensed and are used to reflux the column. The residue gas goes through a NH_3-water wash, a silica gel drier, and an NH_3 refrigerated cooler at 10°C. The condensate and residue gas are sent to a separator, purified, and sprayed into column 2. In this column the residue gas (H_2O, CO, CH_4, C_2H_6) goes overhead and the propane is taken from the kettle. Reflux is obtained with NH_3 refrigeration at -35° and is fed to the top of the column. The propane is removed as product through a cooler and displacement meter to an intermediate tank. The residue gas is expanded to ten (10) atmospheres in the first stage, to five (5) atmospheres in the second stage, and is sent to the cracking plant as power gas residue. Between the first and second stages the gas is sent over a gas heater and finally used for drying the saturated silica gel.

(n) Operation of the Compressor Building.

Because of operating errors and particularly because of flaws in construction a great number of difficulties occurred. By the end of 1942 the coal rich gas compressors were generally satisfactory during their operating time. Both machines were destroyed near the end of 1943 due to the failure of the piston rods, which was traced to faulty construction. Two-stage power gas compressors were substituted as alternates for the Borsig compressors. These had various disadvantages, particularly too weak frames. One machine was strengthened. The refrigerating machine was poorly erected in some respects. Valve plate breakage caused by faulty material was frequent in all machines. One machine sustained damage by failure of lubrication. The rotary blower for Bi-rich gas was often under repair because of the rotor.

(o) Report of Operation of the Power Gas plant.

The power gas plant went into operation in January and April of 1943 without difficulty and has operated without trouble.

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IX. HYGAS PROCESSING. (o)(Cont'd.)

The performance guarantees were in no manner met, particularly the A-plant. Principal faults were poor separation in the columns and a poor performance of the ammonia dephlegmator and ammonia precooler. This was partially remedied by increasing the length of column B-1 and exchanging the dephlegmator of column B-2 for two (2) unit coolers, and providing separators and pumps. The Uhde Company of Dortmunde had guaranteed, and to make good it was necessary to build a now plant.

OPERATING RESULTS

Yield				
	Nat-gasoline		98.0 %	
	Butane		93.0 %	
	Propane		81.0 %	
	? (illegible) ?			
In nat-gasoline		C_4	5.0 %	
		C_5 and higher	95.0 %	
In butane		C_3	5.0 %	(wt.)
	iso	C_4	61.0 %	"
	n	C_4	33.5 %	"
		C_5 and higher	0.5 %	"
In propane		C_2	15.0 %	"
		C_3	12.5 %	"
		C_4	7.5 %	"
Power gas		C_2	4.2 %	"
		C_3	30.0 %	"
		C_4	65.4 %	"
		C_5 and higher	0.4 %	"
Vapor pressure				
	+ 40°		10.2	atm.
	- 15°		1.3	atm.
Hourly quantities				
	Inlet mixed rich gas		4,450.	m^3/hr
	Nat. gasoline		0.9	tons/hr
	Power butane		2.2	tons/hr
	Power propane		1.1	tons/hr
	Residue gas		1,500.	m^3/hr
	Mixed rich gas to cracking plant		550.	m^3/hr

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X. SULFUR PROBLEM.

(a) In order to remove asphalts in a satisfactory manner, a definite partial pressure of H_2S is necessary in the recycle gas stream to the coal stalls. Due to the low sulfur content of the raw coal (0.5 to 0.8 percent) and the diluent oil (0.3 percent), and also due to the heavy sulfur requirement of the iron oxide catalyst, the coal paste at Wesseling has elementary sulfur injected into it amounting to 1.25 to 1.5 percent of solids in the coal paste.

(b) After the conversion in the stall, the sulfur becomes bound chemically with: the iron of the catalyst, the tail gas, the discharge water of the effluent, the distillation and ammonia wash, and the tail gas. It is also to be found in the caustic wash of the rich gas and gasoline. The sulfur in the coking residue and the caustic is lost, while that in the discharge water and tail gas is recovered to a large extent. The discharge water is freed from H_2S by gasification with CO_2.

(c) In the alkazid unit, the tail gas feed for the gas cracking unit and the rich gas for the fuel gas unit are concentrated and stripped of H_2S. The concentrated H_2S (approximately ninety (90) percent) is used for sulfurizing the feed to the gasoline stalls, hence the sulfur soluble in the feed eventually turns up in the crude gasoline, in the gasoline stall rich gas, and in the discharge water. The non-absorbed sulfur is taken back into the alkazid unit. The sulfur losses can be summed up as follows:

(1) Coking residue;
(2) In the purified gas in the alkazid unit due to incomplete washing;
(3) The discharge water from the gasification;
(4) The caustic wash from the raw gasoline.

(d) In the alkazid unit, either H_2S or $H_2S + CO_2$ are absorbed alkazid caustic at room temperature. Upon reheating, the H_2S is stripped out and the caustic used over again. Two kinds of caustic are used, concentrated caustic and M-caustic. The former consists of N-dimethyl amino potassium acetate ($(CH_3)_2-N-CH_2-COOK$) and this is highly selective in absorbing H_2S in contrast to CO_2.

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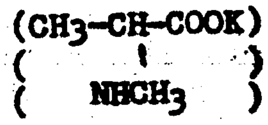
X. SULFUR PROBLEM. (d)(Cont'd.)

M-caustic is principally N-methyl α amino potassium propionate



$$\left(\begin{array}{c} CH_3\text{-}CH\text{-}COOK \\ | \\ NHCH_3 \end{array}\right)$$

and this is equally effective for H_2S and CO_2. The removal and concentration of H_2S occurs as follows (Fig. 26). The lean gas is washed in scrubber W2 with concentrated caustic, removing the H_2S as opposed to CO_2. The absorption in the caustic is determined by titration against H_2SO_4 and the quantity of gas determined. One volume of gas to one volume of caustic is known as "One Point Absorption."

(e) The saturated caustic from scrubbers W2a and W2b is regenerated in columns M1 and M2 by open and coil steam. The relative proportion of the two steam quantities is fixed by the specific gravity of the caustic, which must be kept exact, due to corrosion on one hand and volume contraction on the other.

(f) With regeneration, the H_2S concentration is approximately fifty (50) percent and can be scrubbed within scrubber W4 once again with concentrated caustic. The caustic from scrubber 4 and also from the gasoline stall rich gas washer, W3a and b, are regenerated together, releasing only the H_2S. This concentrate is approximately ninety (90) percent strength and can be used directly for sulfurizing the middle oil.

(g) The gas discharged from scrubber 4 contains approximately twenty (20) percent H_2S. The gas discharged from scrubber W1 goes through the after burning unit in which H_2S is converted into SO_2. The final H_2S content in the SO_2 is very small.

(h) The rich gas from the coal stalls is washed in scrubber W5 with M-caustic which absorbs equally well H_2S and CO_2. The saturated caustic is regenerated in the stripping columns M1 and M2. Due to the high CO_2 content in this gas the H_2S amounts to only fifteen (15) percent and must be concentrated in scrubber W1.

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X. SULFUR PROBLEM. (Cont'd.)

IMPORTANT FACTS ABOUT THE ALKAZID UNIT

H_2S content	g/cu.met	mg/cu.met	Vol/% H_2S	Quantity cu.met/hr
Lean gas raw	8.7			15,000
Lean gas pure		80		
Coal stall rich gas raw	35.			4,000
Coal stall rich gas pure		221		
Gasoline stall rich gas raw	39.			2,400
Gasoline stall rich gas pure		330		
Blower gas	78.			700
Tail gas W1a/b	4.			2,000
Tail gas D1/2			48	800
Tail gas D2/3			91	120
Tail gas M1/2			18	1,000

	Caustic type	Scrubber	Feed Injected cu.met/hr	Recirc. quantity cu./met/hr	Gas co/cc	Steam direct tons/hr	Steam indirect tons/hr	Sp. grav. @ 20° C.
	Concent.	W1	32		16			
Fresh	"	W2	22		23			
caustic	"	W3	16		15			
	"	W4	16		18			
	M	W5	64		—			
	Concent.	D1/2		54	4 - 6	4	3	1,155
Regen.	"	D2/3		32	4 - 6	3,5	2,5	1,155
caustic	M	M1/2		64	7 - 10	4	3	1,175

SULFUR BALANCE

Entrance

Elem. Sulfur	350 tons
S in TK_4	276
S in oils	22
	648 tons

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X. SULFUR PROBLEM. (Cont'd.)

Exit

Coking residue	406 tons
Tail gas from after burner	72
S lost in phenol removal	52
Expansion loss	24
S residue in heating gas	18
S residue in mud gas	17
S residue in tail gas from methane cracker	16
S in NH_3 wash	16
S in exhaust water not recoverable	22
	648 tons
S in 6434 feed	183 tons

XI. RAW AND FINISHED PRODUCTS.

(a) The raw materials used in making the final product are pure lignite, outside oil (tar oils, etc.) and petroleum. Seventy-eight (78) percent of the finished product comes from lignite and the rest from oil. The outside oil is partly used as diluent oil, and partly as feed to the cool stall effluent distillation unit, the boiling range, specific gravity, water and solid content, are fixed. All oils containing either water and more than twenty (20) percent middle oil are passed through the A-distillation unit. The remainder is mixed with diluent oil.

(b) Variations in quality of final product can be made in operational changes: reactor throughput, reactor temperature, coal paste injection, amount of catalyst and boiling range of middle and heavy oil.

(c) Properties of Pure Lignite Charge Stock.

The pure Rheinish lignite is easily decomposed chemically. However, the resulting oils are difficult to hydrogenate, requiring the high pressure seven hundred (700) atmosphere operation in the sump phase. This is apparently due to the high car-

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bon content in the lignite. The lignite seems to be mixed with decayed stumps and plants. The latter did not seriously affect operation after properly sifting the raw coal.

ANALYSIS OF THE LIGNITE

Water content	7.5 %
Ash content	6.0 %
Tar content (Fischer test)	8.0 %

ULTIMATE ANALYSIS		ASH ANALYSIS	
C	67.76 %	SiO_2	2.9 %
H_2	5.10 %	Fe_2O_3	22.5 %
O_2	25.30 %	Al_2O_3	4.1 %
N_2	1.10 %	CaO	45.1 %
S	0.75 %	MgO	4.9 %
		SO_3	20.1 %

The underlined values play an important part in the process.

(d) CaO Content.

This is converted into $CaCO_3$ by the chemical decomposition of the lignite. This results in salt crust or "caviar" formation leading to serious operating difficulties.

(e) O_2 Content.

Due to its high value, twenty-five (25) percent, it uses up large amounts of hydrogen, two-thirds of it being converted into water in the process.

(f) Sulfur Content.

It amounts to only 0.75 percent which is relatively low compared to lignites from middle Germany. Extra sulfur has to be injected to meet the sulfur content requirements of the catalysts.

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XI. RAW AND FINISHED PRODUCTS. (Cont'd.)

(g) Outside Oil.

This consisted of shale oil, petroleum residue, hard coal tars, and lignite tars of aliphatic, naphthenic and aromatic character. Variations in the same produced different products. However, these variations were hardly felt in the final product due to the large part of hydrogenated lignite effluent used and the proper operation of the gas phase catalyst. By useing too much road asphalt (over five (5) percent) as diluent oil, a highly asphaltic product resulted. Best results from hard coal tar occurred when the resulting middle oil end point was reduced from three hundred fifty (350) degrees to three hundred thirty (330) degrees centigrade.

(h) The final products were:

(1) Ordinary Diesel oil;
(2) Marine Diesel oil;
(3) Cold service Diesel oil for winter campaigns in Russia;
(4) Crude gasoline for the DHD plant of I. G. at Ludwigshaven - prehydrogenation only;
(5) Ordinary aviation gasoline;
(6) Ordinary C_3 - C_4 gas for automobiles;
(7) Special aviation C_3 - C_4 gas for use in aviation engines.

INSPECTIONS OF PRODUCTS

Ordinary Diesel oil	
Sp.gr. @ 15° C	0.8 - 0.885
Viscosity - Engler @ 20° C	1.1 - 2.6
Pour point	
Summer not over	- 10° C
Winter not over	- 20° C
Flash point over	21° C
Cetane No. - not under	35

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INSPECTIONS OF PRODUCTS (Cont'd.)

(2) Marine diesel oil	
Sp. gr. @ 15° C	0.840 - 0.870
Viscosity - Engler @ 20° C	1.2 - 2.6
Cloud point	± 0° C
Flash point not under	± 55° C
Cetane No. - not under	35
(3) Diesel oil (Russian quality)	
Viscosity, Engler @ 20° C - not under	1.1
Cloud point, under	- 30° C
Pour point, under	- 35° C
Flash point, over	21° C
(4) Gasoline for D.H.D. unit	
F.B.P.	165° C
(5) Ordinary aviation gasoline	
Sp. gr. @ 15° C	0.725 - 0.750
I.B.P. not under	40° C
10 % min. vol. 10	70° C
50 % " " 10	100° C
90 %	145° C
F.B.P.	165° C
Max. R.V.P.	0.5 @ 37.8° C
API max.	52° C
Octane No.	
Motor method - clear	- 70
+ 0.09 vol. T.E.L.	87
(6) Normal C_3 - C_4 gas for automobiles	
Vapor pressure	
1.4 - 31.8 - minimum	0.7 atm. @ 0 °C
- maximum	16.7 atm. @ 40°C
1.9 - 31.3 - minimum	1.5 atm. @ -15°C
- maximum	16.7 atm. @ +40°C
H_2S - not over	0.2 mg/cu.met.
Organic sulfur - not over	250
Elemental sulfur	negative
Mercaptan (Doctor test)	"
NH_3	"

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XI. RAW AND FINISHED PRODUCTS. (Cont'd.)

(7) Aviation C_3 - C_4 gas for aviation motors

C_4	70 - 80 %.
C_5	20 - 30 %
Max. H_2 content	5 %

Vapor pressure not over 2 atm. @ 0° C
Other specs. as per normal power gas requirements

All the above specs. were met. Only the winter quality Russian Diesel oil failed to meet its cloud point test.

XII. STEELS IN THE HYDROGENATION UNIT.

(a) The great technical development of the high pressure hydrogenation process would be impossible without the existence of suitable steels for the high pressure apparatus. The steels must be safe in regards to the high pressure requirements, but in addition the apparatus must not be too heavy and unmanagable. It must in addition be resistant against H_2 and the corrosive influx of the products of hydrogenation, especially of the contained H_2S. In zones of high temperatures, they must be able to meet the special properties.

(b) These requirements are met only by alloy steels, which have been given a special treatment. Especially suitable are the V_2A steels, which are mixtures containing over twenty-five (25) percent Ni and Cr. The faults of these alloy steels forced the development of other steels with lower impurities. It is to the credit of the I. G. Farbenindustrie that they produced such special steels, having strength meeting the requirements of the high pressure hydrogenation with a metal of lower alloy content. Through a specific heat treatment, the steels are given a structure, which gives them great mechanical strength and high resistance against chemical attack. The treatment consists in prolonging the heating in the austenitic region, quenching and short tempering. The heating and the quenching make the steels hard, but brittle. Through the tempering the hardness and brittleness again will be partially raised. The steels receive by this means a sufficient toughness for working safety.

(c) The added tabular groupings give an insight into the hitherto developed steels and their distribution for individual

HIGH PRESSURE 325 Atm

Applications of the Working Materials

Temp. Stage	Operating Temp. C	Nominal Range	Applicable Material for						
			Tubes	Formed Pieces	Blind Flanges	Screw Flanges	Bolts	Nuts	Lenses
I	0-200	6-16 16-160 200	St.45.29 St.35.29	S2	S2	S1	S3 K4Ms K1,K1MS	S3	S2
II Now 200 - 400°C	200-400	6-200	N8A	N8A	N8A	K4MS,K1, K1MS	K4MS,K1, K1V,K1CV K1MS	S3	N5A
II Previously 200-480°C	200-480	6-200	N8	N8	N8	K3,K3CV	K3,K3CV	S3	N5
III Now 400-510°C	400-510	6-200	N9	N9	N9	K3CV K3	K3CV K3	S3	N5A N5
III Previously 480-510°C	480-510	6-45 58-200	N8 N8V,N10	N8 N8V,N10	N8 N8V,N10	K3,K3CV K3,K3CV, K5,K5V	K3,K3CV K5,K5V	S3 K1MS,K3 K1V,K1CV	N8 N8A

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HIGH PRESSURE 700 Atm

Applications of the Working Materials

Temp. Stage	Operating Temp.°C	Nominal Range	Applicable Working Materials for						
			Tubes	Formed Pieces	Blind Flanges	Screw Flanges	Bolts	Nuts	Lenses
		6-16			S3	S1	S3		S2
		24-160					K4MS	S3	
I	0-200	except 135	K2M	S3	K4MS				
				S3	K1	K1	K4MS	S3,K1,	S3
		135	K2		K1MS	K1MS	K6	K1V,K1CV	
		6-45				K4MS,K1	K4MS,K1		
						K1MS	K1V,K1MS	S3	N5A
II Now 200-400°C	200-400	58-160 except 135	N8A	N8A	N8A	K4MS,K1	K4MS,K1,K1V		
						K1,K3	K4MS	S3,K1,K1V	N8
		135				K3CV	K6	K1CV	N8A
II Previously 200-420°C	200-420	6-160	N8	N8	N8	K3,K3CV	K3,K3CV	S3	
III		6-16	N9			K3CV	K3CV	S3	
Now	400-510	24-45	N10,N8V	N9,N8V	N9,N8V	K5,K5V	K5,K5V	K3,K1V K1CV	N5A
400-510°C		58-160	N9	N8V	N8V	K7	K7	K1MS	N8
III						K7	K7	K1MS	N8A
Previously 420-510°C	420-510	6-160	N10W	N10	N10	K5,K5V	K5,K5V	K3,K1CV	

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XII. STEELS IN THE HYDROGENATION UNIT. (c)(Cont'd.)

working purposes. An attached formulation shows the timely development of the steels, their composition, strength properties, the methods of their testing, as well as the art of the heat treatment. First named are the steels, which would be employed for the cold parts of the apparatus of the original two hundred (200) atmosphere working pressure apparatus. These are ordinary carbon steels, in part with a low Cr addition. For the hot parts of the apparatus were developed (see in part) the N1 to N8 steels. N1 is the standard steel for the high pressure vessels. For all other purposes, N8 will be employed especially for piping at high temperatures. The principal characteristic of these steels is their Cr content which usually amounted to three (3) percent. The remaining elements are Mo and V, which are used in the amount of 0.5 percent. These steels have the advantage of needing only a local tempering after welding, while the later developed steels must be heated in a furnace.

(d) After the introduction of the higher pressures of seven-hundred atmospheres, the strength qualities of S-steels no longer sufficed for cold piping, one bought steels, which had a Brinell hardness of seventy (70) to eighty (80) instead of the hitherto fifty (50) and sixty (60). Such steels would be made under the designation K-steels. They differed from the S-steels through a Cr content of about one (1) percent and a lower Mo composition.

(e) For the hot seven hundred (700) atmosphere apparatus the N8A to N10 and some K-steels were used. Of these K5 and K7 are outstanding. All of these steels contain V. Another characteristic is the somewhat higher C content of the K-steels.

(f) The best developed steel for high temperatures is the N10 steel with a creep strength of sixteen (16) at five hundred fifty (550) degrees centigrade. It is employed for the most stressed tube piping and bends of the seven hundred (700) atmosphere apparatus, especially for the hot preheater tubes.

(g) The lack of tungsten and molybdenum forced the preparation of substitute steels, such as the N8A, N8V, N9, K1CV, K3CV steels. In these, the contents of V and Mn was increased.

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XII. STEELS IN THE HYDROGENATION UNIT. (Cont'd.)

(h) When chrome also became scarce, Si was added. Thus originated the seven hundred (700) atmosphere steels K1MS and K4MS. All of the last named steels could not be used under normal conditions. The added summary about the abailability of the material for the separate apparatus of high pressures are presented to help installation men. The adjacent table "Material summary for high pressure 325 and 700 atmospheres" gives the classification indicating the steels, that would be available for the duration of the war.

THE CONSTRUCTION STEELS IN THE WESSELING HIGH PRESSURE WORKS

For 325 atmospheres	
High pressure hollow vessels	N1
Cold tubes	S2
Hot tubes	N8, N8A, N10
Gas preheater	N8, N8V
Electric preheater	N8, N10
Formed pieces	S2, N8, N8A, N9, N10
Lenses	S2, N5, N5A, N8
Flanges	S1, K1, K3, K3CV, K4MS
Bolts	S3, K1, K3, K3MS, K5
For 700 atmospheres	
High pressure hollow vessels	N1
Cold tubes	K2
Hot tubes	N8, N8A, N10
Gas preheaters	N8, N8V, N9, N10
Formed pieces	N8, N8A, N9, N10
Lenses	S3, N5, N5A, N5C, N8
Flanges	K1, K3, K3CV, K5, K4MS
Bolts	S3, K1, K3, K3CV, K4MS, K5, K6, K7

(i) The preceding exposé of the correct application of the steels is a reliable control for average strength values. The minutest detail must be watched, since the improper application of the smallest parts of the apparatus such as bolts and lens packings can cause trouble.

(j) The supervision starts with the analyses. There are two methods available: the quantitative complete analysis; and the rapid, or so-called spot method. The latter consists in a

STEELS FOR HYDROGENATION I.G. QUALITY

~~[illegible]~~

Number	Alloys	Treatment Conditions	% C	Mn	Si	Cr	[illegible]	Mo	V	Strength Kg/mm²	Min yield pointkg/mm² @ °C. 20	300	350	400	Min Elongation %	Notch Toughness mkg/cm²	Min 400	Creep 450	Strength 500	Kg/mm² 550	@ °C *	Heat Treatment Forging °C	Heating °C	Hardening °C	Cooling Medium	Tempering °C
[illegible]	C	Normal	0.25-0.34	0.60-0.80	0.20-0.35					50-60	37				28	6						1080 - 850	700	870	Air	
[illegible]	C	"	0.15-0.25	0.40-0.60	0.20-0.35					40-48	-				26	10						1100 - 880	680	900	"	600 - 680
[illegible]	Cr	"	0.20-0.25	0.50-0.80Max	0.20	0.20-0.50				50-60	30				26	8						1100 - 850	680	850	"	"
[illegible]	C	"	0.18-0.25	1.20-1.50	0.20-0.40					50-60	30				24	6						"	680 - 700	"	"	500 - 550
[illegible]	Cr	"	0.25-0.30	0.25-0.50Max	0.20	0.20-0.50				50-60	30				26	6						1150 - 800	650 - 700	"	"	600 - 680
[illegible]	C	"	"	"	"					50-60	30				24	6						1050 - 800	"	"	"	500 - 550
[illegible]	Cr Mo	Oil Temper	0.20-0.30	0.40-0.60	0.25-0.35	2.50-3.00		0.20-0.25		65-77	45	35			15	6						1100 - 850	700 - 750	900 - 950	"	650 - 700
[illegible]	Cr Mo	Air "	0.12 Max	0.20-0.50	0.20-0.40	"		0.20-0.30		50-60	30				22 lg	maximum						1050 - 850	750	"	"	700 - 750
[illegible]	CrV	" "	"	0.40-0.60	0.25-0.35	"			0.10-0.20	50-65	35				22 lg	10						1100 - 850	"	980 - 1000	"/oil	"
[illegible]	Cr	" "	"	0.30-0.50	"	"				50-60	-				22 lg	maximum						1050 - 850	"	950 - 980	"	"
[illegible]	CrV	" "	0.1[illegible]-0.20	"	"	"			0.10-0.20	50-60/55-65	30-35		20-27		20-17-18	8 6						1100 - 850	"	980 - 1000	"	"
[illegible]	CrMoV.	" "	"	"	"	3.5 Max.		0.35-0.45	0.10-0.20	60-75	35				18	maximum						"	"	950 - 970	Air	680 - 750
[illegible]	CrNiMoV	Oil "	"	0.20-0.40	"	2.50-3.00	0.40-0.60	0.40-0.60	0.05-0.15	65-80	45			35	18	8	35	30	10			1100 - 900	700 - 780	950 - 970	oil	680 - 750
[illegible]	CrV	" "	0.20-0.28	0.60-0.80	"	"			0.25-0.35	70-85	50			33	16	8.1/5 qu	33					"	"	950 - 980	"	680 - 700
[illegible]	CrMoV	Air "	0.18-0.25	0.40-0.60	"	"		0.40-0.60	0.40-0.50	80-95	55-50				16	10.6 - 8.5			17	13	7.5	1050 - 850	"	1000 - 1050	"	680 - 680
[illegible]	CrMoV	" "	0.18-0.24	"	"	3.00-3.50		0.20-0.30	0.45-0.55	80-95 75-90	55-50				16	10.6 - 8.5			17			"	"	1000 - 1030	OilorAir	660 - 680
[illegible]	CrNiMoV	" "	"	0.20-0.40	"	2.50-3.00	0.35-0.45	0.35-0.45	0.70-0.85	80-95 70-85	55-50				14	10.6 - 8.5		25	20	16	11	1100 - 900	700 - 740	1030 - 1050	"	680 - 720
[illegible]	CrNiMoV	" "	"	"	"	"	0.20-0.30	0.25-0.35	0.80-0.90	80-95 70-85	55-50				14	10.6 - 8.5		25	20	16	11	"	"	"	"	680 - 750
[illegible]	Cr	Water "	0.25-0.28	1.00-1.30	0.50-0.80	1.00-130				70-80	50				16 lg 12qu	7 lg 6 qu						1050 - 850	700 - 720	880 - 850	Water	620 - 660
[illegible]	Cr	" "	0.2			1.0			0.2	70-85	50	38	34	30	17	8	28	15	8			"	700 - 750	950	Oil	600 - 650
[illegible]	MnSi	" "	0.25	1.2	1					70-85	50				16	6						"	"	"	"	"
[illegible]	CrMo	Oil-Air "	0.25-0.28	0.60-0.90Max	0.40	0.90-1.10		0.20-0.25		60-70	38				15	maximum						1100 - 850	"	920	OilorAir	"
[illegible]	Cr	" "	"	0.50-0.80	0.20-0.30	0.90-1.10				60-70	38				15	maximum						"	700 - 780	"	"	"
[illegible]	Mo	" "	"	1.3 -1.5	0.4					55-60	40				18	maximum						"	"	"	Oil	600 - 660
[illegible]	CrMo	Water "	0.25-0.30	0.50-0.70	0.20-0.30	1.0 -1.2		0.14-0.20		70-80	50				16	8						"	"	930 - 950	Water	640 - 680
[illegible]	Cr	" "	0.2	0.7		1.2			0.25	70-80	50				17	8	30	30	10			1050 - 850	700 - 720	950	Oil	600 - 650
[illegible]	MnSi	" "	0.35-0.40	1.1 -1.4	1.1 -1.6					80-90	60	45		40	14	6	15	10	5			1100 - 850	680 - 720	850	"	650
[illegible]	CrMoV	" Oil "	0.20-0.25	0.60-0.80	0.25-0.40	1.3 -1.6		0.50-0.60	0.30-0.40	80-95	65	60	55	50	16	8	45	36	36	8		1100 - 900	700 - 750	980 - 1000	" or Wat.	650 - 680
[illegible]	——	" " "	0.4 -0.5			1			0.2	90	60	45			14	6						1050 - 850	700 - 720	950	Oil	600 - 650
[illegible]	CrMo	" " "	0.3	1.0		1.5			1.2	80-95	60				16	8 - 6	40	30	30	10		"	700 - 720	1000-1030	" orAir	660 - 680

* 5 X 10 70 / 25 - 35 loaded hours.

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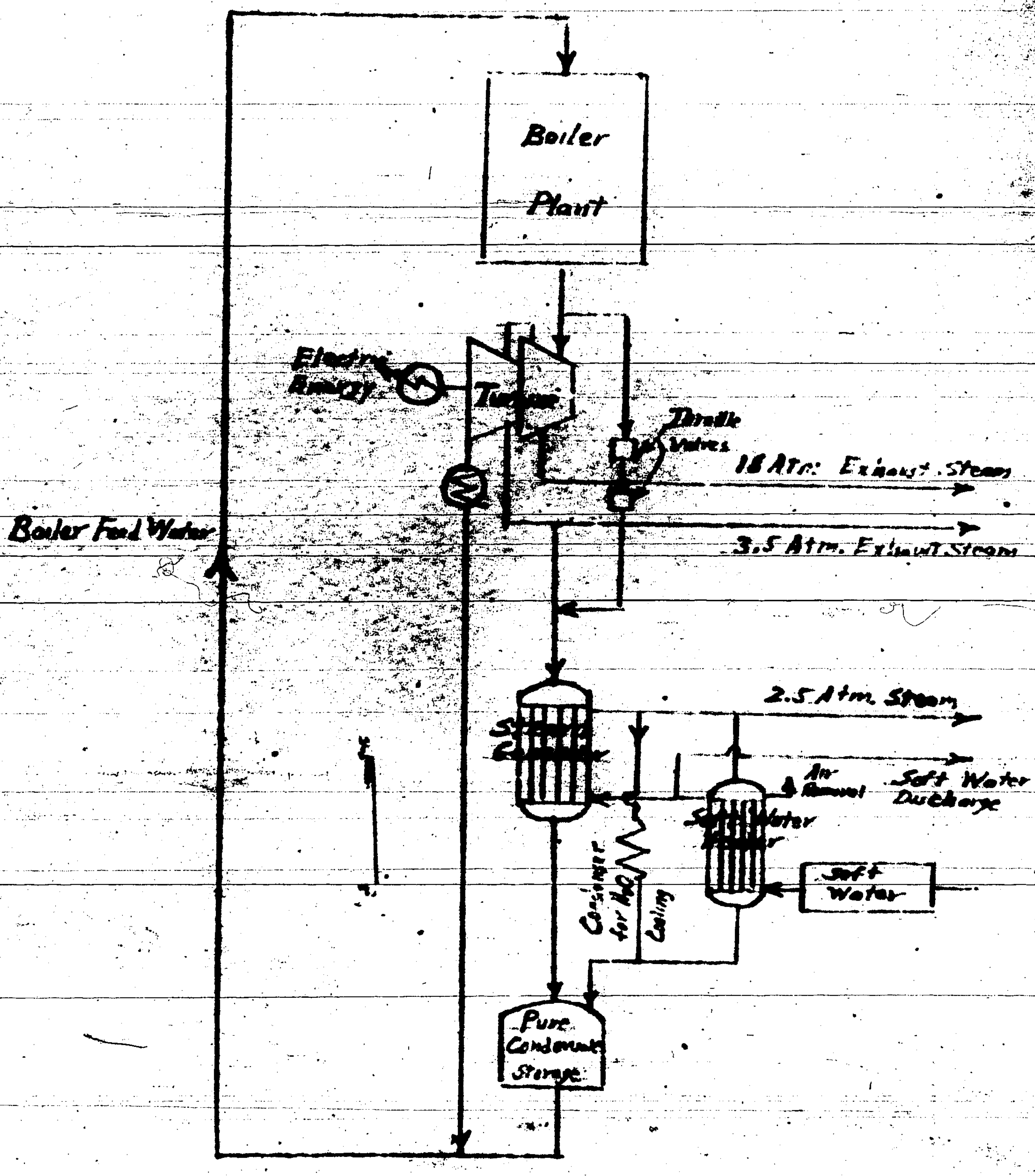
FIG. 21



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XII. STEELS IN THE HYDROGENATION UNIT. (Cont'd.)

moistening of the piece under observation with H_2SO_4, HNO_3, or HCl, and observing the formation of colored spots. In conclusion, all installed apparatus was tested first by the quantitive method and second by the spot method.

(k) Another point of interest is the characteristic of the materials. All larger pieces of apparatus, formed and tube pieces, are marked with stamps, showing the type, the current application, and tests used to show the correct application and testing. With smaller parts, as lense packing, bolts, etc., the material is recognized through grain or similar ways.

(l) The supervision of the correct installation of single pieces of working apparatus is followed colsely by outlines and sketches, on which the technical material data of each construction part is recorded. The lists would be changed after each repair.

(m) It should be stressed that the nearly four (4) years of plant operation not a single working stoppage occurred through material failure or incorrect material application.

C. UTILITY PROCESSES.

I. THE POWER PLANT.

(a) The power plant supplies the factory with steam, power, soft water, amd condensate (Fig. 27). The maximum demands of each of the above quantities is as follows:

(1) Electric energy - 80,000 kilowatt;
(2) Demand of 18 atmospheres steam - 25 tons per hour;
(3) Demand of 3.5 atmospheres steam - 30 tons per hour;
(4) Demand of 2.5 atmospheres steam - 180 tons per hour;
(5) Feed water at 185° C - 50 tons per hour;
(6) Pure condensate 50 - 80° C - 25 tons per hour.

(b) From the above steam quantities, one hundred (100) tons per hour of condensate are returned to the power plant.

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I. THE POWER PLANT. (Cont'd.)

(c) The power plant contains the following units:

(1) Boiler house with coal conveyors and preparation;
(2) Turbo-generators, low pressure steam generator, water purification and pump unit;
(3) Electric control station.

(d) In the boiler house high pressure steam at seventy (70) atmospheres pressure is produced. This is run through turbines, producing electric energy in three (3) stages: at eighteen (18), 3.5, and o.4 atmospheres. The largest quantity is expanded to 3.5 atmospheres whence it goes to an exchanger-generator. By indirect exchange the 3.5 atmosphere steam in contact with 2.5 atmosphere soft water converts the latter into the steam. In this way the total condensate from the turbines is saved for boiler use and is not contaminated with other water streams. The loss and make up of other steam takes place in distillation unit.

(e) The 2.5 atmosphere steam is made from soft water which is made from treated plant water. This is done by decarbonization through milk of lime, Permutit softener, and a heating of above one hundred ten (110) degrees centigrade in order to remove the dissolved oxygen.

(f) In order to care for variations in electric load the turbines were equipped with condensers which allow for increasing the power from the turbines with the same boiler capacity.

(g) The boiler house (Fig. 28) is equipped with five (5) boilers, each capable of producing sixty-four (64) to eighty (80) tons of steam per hour at eighty (80) atmospheres and five hundred (500) degrees centigrade. Four (4) more boilers were almost completed. The boilers are of the flash type (one drum) with integral feed water heater and steam superheater. They also have air preheaters and pulverized coal burners. The temperatures are controlled by Askania regulators, which inject condensate into the superheated steam flow to maintain five hundred (500) degrees centigrade. Boiler feed water is fed through two (2) types of pumps, electric or steam turbine driven. In order to remove scale forming components, a constant blow down of two (2) percent is maintained.

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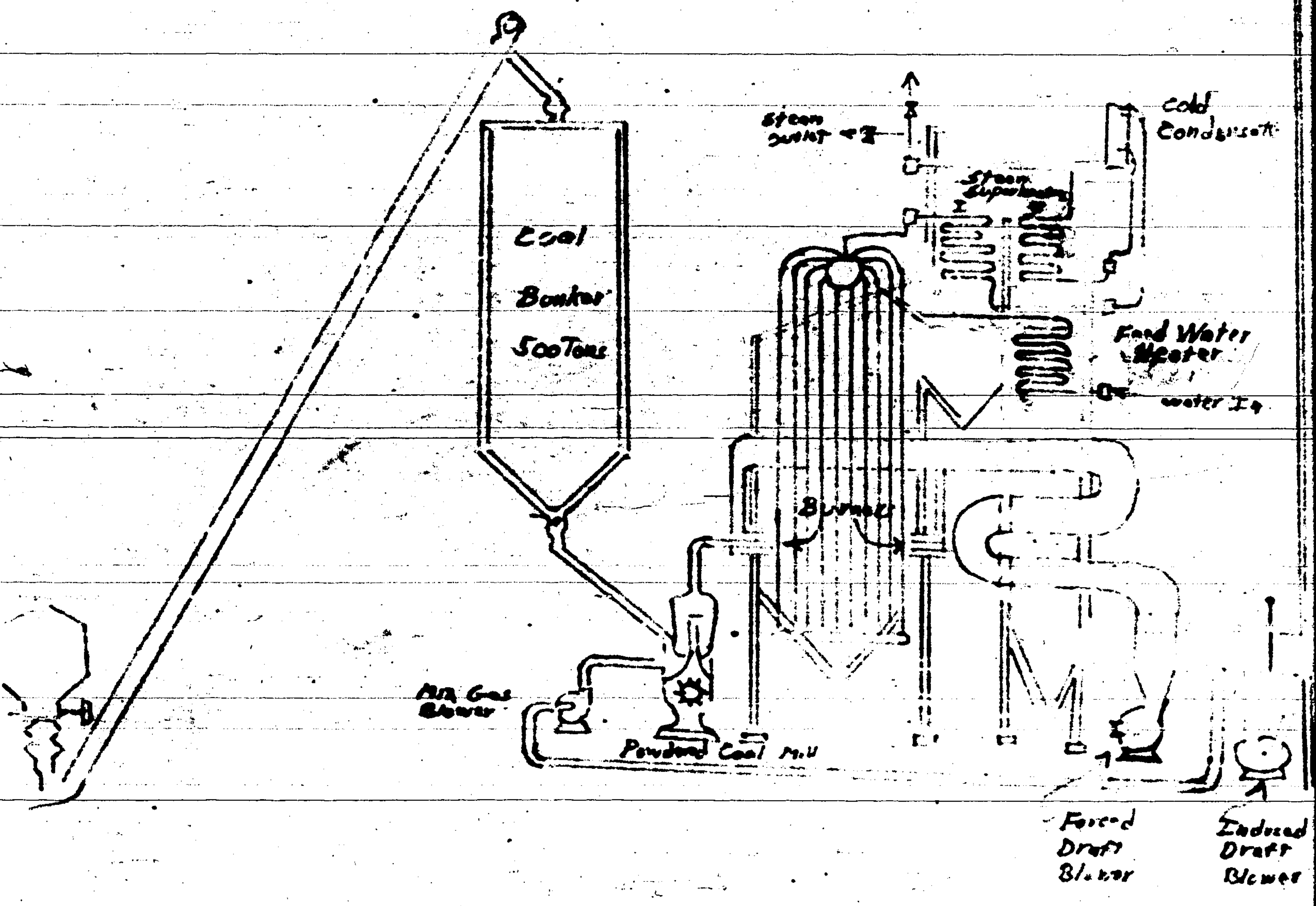
FIG. 28

Boiler House



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I. THE POWER PLANT. (Cont'd.)

(h) The fuel is dried lignite having fifteen (15) percent water content. Also, provision is on hand to use briquette fines and semi-coke dust from the gas plant, as well as excess tail gas from the hydrogenation unit. The coal is transported in special railway cars, in an atmosphere of CO_2. Each boiler is equipped with five (5) pulverizing mills. The combustion gases are removed from the boilers at one hundred eighty (180) to two hundred (200) degrees centigrade through a smoke stack one hundred (100) meters high whose natural draft is augmented by an induced draft fan. The expansion of the boiler house called for a second stack. The ashes are removed from the combustion chamber by a water slurry and pumped into a catch basin.

(i) The original plan called for four (4) steam turbines with condensers. Later two (2) back pressure machines were installed. The turbines discharged ninety-five (95) tons per hour of exhaust, of which thirty-two (32) tons per hour passes through the condensers. In straight condensing operation, a maximum of eight thousand (8,000) kilowatts can be produced. A maximum load requires ninety-five (95) tons per hour of steam which amounts to eighty (80) tons per hour of exhaust at 3.5 atmospheres. Under such operations thirteen thousand (13,000) kilowatts can be produced. For generating one thousand (1,000) kilowatts, twenty (20) tons of steam at eighteen (18) atmospheres or seventeen (17) tons of steam at 3.5 atmospheres or four (4) tons of condensate are required. The generators are so built that when loaded to thirteen thousand (13,000) kilowatts, the resulting power factor is 0.8. The voltage of the generators is six thousand (6,000) volts.

(j) Each turbine has three (3) stages. The first expands from forty (40) to eighteen (18) atmospheres and as such produces the eighteen (18) atmospheres plant steam and the superheated steam for the 2.5 atmosphere steam operation. The temperature of the eighteen (18) atmosphere exhaust is held constant at three hundred (300) degrees centigrade by injecting condensate. The second expansion stage produces 3.5 atmosphere steam which also indirectly produces the 2.5 atmosphere steam for the generator. To cool the condensate the compressor cooler water from the gas plant is used. Its temperature is approximately seventy (70) degrees higher than the temperature of the plant water system.

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I. THE POWER PLANT. (Cont'd.)

(k) All turbines are equipped with over speed trips which automatically operate above three thousand (3,000) revolutions per minute.

(l) The boiler house can continue to supply plant steam even if the turbines are not in operation by means of the throttle stations which reduce the boiler pressure to the various plant requirements.

(m) In order to convert the 3.5 atmosphere extraction steam from the turbine to 2.5 atmosphere plant steam, six (6) exchanger-type steam generators are used. Each can produce forty (40) tons per hour of 2.5 atmosphere steam, and by raising the pressure from 3.5 to 4.5 on the high pressure side, the out-put can be raised from forty (40) to fifty-five (55) tons per hour.

(n) The generator is fed with soft water. In order to remove scale formation, approximately three (3) percent of the soft water is blown down constantly. The soft water is stripped of its oxygen before entering its generator by heating to one hundred five (105) degrees centigrade and then further warmed to one hundred thirty (130) degrees. This heating is done by 2.5 atmosphere steam.

(o) The soft water used in making the 2.5 atmosphere steam is made from plant water which passes through the calcium softener, Permutit unit and de-aerator (Fig. 29).

(p) The softening is done by adding milk of lime in the so-called agitation reactor which is filled with small particles of marble. The plant water is quickly mixed with calcium hydroxide which combines with the total CO_2 content and converts the calcium bicarbonate to calcium carbonate. The result calcium carbonate settles out on the marble balls in solid form. When the marble particles become too large they are renewed.

(q) After leaving the agitation reactor the water passes through a Kies filter in which the large particles are removed, and enters the Permutit filter. This is filled with a zeolite which works by a standard well known process. Finally to remove traces of calcium carbonate, Na_3PO_4 is added. The water is then

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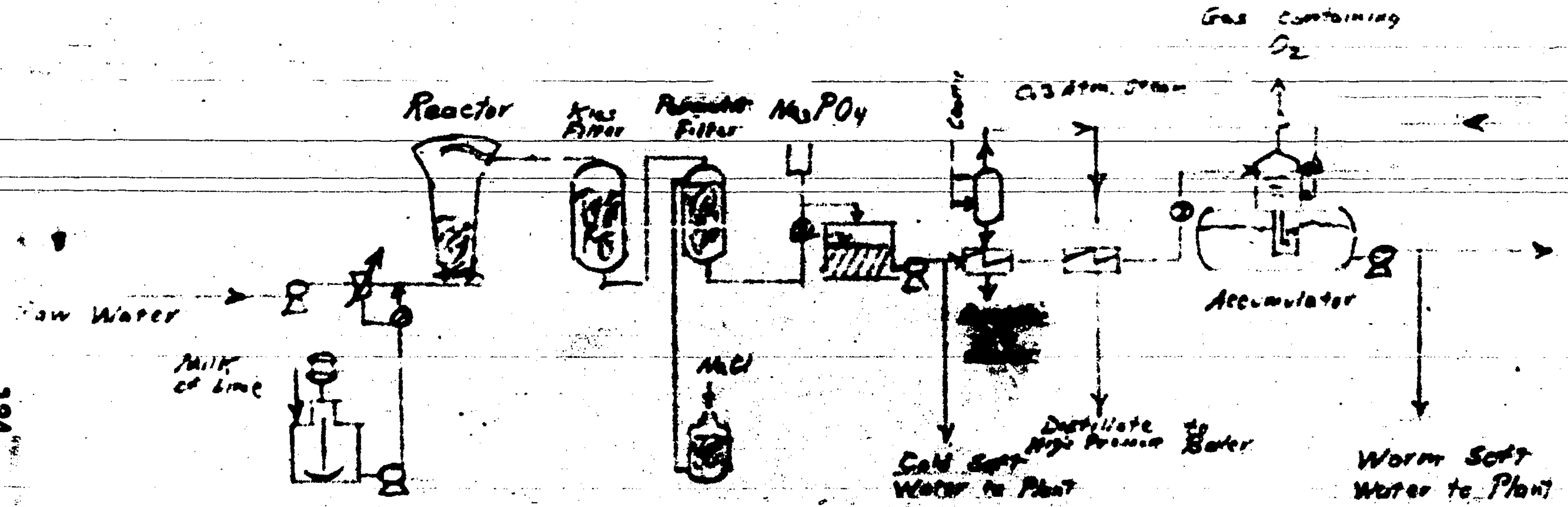
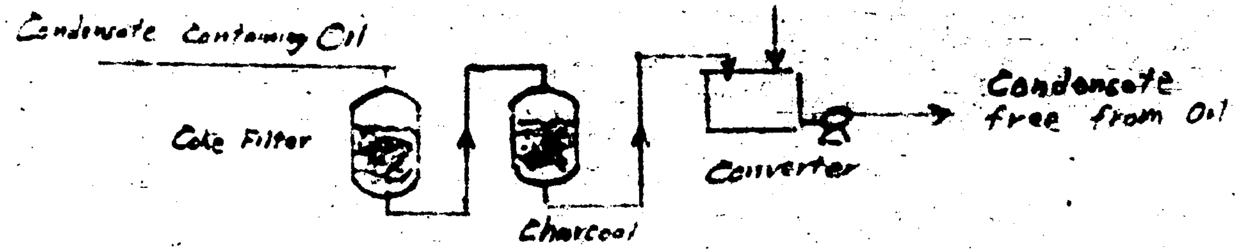
FIG. 29
Flow Sheet of Water Softener



Flow Sheet of Plant Water Unit



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I. THE POWER PLANT. (q)(Cont'd.)

freed of oxygen by heating. The degassed soft water is now taken to the generator and vaporized. In order to prevent scale formation on the tubes, two (2) to three (3) percent of distilled water is constantly added while the same quantity is blown down.

OPERATING DATA 1943

Avg. No. of boilers on stream	4.02	
Avg. load boilers	60.5	tons/hr
Avg. No. of turbines on line	3.05	
Avg. load each turbine	11,542	kw.

FUEL DEMAND

Boiler coal	38.45	tons/hr
H_2O content of coal	15.07	%
H_u - Kg. cal/kg	4,692	

PRODUCTION

70 Atm. Steam

Production	244.11	tons
Used - boiler feed pumps	7.10	
Used - turbines	235.39	
Used - reduction - throttle	1.92	

TURBINE EXHAUST

Condensate	40.58	tons
3.5 atmosphere steam	170.11	tons
18 atmosphere steam	24.70	tons
Loss	-- --	
Total exhaust	235.39	tons

STEAM TO FACTORY

18 atm. steam	14.66	tons
3.5 atm. steam	17.99	tons
2.5 atm. steam	110.88	tons
Condensate - de-oiled	33.46	cu.met.

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I. THE POWER PLANT. (Cont'd.)

STEAM TO FACTORY (Cont'd.)

Turbine condensate	6.24	cu.met.
Soft water - warm	90.61	cu.met.
Soft water - cold	26.10	cu.met.

ELECTRIC ENERGY

Produced in plant	34,862	kwh
Outside power	26,615	kwh
Total required	61,477	kwh
Used in power house	3,015	kwh
Used in plant	54,904	kwh

OTHER FACTS

Steam/coal (ton/ton) (cool 4,500 W.E./kg)	5.78	
70 atm. steam demand/kwh	6.752	
Total coal required/kwh	1.217	
Condenser steam energy	10,144	kw
Total power capacity	34,862	kw

II. TREATMENT OF DISCHARGE WATER.

(a) The discharge water treatment removed the largest part of the impurities in the process water, and thereby prevented the pollution of the Rhine. The discharge water streams are:

(1) Water separated from the coal and gasoline stall effluent chamber products in the discharge water tanks;
(2) Water in coal and gasoline effluent which is obtained in the overhead cuts from distillation;
(3) The condensate from the coking residue;
(4) The wash water from the rich gas washer;
(5) The rinse water from all of the oil treating units.

The impurities are: oil, H_2S, and phenols. The discharge waters were divided into two groups for separate treatments. These are the phenol water and dirty water containing oil (Fig. 30).

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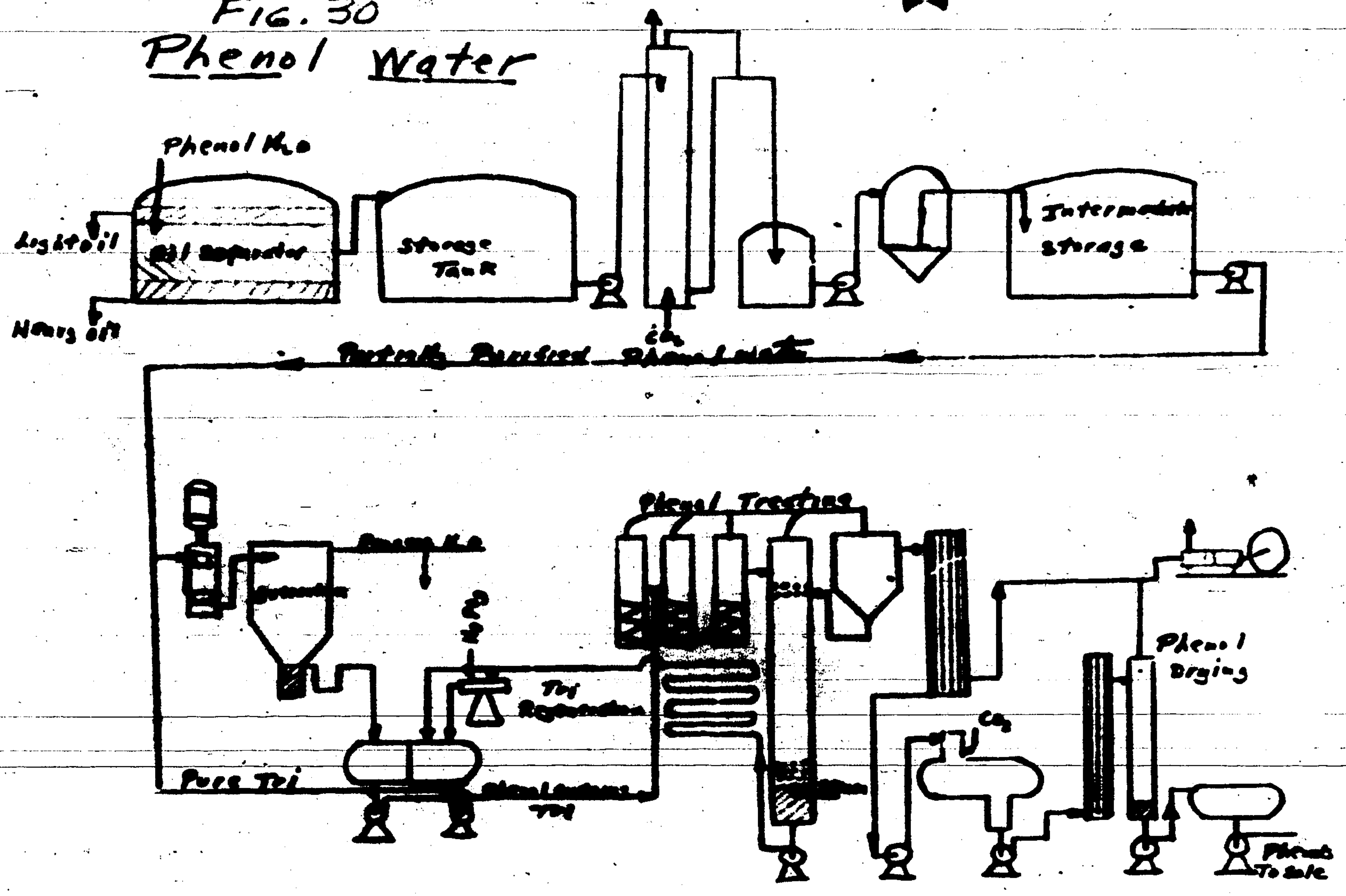
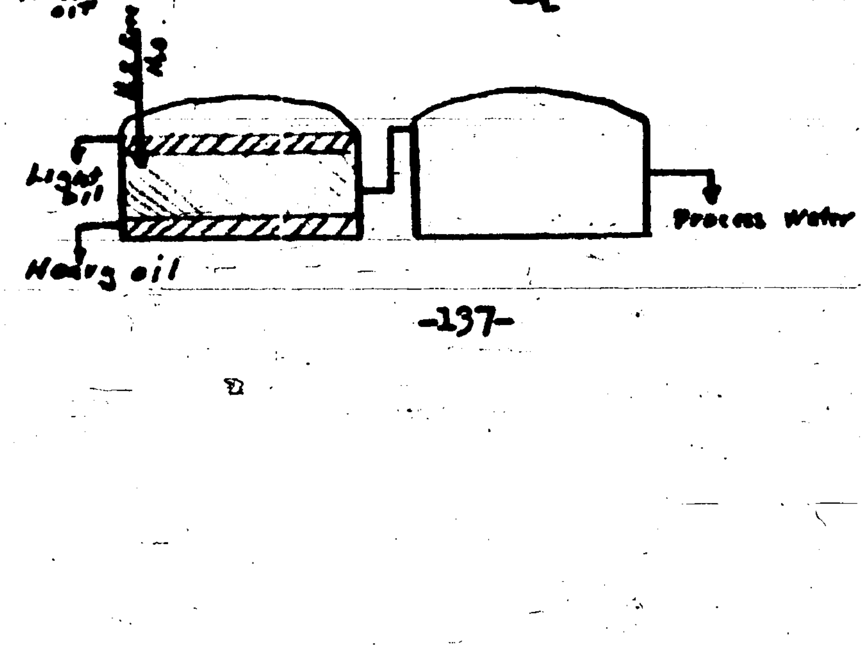
FIG. 30

Phenol Water



Oil-Containing Water



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II. TREATMENT OF DISCHARGE WATER. (Cont'd.)

(b) In the first group belong all waters containing more than one (1) gram/liter of phenol. These are effluent waters of the coal and prehydrogenation chambers, the condensate from the coal effluent and prehydrogenation distillation, and the water produced at the gas plant and the coking kilns.

(c) The second group contains the effluent andd distillation water of the gasoline chambers, the wash water from the rich gas washer, and all of the oil-containing rinse waters.

(d) The purification treatment for the oil-containing dirty water is simple. For H_2S-free water it consists in allowing the oil to settle out. For water containing H_2S the oil is first separated and then it is treated with CO_2 to remove most of the dissolved H_2S.

(e) The water containing phenol is given a somewhat extensive purification which consists of extraction with tricresyl phosphate in addition to the oil separation and the CO_2 treatment. The tricresyl phosphate, called "Tri" for short, is a mixture of triphenyl, tricresyl, and trixylenyl phosphates, whose absorption power depends on the triphenylphosphate content.

(f) A special characteristic of the Tri process is that the extraction medium boils higher than the dissolved phenols, hence these latter must be distilled out of the absorption medium. This operates so that the phenols produced are very pure, while the impurities remain behind as still residue with the Tri. The Tri must next be purified.

(g) In general the operation of the dephenolating unit is: The phenol-containing water was treated at forty (40) degrees centigrade in three (3) mixing chambers and separators located one behind another. Fresh extraction medium was added periodically. The mixing chambers were constructed with slow moving agitators because the Tri tended to emulsify with water when violently agitated. All together the concentration of Tri was about ten (10) percent of the water. The phenol-containing Tri was vacuum distilled to remove the phenols. The Tri remained as still bottoms. The phenols were condensed, the water separated, and

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II. TREATMENT OF DISCHARGE WATER. (g)(Cont'd.)

then vacuum distilled a second time. They were then sold.

(h) The Tri was cooled to about forty (40) degrees centigrade and used for further extraction of phenolic containing water. A fraction of about six (6) percent of the product was centrifuged out to remove impurities, and a second smaller fraction was treated with 0.5 percent phosphoric acid by stirring several hours followed by centrifuging. The dephenolated water was led by a special pipe to the discharge water collection at the Rhine.

(i) Many operating difficulties occurred in the purification of the phenol-containing water from the coal stall effluent, especially when the sludge from the coal chambers overflowed into the effluent. The coal stall effluent could become as dense as the water through the cooling of the latter and then either passed on through the separator or the gravel filter. These disturbances usually led to increased quantity of impurities in the Rhine, since the only remedy was to discharge the water into the Rhine. Once, oil passed through the gravel filter to the extractive vessel and contaminated the tricresylphosphate.

(j) The remedy consisted in preventing the occurrence of the disturbances, for example, as described in the sump phase and coal effluent distillation, the addition of diluent oil to coal effluent produces a deposit. Other points are: the improvement of the apparatus and increased supervision of the high pressure operation, avoiding the addition of emulsion promoting oils, such as heavy oil from the coking residue and unsuitable outside oils to the coal effluent product.

(k) On account of the special properties of the Tri, most higher boiling substances are removed from the water besides the phenols. These materials raised the viscosity of the Tri tenfold inside of three (3) months from the original of three and one-half (3½) E°. This was in spite of the mechanical and chemical purification of a small bleed . The concentration of the impurities then were from forty (40) to fifty (50) percent. At the same time the solubility of the phenolics in the Tri, especially phenol itself dropped sharply, so that the phenolic content of the washed water rose from seven hundred (700) milligrams/liter to nearly three (3) grams/liter.

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II. TREATMENT OF DISCHARGE WATER. (Cont'd.)

(l) Furthermore, the impurities in the Tri tended to cake on the walls of the apparatus. The crust deposits are difficult to remove. It was tried to remove these cakes by circulating hot concentrated NaOH solution, but usually it was necessary to take the apparatus apart.

(m) These difficulties demanded that the Tri be renewed at least every three (3) months. The change was made at suitable intervals to keep the formation of tightly-adhering cokes in check. The product which is drawn off can be regenerated by a high vacuum distillation, which must be used for want of another suitable distillation apparatus. The purified water in the discharge water treatment contained NH_3. This led to the formation of thicker crusts, particularly $CaCO_3$, in the discharge water sewer through its mixing with process water. On this account a pipe line for the impure water was laid to the Rhine in the process water drain.

(n) The disadvantages of the Tri process led to its removal in favor of the "Phenosolven" dephenolation process of Lurgi. Phenosolven is chiefly isobutyl acetate in a mixture of esters that boils lower than the extracted phenols. It is distilled out of theextraction mixture and therefore remains clean. The impurities remained in the phenolic extract and were sold with them. This change in the process produced a far better phenol yield. The phenol content of the treated water was one hundred (100) to two hundred (200) milligrams/liter.

IMPORTANT OPERATING RESULTS

Quantities

Dirty oil from dirty water	8,900 annual tons
Dirty oil from phenol water	2,600 annual tons
Oil containing dirty water	47 M^3/hr
Phenol water	32 M^3/hr
CO_2 used for injection in the water	600 M^3/hr

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II. TREATMENT OF DISCHARGE WATER. (Cont'd.)

H_2S Content

Of the un-gassed phenol water	1.2	g/liter
Of the gassed phenol water	0.2	g/liter
The outlet gases	4	Vol %
Production of phenol oil	950	annual tons

Analysis of Phenol Oils

H_2O	1.2
Mentul oil	2.0
Phenol	31.3
Cresols	43.0
Xylenols	11.5
Rest	11.0

Phenol Content

Of the Phenol water	5.2 g/liter
Of the dephenolated water	1.9 g/liter
Phenol production	63.0 %

Tri Content

Of the outlet water	0.086 g/liter
Of the phenol oils	9.5 g/liter

(d) Miscellaneous.

I. MET AND NOT MET GUARANTEES.

(a) Water Gas Unit	Guarantee Figures	Operating figures at the end of 1943
CO + H_2 - content of the water gas	84 %	84 %
Capacity of the generators	5,500 nm^3/hr	5,250 nm^3/hr
Water gas/briquettes	2,030 nm^3/ton	1.900 nm^3/ton
The heating gas required	780 WE/nm^3 water gas	820 WE/nm^3 water gas
Outside steam required		0.12 kg/nm^3

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I. MET AND NOT MET GUARANTEES. (a)(Cont'd.)

The guaranteed quantities on gas manufacture were never reached. The deficit amounted to approximately five (5) percent, for which the firm of Pintsch was charged with a penalty. This was particularly due to steam requirements.

(b) Fuel Gas Unit.

The guarantee figures for fuel gas unit were completely met when using H_2S steam injection, and when using CO_2 injection the figures were surpassed. At the same time excess steam in the amount of 0.1 kilograms per cubic meter of heating gas was produced.

(c) Gas Cracking Unit.

No guarantee figures on this unit were set up by the manufacturer, but the operating results exceeded those values anticipated and designed. The most noteworthy points were the high production yields and steam production through waste heat recovery which allowed for steam production equal to the steam requirements.

(d) Hydrogenation.

The hydrogenation plant of I. G. was never covered by a guarantee. However, the operating yields from both units exceeded the design quantities. The coal requirements were somewhat higher than anticipated. The hydrogen requirement which had been estimated from pilot plant studies of I. G. were originally set too high. The operating differences expected from using a Rhine lignite instead of mid-German lignite were correctly anticipated.

(e) Other Operations.

In all other operations anticipated full loads were either reached or bettered. This is especially true of utility demands. One exception was the C_3 - C_4 unit which did not meet its guarantees; this failure amounted to forty (40) percent of the designed figures. The firm Uhde was going to build another unit in order to meet the original requirements.

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I. MET AND NOT MET GUARANTEES. (Cont'd.)

(f) Capacity of the Plant.

The production-time curve shows that in 1944 the unit was capable of producing twenty-seven thousand seven hundred (27,700) tons/month of diesel oil and gasoline or two hundred sixty thousand (260,000) tons/year of gasoline and diesel oil. This meant using the complete gas producing capacity. The raw materials were approximately seventy-five (75) percent coal and twenty-five (25) percent oil. From coal alone, two hundred twenty-five thousand (225,000) tons/year of gasoline and diesel oil were produced which was the designed capacity of the unit. The bottle neck was always the hydrogen production. By the addition of outside oil, the capacity of both sump and gas phases rose to the total of two hundred sixty thousand (260,000) tons/year. This use of oil saved hydrogen, as it requires only half as much hydrogen as coal. The sump phase capacity was raised fifty (50) percent by a slight addition to the gas preheater. The gas phase had sufficient reserve capacity for this additional material since the middle oil made from outside oils has less phenols than the coal oil and could even take a throughput thirty-five (35) percent over the designed figure. In using coal, the capacity of the unit is two hundred twenty-five (225,000) tons/year diesel oil and gasoline while with outside oil it is three hundred sixty thousand (360,000) tons/year of the same. To convert the latter quantity to aviation gasoline, a fifth gasoline stall would have to be built.

II. AIR ATTACKS AND COUNTER MEASURES TAKEN.

(a) Protection for Men and Machines.

When the plant was built, many air raid shelters were included in the work. Besides these, a considerable number of walls were built both inside and outside of buildings to protect machines. The turbines and boiler plant were given special protection. All tanks containing inflammable material were specially constructed and had extra heavy dykes and run off ditches.

(b) Blackout.

Special means for blacking out the plant were undertaken, either semi- or complete. Under normal blackout conditions,

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II. AIR ATTACKS AND COUNTER MEASURES TAKEN. (b)(Cont'd.)

special lights kept buildings in semi-darkness, while only the repair shops were kept fully lit. At the approach of enemy planes, the blackout was completed by cutting off the lighting current. Discipline among the workmen during air raids was excellent. No damage was received due to blackout errors.

(c) Air Raid Wardens and Their Work.

Suitable air raid defence was always available. No one shirked his responsibility and the posts were always completely manned. The air raid protection procedure was minutely worked out and was constantly being improved. Warning from the outside was conveyed quickly and efficiently to the central station by the Army, with whom good cooperation always existed. The information was relayed to the whole plant by a siren alarm except to the high pressure unit and boiler house which was by telephone, giving the latter instantaneous notice.

(d) Operation Procedure.

The most important detail is the blowing down of the unit. This was done in two stages "Safety Operation" and complete depressuring. The former assumed on receipt of warning that planes were near, while the latter was only resorted to just before or after bombs started to fall. "Safety operation" requires isolating the units in the plant from one another, hence making indirect damage impossible or unlikely. It disconnects the main plant from outside power supply and stops the feed to the gasoline stalls of the gas phase. It also stops the coal paste injection in the sump phase, and substitutes diluent oil for the same. Under extreme conditions even these units can be disconnected from the power plant in a few seconds. The procedure was so well executed that "safety operation" could be carried out in two minutes and complete blow down in another few seconds. Such results were made possible by placing all control valves and power switches in one air raid shelter and at one switchboard in the power house. The same reliability in blowing down the unit existed in resuming operations. Production was completely restored after four (4) to five (5) hours. Hence operations were broken and resumed thirty-one (31) times. The methods were carried out that damage was limited to one gas holder and one small explosion in the gas plant.

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II. AIR ATTACKS AND COUNTER MEASURES TAKEN. (Cont'd.)

Loss of Production Due to Enemy Air Raids		Loss of Finished Product	
5/29/42	Safety operation (attack on Cologne, loss of outside power - several days)	300	tons
10/15/42	Bombs dropped on gas plant	8,300	"
1/23/43	Safety operation (outside power off)	600	"
2/14/43	Safety operation (outside power off)	250	"
2/23/43	Loss of all outside power	450	"
6/27/43	Blow down complete (1 stall coked up and had to be taken down)	700	"
7/4/43	Safety operation with loss of power	300	"
7/9/43	Safety operation with loss of power	100	"
7/30/43	Safety operation with loss of power	150	"
8/12/43	Safety operation with loss of power	150	"
8/13/43	Complete power failure (all stalls coked up despite quick operation)	5,000	"
8/17/43	Safety operation - twice	150	"
8/22/43	Safety operation	100	"
9/10/43	Outside power failure	100	"
9/15/43	Several days outside power lost due to damage to public utility	800	"
10/3/43	Damage to briquette conveyer	20	"
10/14/43	Safety operation	120	"
10/20/43	Safety operation	80	"
10/23/43	Several days lack of briquettes (main water conveyer in mine damaged)	200	"
11/3/43	Safety operation	150	"
11/19/43	Safety operation	150	"
11/27/43	Outside power failure (oil circulating pumps out)	200	"

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II. AIR ATTACKS AND COUNTER MEASURES TAKEN. (Cont'd.)

Loss of Production Due to Enemy Air Raids		Loss of Finished Product
11/30/43	Safety operation	150 tons
1/7/44	Safety operation	100 "
1/24/44	Safety operation	150 "
3/4/44	Safety operation	150 "
4/22/44	Safety operation	150 "
5/20/44	Safety operation	100 "
5/24/44	Safety operation	100 "
5/26/44	Safety operation	100 "
5/28/44	Safety operation	100 "
6/3/44	Safety operation	150 "
6/13/44	Safety operation (failure of outside power transformers)	2,080 "
6/22/44	Safety operation and blow down	970 "
6/27/44	Safety operation	250 "
7/10/44	Safety operation	150 "
7/11/44	Safety operation	150 "
		23,220 tons

The total production during this time was 455,356 tons, so that air raids caused a loss of 5.1 percent.

III. AIR ATTACK OF JULY 18, 1944.

(a) In the night of July 18-19, 1944 a heavy air attack was made on the plant. About one thousand (1,000) high explosive bombs, mostly five hundred (500) pound, fell inside the manufacturing plant. On the south west the boiler house was heavily hit.

(b) The account of the attack was as follows: at 12:55 a.m. first alarm, at 1:03 a.m. "safety operations" was sounded and word was passed, "Attack headed for the plant."

(c) 1:07 a.m. full blow down was given after a red flare was dropped over the plant. Seconds later the bombs started to drop. They came in three waves and lasted about twenty (20) minutes.

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III. AIR ATTACK OF JULY 18, 1944. (Cont'd.)

(d) The attack was made easy for the aviators by the lighted conditions, since the artificial fog was started too late. The reason for not starting the fog is unknown. The manufacturing units were brilliantly lighted up by the flares. Brilliant fires were started after the first bomb attack.

(e) Safety operations and emergency shut down proceeded satisfactorily, despite the short interval of four (4) minutes for doing same and taking air raid shelter.

(f) The same satisfactory conditions obtained for the several men in the power house, who had to remain at their posts as long as possible. Nevertheless, they were in their shelters at the start of the bomb falling. Of the six hundred (600) workmen, there were three (3) deaths. These all occurred through one explosion.

(g) On account of the severity of the attack, the water and electric utilities and telephone lines were down. Likewise the destruction of the radio tower made it necessary to send for aid from Cologne.

(h) The aid men and wardens were brought partly by Intelligence and part came by themselves. The fire was spread by numerous explosions, and through the many hours of fighting there was an extremely thick fog. It followed from the Rhine back to Urfeld. Fire water was taken from DHD tanks filled with water, out of the Rhine through a short finished water line, and out of the ash settling basins of the gas works. Great fires spread in the tank farm where four (4) full tanks were located. Also fires spread in the coal mill and the bunkers of the gas works. Besides, there were a series of small fires in the vicinity of the high pressure, the distillation, and the power gas units. The little fires were quickly extinguished, but the large ones lasted to the following noon.

(i) The following damage occurred: Great destruction in the gas production unit, in the coal mill, in the water gas conversion, in the compressor building, in the CO purification, in the recycle pumps used for hydrogenation, in the tank farm, and the pump house for heavy oils. Almost all gasoline was destroyed.

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III. AIR ATTACK OF JULY 18, 1944. (Cont'd.)

The smaller gas holder for N_2 and H_2S remained almost undamaged. The cracking, distillation, power gas, dephenolating units were less heavily damaged. Four (4) large tube breaks and a larger number of splits occurred. The fresh water, drinking water, and discharged water lines were broken in many places, also the telegraph and telephone lines.

(j) About twenty (20) percent of the plant was destroyed. The capacity was greatly hurt because the buildings had been hit so heavily.

(k) In ten (10) weeks of accellerated repair work, the plant was restored to forty (40) percent of production.

(l) On October 3 and 11, 1944 two more attacks followed and at each about sixty (60) bombs of one thousand pounds fell on the plant. These caused damage in the high pressure, tank farm, and power house units.

(m) On October 6, 1944 the plant was closed. Of all the bombs dropped on the July 18, 1944 raid, two hundred (200) were duds.

IV. LIST OF IMPORTANT MANUFACTURERS OF MACHINES AND EQUIPMENT.

GAS PRODUCING UNIT

Water gas unit	Pintsch - Berlin
Producer gas unit	Pintsch - Berlin
Piping and steel work	Kolsch - Folserwerke, Siegen
Furnace lining	Dr. Otto, Bochum
	Koppers, Essen
Gas scrubber	Theissen, Munchen
Gas and air blowers	Jager and Co., Leipzig
Dust removal and cleaning	Lurgi, Frankfurt
Tar pumps	Weise, Sohne, Halle
Ash removal	Nacher, Chemnitz
Conveyors	Pohlig, Koln-Zollstock
Producer and water gas blowers	Schiele, Eschborn/Taunus

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IV. LIST OF IMPORTANT MANUFACTURERS OF MACHINES AND EQUIPMENT. (Cont'd.)

Fittings and cocks	Zimmermann u. Jansen, Duren
Gas holders	Neumann, Eschweiler
Tanks	Neumann, Eschweiler
Cooling towers	Otto Estner, Dortmund
Redler conveyors for dust and ashes	Gebr. Buhler, Dresden
Conveyor belt	Clouth, Koln-Nippes

BOILER HOUSE

Steam boilers	Durr A. G., Ratingenb. D'dorf Walther, Koln-Dellbruck
Boiler feed pumps	Halberg, Ludwigshafen
Boiler feed turbines	Borsig, Berlin-Tegel
Coal conveyors	Maschinenfabrik, Magdeburg,K.S.G. Berlin
Fire brick lining	Karrenberg, Dusseldorf
Steam lines	Seiffert, Eberswalde
Burner control	Askania, Berlin
Temperature control	A.E.G., Berlin
Flow regulators	V.A.G., Mannheim
Superheated steam equipment	Amag-Hilpert, Nurnberg Schaffer u. Budenberg, Magdeburg
Boiler feed water treatment	Permutit, Berlin
Blowdown (?)	Natorp u. Eberhardt, Hohenturm b. Halle
Turbines	A.E.G., Berlin
Water pumps	Ritz u. Schweitzer, Schwabisch-Gemund
Condensate	Vogel, Wien-Stockerau
Low pressure tanks	Feld u. Halm, Bendorf

CONVERSION, COMPRESSORS
CO_2 AND CO PURIFICATION

Methane cracking	
Organic sulfur removal	Bamag, Berlin
Exhaust gas blowers	Kuhle, Kopp u. Kausch Frankenthal
Air blowers	Schiel, Eschborn i. Ta.
Boilers	Oschatz, Merane i. S.

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IV. LIST OF IMPORTANT MANUFACTURERS OF MACHINES AND EQUIPMENT. (Cont'd.)

Regenerators - 700 and 325 atm.	Friedr. Krupp, Essen D.H.H.V. Dortmund-Horde Bocumner Verein, Bochum Pres. u. Walzwerk, Reisholz
Heat removers - 700 atm.	D.H.H.V. Dortmund-Horde
Product collectors	Bochumer Verein, Bochum Pres. u. Walzwerk, Reisholz
Surge tanks	Deutsches Rohrenwerk, Dusseldorf
Preheater construction	Eisenwerke, Kaiserlautern
Hairpin tubes - 700 atm.	I. G. Ludwigshafen, Leuna
Hiarpin tubes - 325 atm.	I. G. Ludwigshafen, Leuna
Exchanger bundles	Leuna-Werke Hydrierwerke, Politz Chemische Werke, Huls
Appurtenances	I. G. Ludwigshafen
Circulating blowers	Schiele, Escheborn i. T.
Gas coolers - 700 atm.	I. G. Ludwigshafen
Air coolers	I. G. Ludwigshafen
Mud coolers	I. G. Ludwigshafen
Gas cooler - 325 atm.	Deutsche Rohrenwerke, Dussledorf
Reactor crane	Demag, Duisburg
High pressure fittings - 700 atm.	I. G. Ludwigshafen
High pressure fittings - 325 atm.	I. G. Ludwigshafen
High pressure piping	I. G. Ludwigshafen Rheinmetall-Borsig, Dusseldorf Ruhrstahl, Witten Henrichshutte, Hattingenu, Wolking Mannesmann, Dusseldorf, Remscheid Deutsche Rohrenwerke, Dusseldorf
Tool wagons	Fuchs Waggon, Heidelberg
Electric preheater	I. G. Ludwigshafen
Electric transformers	Koch und Sterzel, Dresden
Electric equipment	Ges. f. Elektroschweisung, Dortmund
Other cranes	Fredenhagen, Offenbach
Conveyors	Gebr. Wohr, Unterkochen/Wttbg.

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IV. LIST OF IMPORTANT MANUFACTURERS OF MACHINES AND EQUIPMENT. (Cont'd.)

Boiler feed units (pumps)	K.S.B. Frankenthal
CO_2 compressor 0.4 atu	C. Enke and Co. Schkeuditz
	Balcke, Frankenthal
Combustion unit for N_2 production	Bamag, Berlin
H_2 compressors	Maschinenfabrik Surth
Conversion	Bamag, Berlin
Pump units	ther Amag-Hilpert jetzt
	K.S.B. Frankenthal
Water gas blowers	C. Enke and Co., Schkeuditz
Heating gas blowers	C. Enke and Co., Schkeuditz
Heating gas blowers Bau 144	C. Enke and Co, Schkeuditz
Heating gas blowers Bau 38	C. Enke and Co., Schkeuditz
	I. Jager, Chemnitz
Compressors	Halberg A. G. Ludwigshafen
Boosters	Ehrhard u. Schmer, Saarbrucken
	Demag, Duisburg
CO_2 purifier	Gutehoffnungshutte, Sterkrade
Pump units	Halberg A. G. Ludwigshafen
Pelton turbines	Escher Wyss, Ravensburg/W.
CO purifier	PreB-u. Walzwerk, Reisholz
Press pumps	Gutehoffnungshutte vorm.
	Haniel u. Lueg, Dusseldorf
Expansion engine	Leuna-Werk, Merseburg
Vacuum pump	K.S.B. Frankenthal
Tanks	Wilhelmshutte, Sprottau
Cooling unit	Mansfelder Maschinenfabrik,
	Mansfeld
Booster	Eslinger Maschinenfabrik,
	Eblingen
	Demag, Duisberg
Oil purification equipment	Bergedorfer Eisenwerke,
	Bergedorf b. Hamburg

HYDROGENATION - HIGH PRESSURE

Coal reacors and washers - 700 atm.	Friedr. Krupp, Essen
Coal reactors	D.H.H.V. Dortmund-Horde
Gasoline reactors - 325 atm.	D.H.H.V. Dortmund-Horde

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IV. LIST OF IMPORTANT MANUFACTURERS OF MACHINES AND EQUIPMENT. (Cont'd.)

Rotating furnaces	Krupp, Grusonwerk, Magdeburg
Furnace lining	Tonwerk, Beibrich-Wiesbaden
Reducing gears	Friedr. Krupp, Essen
Burners	Wistra G.m.b.H.
Preheater and steam superheater	Walther, Koln-Dellbruck
Crane units	W. Fiebig, Waldenburg/Schl.
Residue pumps	I. H. Naher, Chemnitz
Other cranes	E. Holscher, Rechlinghausen
Circulating and fresh gas blowers	Kleinschanzlin & Becker, Frankenthal

DISTILLATION

Distillation units A1, A2, A3	Uhde, Dortmund
Distillation units B1, B2, B3	Uhde, Dortmund
Distillation unit B4	Maschinenfabrik Brunn, Konigsfeld
Stabilizers 1 & 2	Lurgi, Frankenthal/M.
Hot oil pumps up to 40 atm.	K.S.B. Frankenthal
Water pumps	Hesse, Chemnitz
Pumps for cold products	Weise, Sohne, Halle
A3 column	Ganzler, Duren
Tanks 1000, 2000, 3000 cu. meters	Munk & Schmitz, Koln
Tank 500 cu. meters	Dingler-Werke, Zweibrucken
Centrifugal blowers	Schiele, Eschborn, i. Ta.
Power gas storage tanks	Bamag, Bayenthal G.m.b.H. Sterkrade
Power gas scales	Dopp, Berlin
Weighing lorry	Schmidt, Dusseldorf
Other lorries	Schmidt, Dusseldorf

HYGASVERABEITUNG und PHENOLWASSERREINIGUNG

Alkazid unit	Dr. Otto, Bochum
Hot and cold caustic pumps	Amag-Hilpert, Nurnberg
Oil scrubber	Bamag, Berlin
Organic sulfur purifier	Bamag, Berlin
Sodium hydroxide wash	Bamag, Berlin
Caustic pumps	Amag-Hilpert, Nurnberg
Hard steel-nozzles	Wallram, Essen
Electric controls for valves	A.E.G. Berlin

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IV. LIST OF IMPORTANT MANUFACTURERS OF MACHINES AND EQUIPMENT. (Cont'd.)

De-pressure vessels 50 and 100 atm.	Pintsch, Berlin D.R.W. Dusseldorf Mittledeutsche Stahlwerke Riesa
Repair of tube bundles	Chemische Werke, Huls Leuna-Werke
Hairpin tubes - 700 atm.	Leuna-Werke
Hairpin tubes - 325 atm.	I. G. Ludwigshafen
Paste and presses	BMAG vorm. Schwartzkofpff, Berlin
Middle oil injection pumps - 350 & 700 atm.	Balcke, Frankenthal
High pressure circulating pump - 60 atm.	Halberg A. G. Ludwigshafen
Expansion engine	Leuna-Werke

HYDROGENATION LOW PRESSURE

Discharge units	Gebr. Buhler, Dresden Maschinenfabrik Buckau
Conveyor units	Gebr. Buhler, Dresden
Mill units (sieve rolls, & Konzentra mill)	Krupp, Grusonwerke, Magdeburg
Automatic balancers	Schenk & Co., Darmstadt
Agitator vessel	W. Dohmen, Eschweiler
Product pumps	K. S. Eddesse, Oeschersleben
Mud centrifuges	Bergedorfer Eisenwerke, Bergedorf
Widia-nozzles (Wie dremant)	Krupp, Essen Deutsche Edelstahlwerke, Krefeld
Sand separators	Eisenwerke, Kaiserlautern
Dirty ore centrifuge	I. Haubold, Chemnitz
Circulating pumps	Weise, Sohne, Halle Hesse, Chemnitz
Screw conveyor ovens	Uhde, Leuna
Screw conveyor cranes	Peninger Maschinenfabrik und Liebig, Leipzig
C_3 - C_4 unit	Uhde, Leuna
C_3 - C_4 pumps	K.S.B. Frankenthal
C_3 - C_4 compressors	Maschinenfabrik, Surth

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IV. LIST OF IMPORTANT MANUFACTURERS OF MACHINES AND EQUIPMENT. (Cont'd.)

Drives	Westdeutsche Getriebebaugensellschaft (Ges. Existiert night mehr)
Carbon rich gas compressors	Maschinenfabrik, Surth
Cooling unit	Rehinkalte, Dusseldorf
Drives and cooling compressors	Tacke, Rehine Westf. Westdeutsche Getriebebauges
Gasoline rich gas blowers	C. Enke, Schkeuditz, Leipzig
C_3 - C_4 gas holders	Opbergen, Neuss Gutehoffnungshutte, Sterkrade
Phenol removing unit	Dr. Otto, Bochum
Gear pumps	Neidig, Mannheim
Vacuum pumps	K.S.B. Frankenthal
Oil separators	Schumann, Leipzig
Packed towers	Dinglewerke, Zweibrucken
Dirty water pumps	K.S.B. Frankenthal Weise, Sohne, Halle Amag-Hilpert, Nurnberg
Water tanks	Dinglewerke, Zweibrucken Kolsch-Folzerwerke, Siegen

V. FUEL ADMINISTRATION IN THE GERMAN GOVERNMENT.

(a) The head of all industry in Germany is Dr. Speere. Under him in charge of the chemical industries is Dr. Krauch, the chairman of I. G., who corresponds to the head of our W.P.B. The industries are broken down in the following groups:

(1) Oil,
(2) Aluminum,
(3) Hydrogenation,
(4) Nitrogen,
(5) Explosives.

(b) The planning for all armaments under Speere is done by Herr Kehl, chairman of the planning division.

(c) As well as the above mentioned persons there is Herr Geilenberg, personally picked by Hitler, and responsible only to him, who is in charge of exploiting all hydrogenation plants.

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V. FUEL ADMINISTRATION IN THE GERMAN GOVERNMENT. (Cont'd.)

He is responsible for the Geilenberg Plan which:

(1) Repairs plants,
(2) Builds new ones.

Geilenberg was responsible for the decision not to repair Wesseling and moving the workmen elsewhere.

(d) Product Destination.

All of the men at Wesseling seemed ignorant of the ultimate destination of the plant's output. However, the following information was given:

(1) Motor gasoline - shipped to Berlin, Duisberg, Köln, Mannheim to large tank farms - Standard, Shell, etc. Some lead was apparently added.
(2) Diesel oil - sent by canal to Holland, Antwerp and Ghent. Orders came from the Zentral Büro.
(3) Aviation gasoline - destined for plants called WIFO - Munich and Duisberg. Some went to Ruhr Oil Co. at Bothrop.
(4) Special 165° C aviation gasoline went to D.H.D. unit at Ludwigshafen. Here the naphthenes were dehydrogenated to aromatics.

(e) New Underground Installations of Hydrogenation Plants.

The underground installations go by the code name "Schwalbe". They are supposedly five in number. Two are in the Elbe valley, between Dresden and Aussig, in the Elbe Sandstein Gebirge, on both sides of the river. One is near Buckeburg and Minden in a natural cave. The fourth is in Thuringia at Berga Kelbia and the fifth, belonging to I. G., is in the Harz mountains in the old gypsum quarries at Niedersachswerfen. The latter also has an A. T. unit (Alkylation Plant).

Prepared by:

L. H. MULIT,
Lieut. Comdr., USNR,

R. C. ALDRICH,
Lieut., USNR.

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U·S·NAVAL·TECHNICAL·MISSION·IN·EUROPE

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CNO ltr. Op-23-PT,
Serial 327P23,
dated 22 October, 1945

80274

TECHNICAL REPORT No. 105-45

THE PRODUCTION OF TETRAHYDROFURAN INTERMEDIATES

JUNE 1945

U·S·NAVAL·TECHNICAL·MISSION·IN·EUROPE

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U. S. NAVAL TECHNICAL MISSION IN EUROPE
c/o Fleet Post Office
New York, N. Y.

File: A9-16(3)(10/Hs)

Serial: 533

1 July 1945

[redacted]

From: Chief, U. S. Naval Technical Mission in Europe.
To : Chief of Naval Operations (OP-16-PT).

Subject: U. S. Naval Technical Mission in Europe Technical Report No. 105-45, The Production of Tetrahydrofuran Intermediates - Forwarding of.

Enclosure: (A) (HW) Copies of subject report.

1. Enclosure (A) is forwarded herewith.

HARRY D. HOFFMAN,
Captain, USN,
Acting.

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TECHNICAL REPORT No. 105-45

THE PRODUCTION OF TETRAHYDROFURAN INTERMEDIATES

JUNE 1945

U. S. NAVAL TECHNICAL MISSION IN EUROPE

80277

[redacted]

THE PRODUCTION OF TETRAHYDROFURAN INTERMEDIATES

1. Summary.

The information contained herein was obtained during an interrogation of Dr. Dorer of the I.G. Farbenindustrie plant at Ludwigshafen on 28 May 1945. Tetrahydrofuran is produced as an intermediate for other syntheses. The principal uses to date have been as a monomer for a polymeric synthetic lubricant and for butyrolactone production. The latter is a relatively high boiling ketone for solvent purposes. An intermediate in the production is butandiol - 1, 4 which has been used in the laboratory preparation of a polymer for a nylon substitute. This work was described by Dr. Pöhme of the I.G. Farbenindustrie plant at Leverkusen. No large scale work was done on this process so no details of equipment or process can be given. The product is quite new and still remains to be exploited by further laboratory work in Germany. The chemistry of the synthesis is given below. It is suggested that this information be made available to interested laboratories for a more critical evaluation and possible exploitation, if the resin possesses any desirable features, either from its physical properties or manufacturing advantages. It does not appear that tetrahydrofuran would become a very inexpensive building block because of the raw materials, acetylene and formaldehyde. The process requires three (3) steps each of which has an efficiency between 90 and 95 percent, resulting in an overall efficiency between 73 and 86 percent. The equipment requirements are easily met in that no extreme temperatures or pressures are employed and the operations are similar to techniques commonly used. The Nylon substitute, a POLYURETHANE, is described in detail in the attached report "Polyurethane" by Dr. O. Bayer, Leverkusen I.G. Werk, 24 September 1941.

2. Details.

(a) Tetrahydrofuran is produced by a liquid phase reaction of 30 percent aqeous formaldehyde with acetylene in the pressure of a catalyst containing 12 percent copper and 3 percent bismuth deposited simultaneously on silica gel. The conditions for the reaction are as follows:

Temperature	100° C
Pressure	5 Atmospheres

Acetylene is fed continuously to an agitated autoclave containing the formalin and catalyst until the stoichiometric quantity has been reached.

2. Details (a) (Cont'd.)

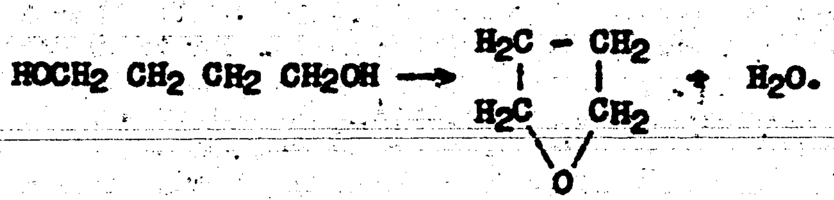
The catalyst is removed by filtration and recycled. The yield is alleged to be 92 percent. The crude product from this step is hydrogenated in the liquid phase with a suspended catalyst which contains:

Nickel	15 to 16 percent.
Copper	5 percent.
Chromium	0.6 percent.

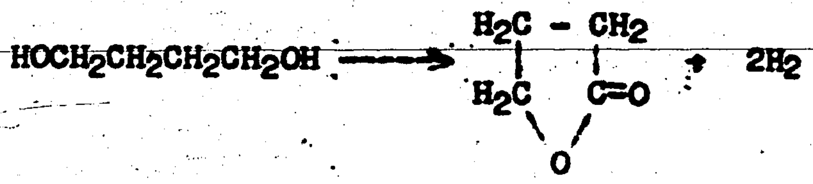
deposited on an inert carrier of kieselguhr. Excess hydrogen above the quantities called for in the following equation is used and the temperature of hydrogenation is maintained at 100 to 120 degrees centigrade. The product is butylene glycol - 1, 4

$$HOCH_2 - C \equiv C - CH_2OH + 2\ H_2 \rightarrow HOCH_2\ CH_2 - CH_2{-}CH_2OH.$$

The specified yield in this step is 96 percent. The catalyst is again removed by filtration. The third step is the dehydration of butylene glycol to tetrahydrofuran.



This is a liquid phase reaction utilising one percent by weight of phosphoric acid as the catalyst. The dehydration takes place at 270 degrees centigrade and the tetrahydrofuran is removed as distillate as rapidly as formed. The yields are given as 95 percent or higher. Butyrolactone is produced from the above compound butylene glycol - 1, 4 by liquid phase dehydrogenation in the presence of a suspend catalyst of 8 percent pure copper on an inert carrier of silica gel. The butyrolactone and hydrogen are continuously removed as the reaction proceeds.



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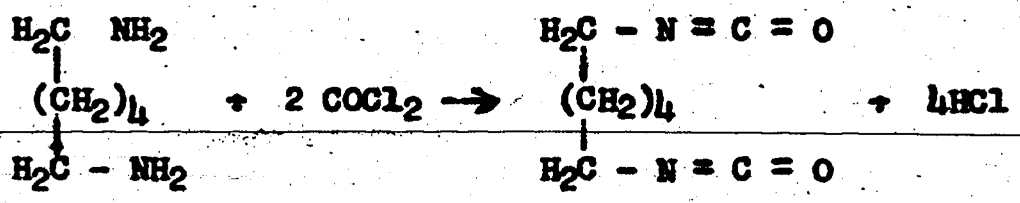
2. Details (a) (Cont'd.)

The nylon substitute mentioned in the summary is closely related to nylon in that hexamethylene diamine - 1, 6 is used in the synthesis. This diamine is made in the conventional manner used in the United States that is from adipic acid thru the nitril and hydrogenation with Raney Cobalt catalyst in batch liquid phase reaction at 150 degrees to 180 degrees centigrade and 100 atmospheres.

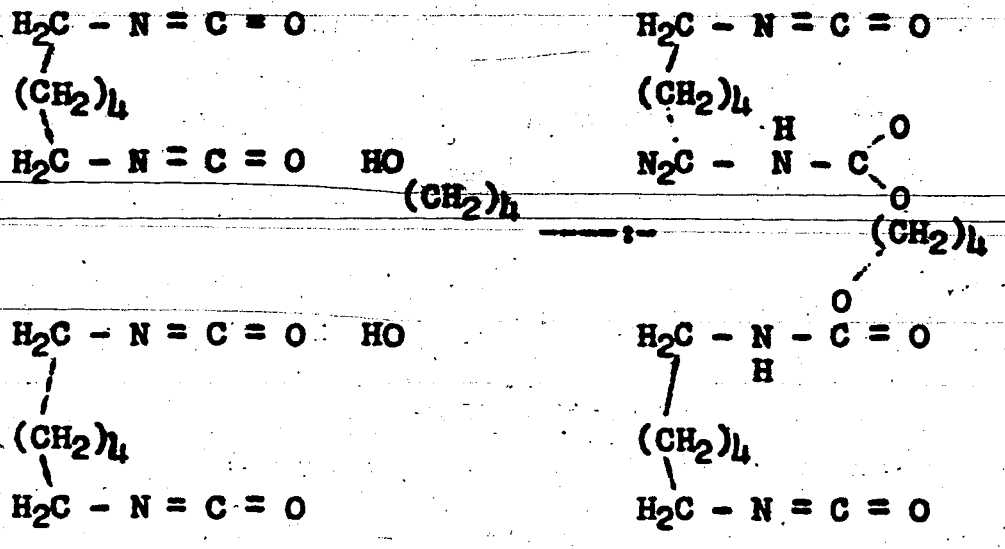
(b) The hexamethylene diamine is reacted with phosgene according to the following equation:



$$\begin{array}{l} H_2C\ \ NH_2 \\ \ \ | \\ (CH_2)_4 \\ \ \ | \\ H_2C - NH_2 \end{array} + 2\ COCl_2 \rightarrow \begin{array}{l} H_2C - N = C = O \\ \ \ | \\ (CH_2)_4 \\ \ \ | \\ H_2C - N = C = O \end{array} + 4HCl$$

to give the diisonitril shown in the equation. This isonitril is reacted with butanediol - 1, 4 to give an alkyd type of polymer by the interaction of 2 polyfunctional molecules. The mechanism of the reaction and structure of the product was believed by Dr. Pocheme to be as follows:

The hydrogen of the hydrox 1 group on the alcohol adds to the nitrogen atom of the isonitril and the remainder of the alcohol links to the carbon atom as follows:



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2. Details (b) (Cont'd.)

Obviously this reaction can continue to build long chains on the available terminal isonitril groups shown in the above equation in the manner of typical alkyd polymers.

Prepared by:

F.H. ROBERTS,
Technician.

[redacted]

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Copies of "POLYURETHANE"
report can be supplied by:

CIOS - London

CNO (OP-16-PT)
U.S. Navy Dept.

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Exemplar Nr. 2

POLYURETHANE

Dr. O. Bayer

Leverkusen - I. G. Werk

Vortrag

gehalten auf der T-A-Sitzung zu Frankfurt a. M.

am 24. September 1941.

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ÜBERSICHT

8C284

Polyurethane

Hochmolekulare Verbindungen werden bekanntlich nach zwei grundlegenden Verfahren entweder durch Kondensation oder durch Polymerisation hergestellt.-

Die charakteristischen Merkmale des Kondensationsverfahrens sind :

1.) eine große Anzahl kleiner Molekule mit mindestens je 2 funktionellen Gruppen reagieren unter Austritt eines niedermolekularen Reaktionspartners, wie beispielsweise Wasser, Salzsäure, NaCl, Alkohol u.dgl. miteinander.
2.) zur Erzielung des makromolekularen Zustandes werden vielfach recht robuste Reaktionsbedingungen, wie beispielsweise hohe Temperaturen, Kondensationsmittel usw. angewandt. Infolgedessen sind die erhaltenen Kunststoffe in den allermeisten Fällen Gemische der verschiedensten Kondensationsstufen.-
3.) Wertvoll und für die Kondensationsreaktion bemerkenswert ist die Möglichkeit, beliebige Kondensationszwischenstufen abfangen und diese gegebenenfalls unter bleibender Verformung bis zur Endstufe, sei es als Pressfertigung, Giessharz oder unschmelzbaren Lacküberzug, ausreagieren lassen zu können. Auch Mischkondensate lassen sich aus den verschiedensten Vorkondensationsprodukten herstellen.-

Typische Kondensationsprodukte aus der Reihe der 2-dimensionalen linearen Hochpolymeren sind beispielsweise die Thiokole aus $ClCH_2CH_2Cl + Na_2S_{4,5}$, die Superpolyamide, die man durch Kondensation aus Adipinsaure und Hexamethylendiamin mit einem Mol.Gew. von lo-2o ooo herstellt; ferner, um nur einige Beispiele aus der Gruppe der wichtigsten 3-dimensionalen, d.h. der völlig vernetzten Kunststoffe, zu nennen, die ausgehärteten Bakelitharze, die Harnstoffformaldehydharze, die Glyptale u.a.m.-

Zum Unterschied von dem Kondensationsverfahren ist das Wesen der Polymerisations-Reaktion:

1.) die scheinbar glatte Aneinanderlagerung vieler Moleküle (bis zu ca. 5000 im linearen Aufbau) monomerer Verbindungen zu dem hochmolekularen Polymerisat. Dieses besitzt die gleiche prozentuale Zusammensetzung wie das Monomere. Die Polymerisation ist eine außerordentlich empfindliche Reaktion, die aller Wahrscheinlichkeit nach durch eine Verschiebung eines aktivierten Wasserstoffatoms von Molekül zu Molekül des Monomeren zustande kommt. Sie verläuft im Gegensatz zur Kondensation äußerst milde. Kinetisch gesehen, ist sie eine reine Kettenreaktion.-

2.) Typisch für die Polymerisationsreaktion ist ferner die Tatsache, daß man immer nur das Endprodukt einer Polymerisation fassen kann und daß es nicht möglich ist, wie bei der Kondensationsreaktion noch reaktionsfähige Zwischenstufen abzufangen bezw. von Di-, Tri- oder Tetrameren auszugehen und diese weiterhin untereinander oder mit dem Monomeren zu hochpolymeren Verbindungen weiter zu polymerisieren. Im Gegenteil, derartige Zwischenstufen wirken sich in isolierter Form oft sogar als Polymerisationsgifte aus, wie dies beispielsweise bei der Polymerisation des Isobutylens zum Oppanol der Fall ist.-

3.) Ein weiteres wesentliches Merkmal der Polymerisation ist, daß man praktisch nur von reaktionsfähigen Vinylverbindungen oder Dienen ausgehen kann und aus diesen entweder gradkettige oder vernetzte Polymere erhält, die alle durch direkte Kohlenstoff-Kohlenstoff-Verknüpfung zustande gekommen sind. Die Mischpolymerisation zweier oder dreier verschiedener polymerisationsfähiger Verbindungen ermöglicht wohl eine weitgehende Variationsmöglichkeit (Igelite, Buna usw.), schließt aber den hochmolekularen Aufbau über Heteroatome praktisch aus. In ganz wenigen Ausnahmefällen sind zwar auch reine Polymerisationsreaktionen über Heteroatome bekannt geworden. Es sei hier auf die Polymerisation stark gespannter Ringsysteme wie z.B. Aethylenoxyd, Aethylenimin und Caprolactam hingewiesen und an die Vulkanisation des Kautschuks erinnert, die man ja auch als Weiterpolymerisation unter Vernetzung zwischen dem linearen Kautschuk-u.dem Schwefelmolekül formulieren muß.-

Obgleich nach diesen beiden Grundreaktionen die verwirrende Fülle unserer Kunststoffe hergestellt wird, mangelte es noch an einer universellen Polymerisationsmethode, die gleichzeitig die Möglichkeiten und die Vorzüge der Kondensations- und der klassischen Polymerisationsverfahren in sich vereinigt, die es also ermöglicht, ausgehend von beliebigen bi- und polyfunktionellen niedermolekularen Verbindungen bezw. von Vorkondensaten bezw. Vorpolymerisaten durch reine Additionsreaktionen beliebige Endstufen bezw. Kunststoffe mit gewünschten Eigenschaften zu erzeugen.-

Eine solche haben wir nun im Jahre 1937 in dem sogenannten Polyurethan-Polymerisations- oder dem Diisocyanat-Verfahren aufgefunden und seitdem weiter ausgebaut.- (Anm. J 59 592 v. 11 Nov. 1937).

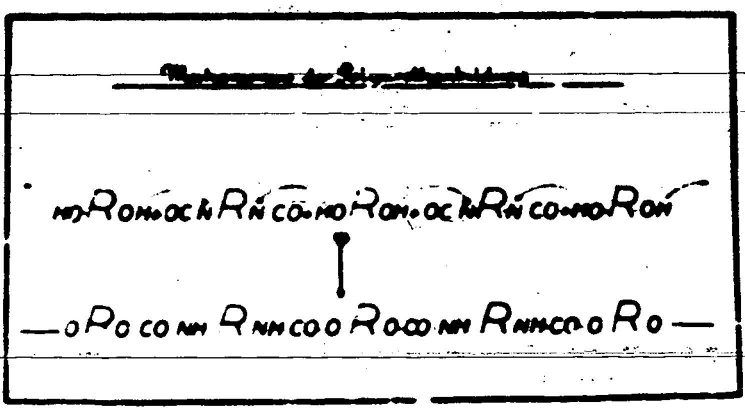
Die Grundlagen des neuen Verfahrens sind folgende:

Wurtz hat bereits im Jahre 1848 gefunden, daß sich

$C_2H_5N{=}C{=}O$ glatt an C_2H_5OH zu $C_2H_5NHCOO\,C_2H_5$

und an $R\,\underset{R_1}{N}H$ zu $C_2H_5NH\,CO\,N\genfrac{}{}{0pt}{}{R}{R_1}$

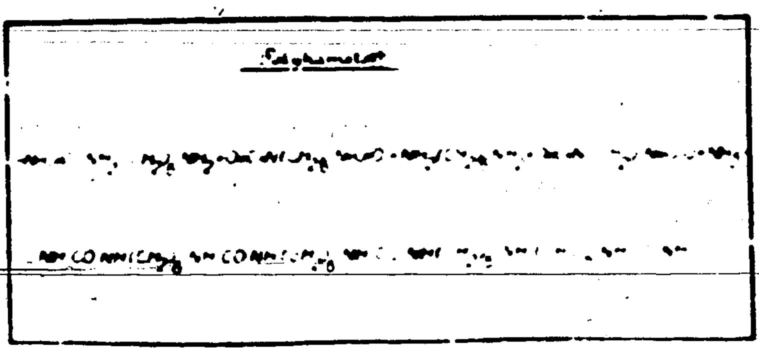
unter Verschiebung des Wasserstoffatoms der Hydroxyl- bzw. Aminogruppe an das Stickstoffatom der Isocyanatgruppe addiert. A.W. Hoffmann bestätigte diese Beobachtungen in der aromatischen Reihe mit dem Phenylisocyanat im Jahre 1849. Wollte man diese quantitativ und unter starken Wärmetönungen verlaufenden Reaktionen für die Kunststoffchemie nutzbar machen, so mußte man Diisocyanate herstellen und diese an Glykole, Diamine, Polyoxy- oder an Polyaminoverbindungen addieren. Sie erkennen bereits an dem einfachsten Reaktionsschema eines Diisocyanats mit einem Glykol, daß hier



eine Reaktion vorliegt, die sich zu der reinen Polymerisationsreaktion weitgehend in Parallele setzen läßt. Ein wesentlicher Unterschied gegenüber den üblichen Polymerisationsverfahren besteht aber darin, daß die Molekülverknüpfungen nicht ausschließlich über Kohlenstoffatome, sondern über die Heteroatome Sauerstoff, Kohlenstoff und Stickstoff zustandekommen und bei der ungeheuren Fülle, allein der Polyoxyverbindungen, eine Anwendungsbreite besitzen, wie man sie bisher weder mit dem Kondensations- noch mit dem Polymerisationsverfahren bestreiten konnte.-

Nachdem nun die Carotherschen Arbeiten über die Superpolyamide bekannt geworden waren, bestand innerhalb der I.G. das vordringliche Problem, etwas Gleichartiges oder noch Besseres zu schaffen, das von den Dupont'schen Patenten unabhängig war.-

Wir haben uns daher zunächst ausschließlich der Addition von Diisocyanaten an Diamine und an Glykole zugewandt, um auf diese Weise hochmolekulare lineare Polyharnstoffe bzw. Polyurethane herzustellen. Dabei stellte sich nun heraus, daß man unter Verwendung langkettiger aliphatischer Diamine und aliphatischer Diisocyanate



[redacted]

nur unschmelzbare und stark hydrophile Polymere erhält, die im Schmelzspinnprozess nicht verarbeitet werden können und demnach auch für die Kunststoffchemie praktisch ausscheiden. Ein auf diese Weise hergestellter basischer Polyharnstoff findet jedoch als Animalisiermittel für Kupferkunstseide technische Verwendung.-

Dagegen erwiesen sich die linearen Polyurethane als recht vielseitig verwendbare Kunststoffe, mit zum Teil noch wertvolleren Eigenschaften, als sie die Superpolyamide besitzen.-

Aus der großen Zahl der hergestellten linearen Polyurethane möchte ich nur einige charakteristische anführen. Technisch am leichtesten zugänglich ist das Polyurethan aus 1.6-Hexandiisocyanat + 1.4-Butylenglykol

[illegible]

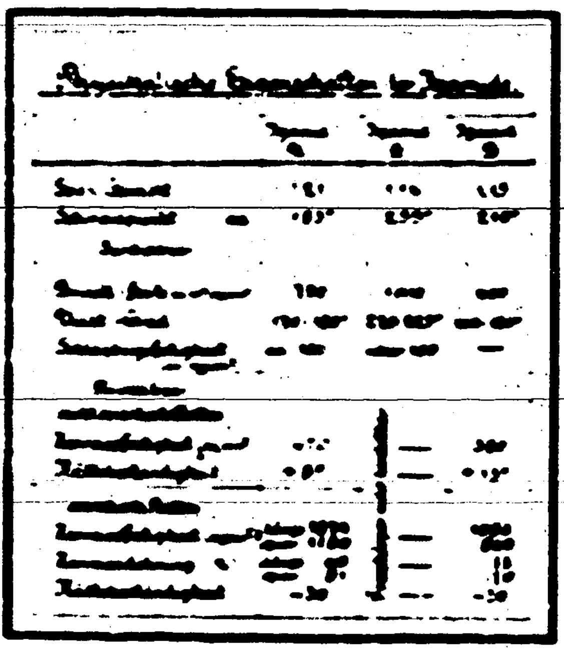
Es erwies sich für die Herstellung von Seide, Kunststoffen und vor allem von Borsten besonders geeignet. Technisch wird es dargestellt durch Addition von 1 Mol reinstem 1.6-Hexamethylendiisocyanat an 1 Mol 1.4-Butylenglykol in Monochlorbenzol-Lösung, wobei die Addition bezw. die Polymerisation unter starker Wärmetönung (5. Kal. pro Mol oder 205 Kal/kg Polyurethan) verläuft. Nach etwa 1-stündiger Reaktionsdauer scheidet sich das Polyurethan als feines, sandiges Pulver in praktisch quantitativer Ausbeute ab. Je nach der Reaktionstemperatur und Verweilen im gelösten Zustand, die man durch Zugabe von Dichlorbenzol usw. einstellen kann bezw. durch Kettenabbruch mit monofunktionellen Verbindungen, hat man es in der Hand, Polyurethane der verschiedensten Polymerisationsgrade zu synthetisieren.

Die Eigenschaften und Unterscheidungsmerkmale eines solchen Polyurethans, das als <u>Igamid U</u> für Kunststoffe mit einem [illegible] von [illegible] und als <u>Perlon U</u> mit einem K-Wert von 55-60 in Form von Seide und Borsten in den Handel kommt, gegenüber Nylon und Perluran-Material sind folgende:

Infolge seiner Darstellung, der Polymerisation im Lösungsmittel und Ausfallen nach Erreichung eines bestimmten Polymerisationsgrades ist das Igamid U polymer einheitlicher als die durch Kondensation erhaltenen Superpolyamide. Dies kommt beispielsweise durch die nahe beieinanderliegenden Erweichungs- und Schmelzpunkte zum Ausdruck.

[illegible] z. Zt. technisch [illegible] verspinnbaren und linearen Superpolymeren besitzt Perlon U den niedrigsten

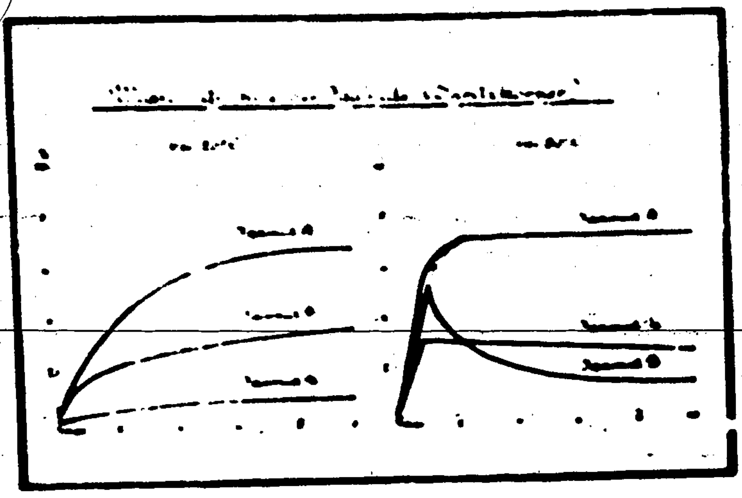
Schmelzpunkt, etwa wie Acetatseide, was fur eine Reihe von textilen Verwendungszwecken unerwunscht ist.-



Die Festigkeiten der aus den Polyurethanen hergestellten Faden und Borsten sind praktisch gleich denen der Superpolyamide. Im Laboratorium wurden mit Perlon U Spitzenfestigkeitswerte bis zu 7.5 g/den. erhalten (Naturseide 3.5 g/den). Es gelingt also auch hier, Faden zu erzeugen, die die Festigkeit von bester Naturseide um uber 100% ubertreffen.-

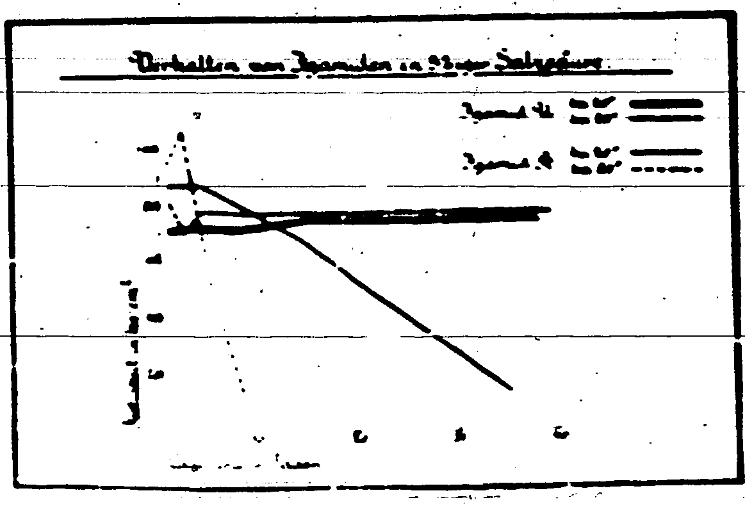
Besonders charakteristisch fur Igamid U und alle ubrigen

- Polyurethane und ihr niedriges Wasseraufnahmevermogen -



Mit steigender CH_2 Gliederzahl in der Polyurethankette vermindert sich zwar das Wasseraufnahmevermogen noch beträchtlich, gleichzeitig sinken aber, da das Molekul immer paraffinähnlicher wird, sowohl Festigkeiten als auch die Schmelzpunkte stark ab.

Auch in den elektrischen Eigenschaften und in der Wetterbeständigkeit sind die Polyurethane den Polyamiden überlegen. Ferner zeichnen sie sich durch eine erhöhte Beständigkeit gegenuber Säuren aus



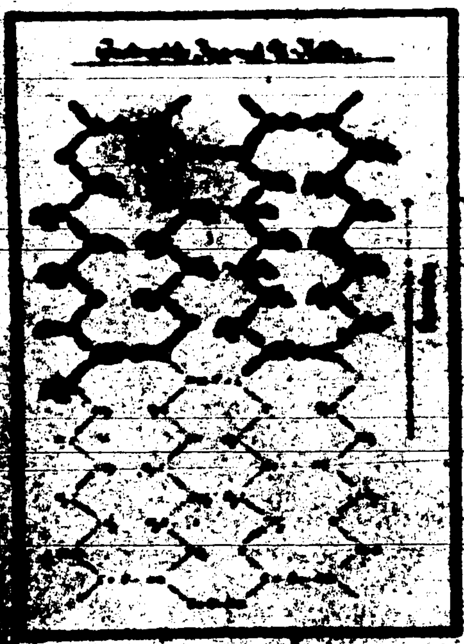
Diese speziellen Eigenschaften in Verbindung mit den übrigen guten Eigenschaften der Superpolyamide machen das Igamid U auch im Kunststoffsektor zu einem wertvollen, hochschmelzenden Thermoplasten. Die daraus hergestellten Spritzlinge sind gegenüber Wasser und Luftfeuchtigkeit unempfindlich und vor allem maßhaltig. All diese Eigenschaften werden dem Igamid U bezw. Perlon U im technischen Sektor eine Reihe von Spezialanwendungsgebieten, wie z.B. in der Herstellung koch- und säurefester Filtertucher, Säure- und lostbestandiger Anzüge, Treibriemen, Taue, Kabelisolierungen usw. erschließen. Auf dem Textilgebiet wird sich beispielsweise das geringe Wasseraufnahmevermögen der Polyurethane für manche Verwendungszwecke, wie z.B. für Unterwäsche nachteilig und für die Herstellung von hydrophoben Damenstrümpfen vorteilhaft auswirken.-

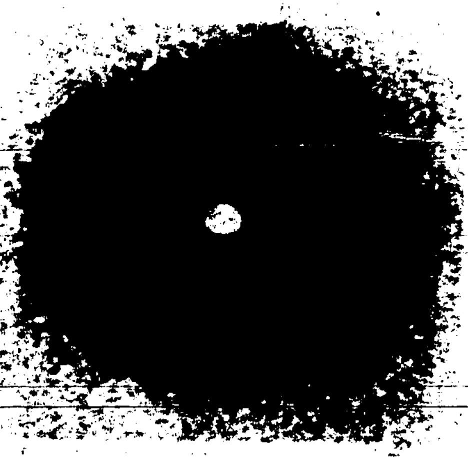
Perlon U stellt infolge seiner Härte, seiner metallsaitenähnlichen Elastizität und seiner Unempfindlichkeit gegenüber Feuchtigkeit im Temperaturbereich bis zu ~ 6o° ein wertvolles Material zur Herstellung von Borsten und Rosshaar dar.- Auch in seinem färberischen Verhalten unterscheidet sich Perlon U von den Superpolyamiden; da es keinerlei basische Gruppen enthält, ist es auch nicht wie diese mit sauren Farbstoffen, sondern nur noch mit Acetatseide- bezw. Suspensionsfarbstoffen anfärbbar. Infolge des Fehlens basischer Gruppen ist Igamid U auch in der Schmelze gegen Luftsauerstoff ganz erheblich unempfindlicher als die Superpolyamide, sodass eine Bräunung des Materials beim Aufschmelzen, Verspritzen und Verspinnen auch bei unvollständigem Luftausschluß nicht eintritt.-

In seinen übrigen physikalischen Phänomenen und seiner Weiterverarbeitung, wie z.B. in seiner Verstreckbarkeit auf über 400% seiner ursprünglichen Länge unter Orientierung der Molekülketten, seiner bleibenden Verformung unter Einwirkung von kochendem Wasser unter gleichzeitiger starker Spannung (board setting), ähnelt es weitestgehend den Superpolyamiden.-

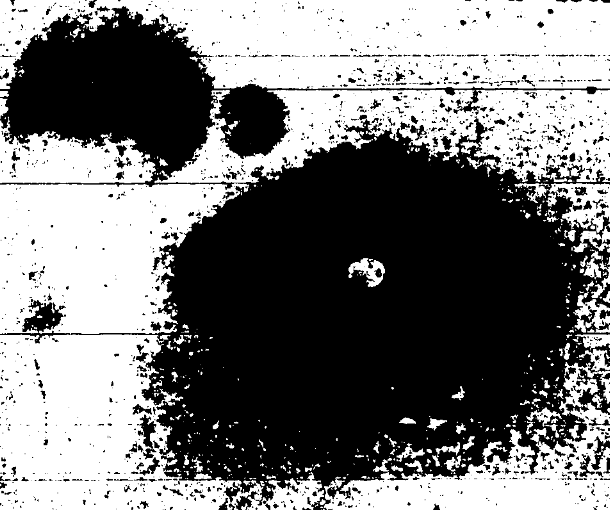
[illegible]

[illegible]





a) im unorientierten Zustand



b) im orientierten Zustand

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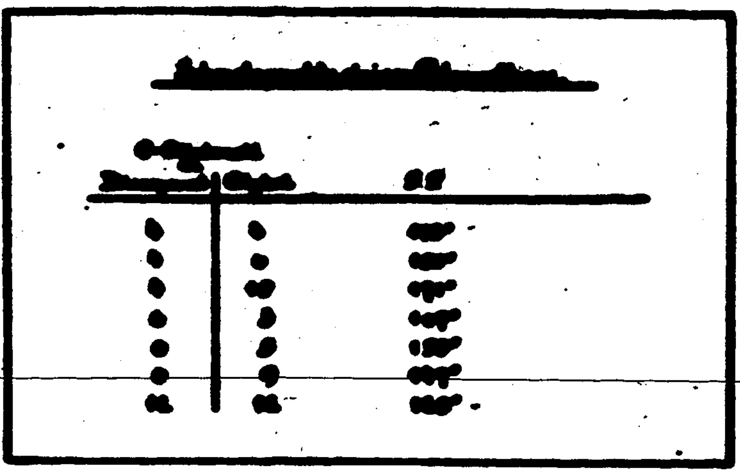

[illegible]

[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]
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Polyurethan-Ketten

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Polyurethan Ketten

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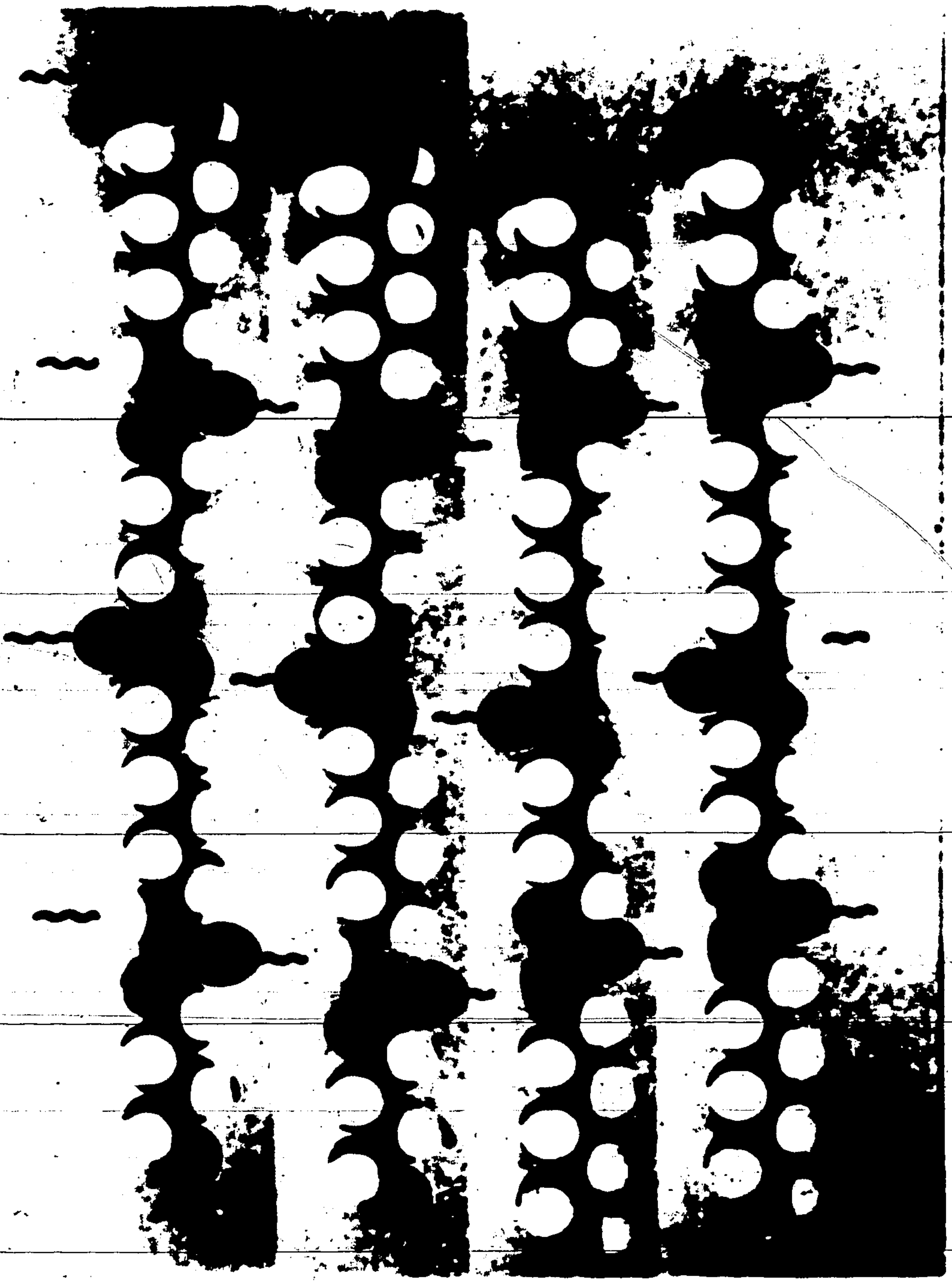


Das verspinnbare Polyurethanmolekül besitzt eine etwa 25 mal so große Kettenlänge als obiger Ausschnitt

13-B

Ausser diesem Igamid U bezw. Perlon U werden noch folgende Typen technische Bedeutung erlangen :

Das Polyurethan aus dem 1.4-Butan-diisocyanat + 1.4-Butylenglykol. Es besitzt praktisch die gleichen Eigenschaften wie Igamid U, schmilzt jedoch um 12° höher (F.P. 194°). Wahrscheinlich wird es auch billiger als Igamid U einstehen und uns durch die Totalsynthese des 1.4-Diaminbutans aus Acetylen und Blausäure unabhängig von der Phenol- bezw. Benzolbasis machen.-

Von diesen einheitlichen Polyurethanen, die in ihren niederen Gliedern in allen Lösungsmitteln in der Kälte völlig unlöslich und nur in einem Phenol-Wassergemisch (9o:lo) löslich sind, unterscheiden sich die Mischpolyurethane, die unter Verwendung eines Gemisches der Glykol- oder der Diisocyanat-Komponenten hergestellt werden, durch ihre gute Löslichkeit in Chlorkohlenwasserstoffen, sogar schon in der Kälte, einen niedrigeren Schmelzpunkt, ein größeres thermoplastisches Bereich, größere Weichheit und bessere Verträglichkeit mit Weichmachern.-

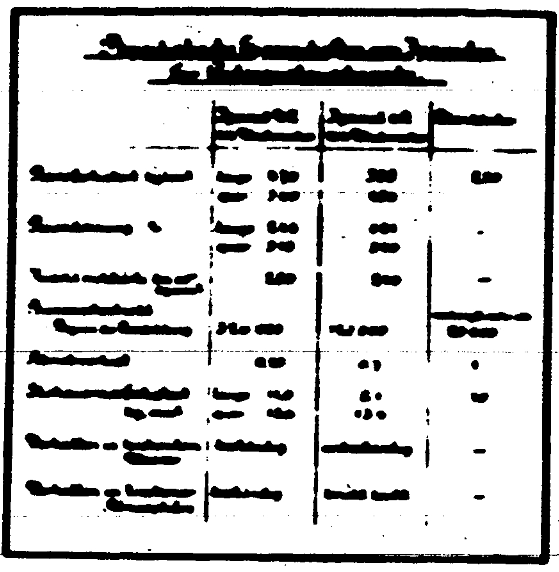
Sie sind damit die gegebenen Materialien zur Herstellung von Filmen, Folien und Lederaustauschstoffen.-

Ein Igamid U, in dem nur lo Mol % des Butylenglykols durch Methyl-1.6-hexandiol ersetzt sind, ist erheblich thermoplastischer und infolgedessen auch leichter verspritzbar als das einheitliche Material. Wichtig ist ferner, daß man es ohne Lösungsmittel einfach durch Zusammenschmelzen der Komponenten herstellen kann.-

Es hat sich im großen und ganzen als praktisch gleich herausgestellt, welche Glykole man in Verbindung mit dem billigen 1.4-Butylenglykol mischpolymerisiert. Als Lederaustauschstoff ist Igamid UL, ein Mischpolyurethan, zur Fabrikation vorgesehen, das durch

Zusammenschmelzen von 1 Mol 1.6-Hexandiisocyanat + 1/2 Mol 1.4-Butylenglykol + 1/2 Mol Methylhexandiol erhalten wird. Ein Mischpolymerisat mit ganz ähnlichen Eigenschaften ist beispielsweise aus 1/2 Mol 1.4- + 1/2 Mol 1.6-Diisocyanat und 0,8 Mol 1.4-Butylenglykol + 0,2 Mol Methylhexandiol aufgebaut.-

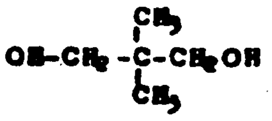
Igamid UL ist ein sehr weiches, in Chloroform-Alkohol-Gemischen leicht lösliches Material In vielen seiner Eigenschaften ist es dem Blank-Leder erheblich überlegen.



Vor den übrigen Igamid-Marken, die als Lederaustauschstoffe in Frage kommen, besitzt es eine etwas höhere L-Festigkeit und vor allem den Vorzug, praktisch unempfindlich gegen Wasser zu sein.

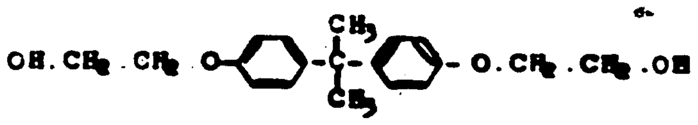
also nicht mehr die Neigung zum Brechen bei extremer Trockenheit bezw. beim Erhitzen in Wasser zu zeigen.-

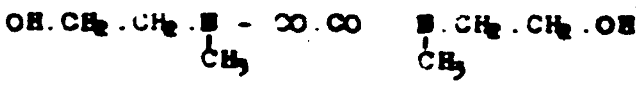
Aufgrund seiner elastischen Eigenschaften ist das Polyurethan aus 1 Mol 1.6-Diisocyanat + 1/2 Mol 1.4-Butylenglykol + 1/2 Mol



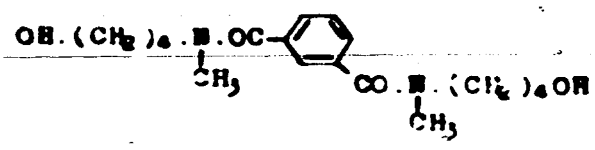
$$OH{-}CH_2{-}\underset{CH_3}{\overset{CH_3}{C}}{-}CH_2OH$$

besonders zum Imprägnieren und Cachieren von Geweben geeignet. Andere interessante Polyurethan-Typen, die sich noch in Durchprüfung befinden, werden zum Teil hergestellt aus den billiger einstehenden aromatischen Diisocyanaten + aliphatischen Glykolen oder aus aromatischen Glykolen mit Heteroatomen, wie z.B.





$$OH.CH_2.CH_2.\underset{CH_3}{N} - CO.CO \quad \underset{CH_3}{N}.CH_2.CH_2.OH$$



oder aus aliphatischen linearen Polyestern mit freien Hydroxylgruppen usw.. Sie werden als Elektroisolierfolien, kochfeste Wursthäute, Trägermaterialien für fotografische Filme und für militärische Zwecke usw. praktische Anwendung finden.-

Im Rahmen dieses zusammenfassenden Vortrages kann ich leider nicht auf die zahlreichen speziellen Verarbeitungs-Verfahren und Anwendungsgebiete fur die Polyurethane eingehen. Nebenbei sei nur erwahnt, daß eine ganze Reihe schwieriger und neuer Probleme bei der Herstellung und Verarbeitung der Polyurethane auftauchten, wie beispielsweise die Herstellung von Polyurethanen mit bestimmten K-Werten, die Stabilisierung des Materials in der Schmelze gegen Weiterpolymerisation und auch Abbau u.s.m. . Es mußten neue Charakterisierungsmethoden, neue Weichmacher, Stabilisierungsmittel usw. geschaffen werden.-

In der Herstellung der Polyurethane und in ihrer Verwendung auf dem Folien- und Kunststoffgebiet sind wir von den Dupont'schen Polyamid-Schutzrechten völlig unabhängig. In ihrer Verarbeitung auf Seide und Borsten ist es uns in Zusammenarbeit mit Dormagen und Wolfen gelungen, Patent-unabhängige Verarbeitungs-Verfahren aufzufinden.-

Die Patentlage in USA ist allerdings noch ungeklart. Dupont hat nämlich, nachdem wir ihm von unseren Arbeiten bereits in einem sehr fruhen Stadium Mitteilung gemacht haben, in USA die Polyurethane ebenfalls zum Patent angemeldet.-

Igamid U wird praktisch nicht teurer als die Superpolyamide einstehen. Dadurch spart die I.G. kunftighin ganz wesentliche Lizenz-Beträge ein. Außerdem werden wir mit den neuen

[redacted]

Materialien auch von den territorialen Bindungen des Polyamid-Vertrages frei werden.-

Die linear aufgebauten Polyurethane sind praktisch alle Thermoplaste, also in der Hitze oder mit Lösungsmitteln bzw. Weichmachungsmitteln verform- und verarbeitbar. Lässt man jedoch Diisocyanate auf Verbindungen mit mehr als 2 reaktionsfähigen Wasserstoffatomen, wie z.B. auf Glycerin, Acetylcellulose, Polyester mit freien Hydroxylgruppen, Polyvinylalkohol usw., einwirken, so entstehen 3-dimensionale Makromoleküle, die sowohl in allen organischen Lösungsmitteln unlöslich als auch unschmelzbar sind. Als solche sind sie für die Kunststoffchemie nur sehr beschränkt verwertbar (Giessharze und nur mit spanabhebenden Werkzeugen bearbeitbar). Will man daher diese, bei der großen Fülle der bekannten Polyoxyverbindungen herstellbaren Kunststoffe praktisch verwerten, so muss man ihre Addition an Diisocyanate während des Fertigungsprozesses vornehmen. Man muss also für die wichtigsten Anwendungsgebiete im Lack- und Kunststoffsektor die beiden Komponenten entweder auf dem zu überziehenden Gegenstand oder unter bleibender Verformung unter Druck, ähnlich den Formaldehydpressmassen, ausreagieren lassen. (Anm.J. 66 687).-

§ Ein Isocyanatlack wird z.B. durch Lösen eines Polyalkohols und eines Diisocyanates etwa im Verhältnis 4:3 der OH- und Isocyanatgruppen in einem hydroxylgruppenfreien Lösungsmittel, gegebenenfalls unter Zusatz von Pigmentstoffen hergestellt. Eine

80363

derartige Lacklösung wird dann aufgespritzt und durch Stehenlassen bei Zimmertemperatur oder durch Erhitzen auf Temperaturen bis zu 160° eingebrannt. Dabei entsteht ein völlig unlöslicher und unschmelzbarer Lacküberzug, dessen Elastizität und Härte man je nach der Verwendung von überwiegend aliphatischen oder aromatischen Komponenten beliebig einstellen kann.-

Selbstverständliche Voraussetzung für diese Arbeitsweise ist natürlich, daß die Reaktionskomponenten bei gewöhnlicher Temperatur nicht schon vorzeitig miteinander reagieren, da sonst die Lacklösungen verqualien. Diese Forderung wird von einigen Diisocyanaten befriedigend erfüllt. Die frisch hergestellten Lösungen sind je nach den Bedingungen und den Ausgangsmaterialien viele Stunden, oft sogar Tage lang, haltbar.-

Es wurde nun weiterhin gefunden, besonders bei Anwendung von organischen Cellulosederivaten, daß die Haltbarkeit durch gewisse "Stabilisatoren" erhöht werden kann. Solche sind z.B. in organischen Lösungsmitteln lösliche Azofarbstoffe und gewisse sauer reagierende Verbindungen, wie Thioharnstoff und seine Derivate (Anm. J. 6/ 162).-

[redacted]

80304

Von den technisch zugänglichen Diisocyanaten kommen folgende für die praktische Verwendung in Frage, die nach ihrer Reaktionsfähigkeit angeordnet sind :

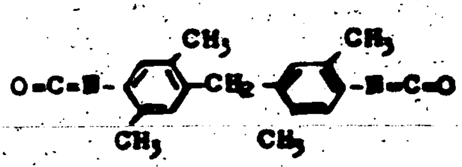
1.) 1-Chlorphenylen-2,4-diisocyanat

2.) m-Toluylendiisocyanat

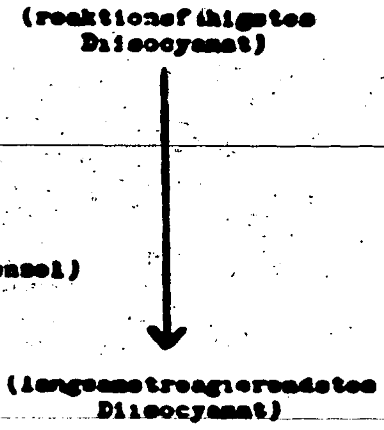
3.) 1.6-Hexandiisocyanat

4.) Diisocyanat aus Dianisidin
F.P.126° (+ 1/2 Mol Krist.-Chlorbenzol)

5.)

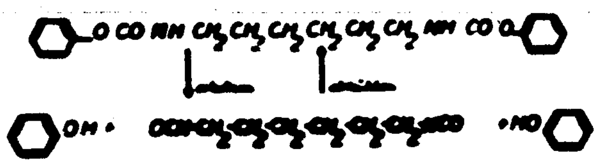


F.P. 129°

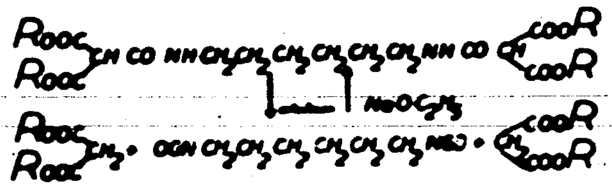


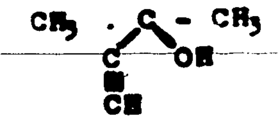
Die Frage der Haltbarkeit von Lackansätzen nach dem neuen Verfahren kann auch von einer grundsätzlich anderen Seite angefaßt werden. Man kann nämlich statt der Diisocyanate auch Verbindungen verwenden, die in der Hitze wie Diisocyanate reagieren, d.h. unter Bildung von Diisocyanaten aufgespalten werden. Es sind das beispielsweise die den Diisocyanaten entsprechenden Bisphenylurethane, die man entweder aus einem Diisocyanat und Phenol oder aus Chlorameisensäurephenylester und einem Diamin gewonnen werden kann.

[illegible]



Auch eine andere Körperklasse ist für den gleichen Zweck verwendbar, es sind dies die Addukte aus Diisocyanaten und Malonester bzw. Acetessigester z.B.



die ebenfalls beim Erhitzen zurückspalten. Andere geeignete, [illegible] additive Addukte lassen sich aus Diisocyanaten + Phenylmethylpyrazolon, Diphenylamin oder  $CH_3 \cdot C(OH)(C \equiv CH) - CH_3$ herstellen.

Weiterhin ist auch aus Hexan-1.6-diisocyanat + 1 Mol Ammoniak ein spaltbares Addukt herstellbar.-

Diese "verkappten Diisocyanate" besitzen den großen Vorteil, daß ihre Lackansätze unbegrenzt haltbar sind. Ja, man kann sogar hydroxylgruppenhaltige Lösungsmittel mitverwenden, da diese meist vorher verdampfen, ehe die Rückspaltung zum Diisocyanat eintritt. Dagegen tauscht man den Nachteil einer höheren Einbrenntemperatur ein und die oft weniger angenehme Tatsache, daß unerwünschte Spaltstücke auftreten. Es zeigte sich aber bei größeren Versuchen, dass z.B. das auftretende Phenol bzw. der entstehende Malonester und seine Zersetzungsprodukte beim Einbrennen mitverdampfen und nicht weiter stören. Mit diesen Mitteln kann man allerdings die Vernetzung besser bis zu einem bestimmten Grad treiben als mit freien Diisocyanaten, da keineswegs die völlig vernetzten Polyurethane immer das Optimum darstellen.-

Aus der riesigen Fülle der billig herstellbaren Polyoxyverbindungen haben sich folgende besonders bewährt :

1.) Ein verseiftes Mischpolymerisat aus 80% Vinylchlorid + 20% Vinylacetat.
2.) Ein durch Vakuumveresterung hergestellter hydroxylgruppenhaltiger Polyester aus ca. 3 Mol Adipinsäure bzw. Thiodipropionsäure, Phtalsäure usw. und [illegible] Mol Trimethylolpropan, 1.2.4-Trioxybutan usw.. Durch Mischen der Säurekomponenten hat man es in der Hand, die Elastizität in weiten Grenzen variieren zu können.
3.) Die Luphene,
4.) Benzylcellulose,
5.) Kondensationsprodukte aus den Esterglykolen gemäß 2 + sauerstoffreiche Xylolformaldehydharze.-

Zusammenfassend besitzen die neuen Lacküberzüge aufgrund eingehender Prüfungen der Lackabteilungen von Le und Lu folgende Vorzuge

1.) gegenuber den Alkydallacken lassen sie sich bei erheblich niederen Temperaturen z.T. sogar schon bei Zimmertemperatur "einbrennen" und kommen daher auch fur eine bisher in dieser Qualitat nicht ausfuhrbare Lackierung von Papier, Textilmaterialien, Leder, Holz, Gummiwaren, Kunststoffen usw. in Frage.-
2.) Sie besitzen eine Variationsbreite in den Eigenschaften, wie sie durch andere Lacke oft nicht zu erzielen ist.-
3.) Sie zeichnen sich durch eine ungewöhnliche Haftfestigkeit auf der Unterlage und durch einen sehr hohen Glanz aus und sind in den meisten Fallen sehr kaltebestandig Wasserfestigkeit und Pigmentbindevermogen, Wetterbestandigkeit und Lösungsmittelbestandigkeit sind hervorragend.-
4.) Da die Diisocyanatgruppen mit allen beweglichen Wasserstoffatomen, die ja die elektrische Leitfähigkeit bedingen, reagieren, weisen die Diisocyanatlacke einen hohen elektrischen Widerstand (spez.Widerstand 10^{15}- 10^{16} Ohm x cm) und auch eine bemerkenswert gute Kriechstromfestigkeit auf, was für die Herstellung von Kabellacken von besonderer Bedeutung ist.-

Nachteilig fur das neue Lackierungsverfahren sind :

1.) die geringe Haltbarkeit der fertigen Lacklösungen. Sie müssen an einem Tag verarbeitet werden.-
2.) Die Verwendung von hydroxylgruppenfreien Lösungsmitteln und der vollige Ausschluß von Wasser.

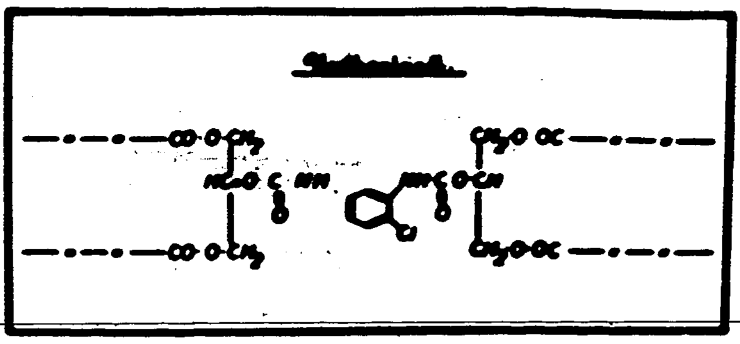
3.) Der bisweilen stechende Geruch der niedermolekularen Diisocyanate

Das gute Haftvermögen, die hohe Elastizität und die Kochbeständigkeit einiger Isocyanatlacke lassen sie besonders als Ueberzüge auf Tiefziehblechen fur Konservendosen geeignet erscheinen. Da die Vernetzung ohne Abspaltung von Reaktionspartnern verläuft, besitzen die Lackuberzüge ausserdem eine hohe Gasdichtigkeit. Bemerkenswert fur die Diisocyanatlacke ist weiterhin ihre gute Lostbeständigkeit, die die des Oppanols sogar noch erheblich ubertrifft. Ein damit imprägniertes Papier (1 m² wiegt 66 g) mit einer Lackeinlagerung von nur 14 g/m² besitzt einen L-Wert von 13 St.(!) nach MR 30 und von 4 St. nach MR 50. Die Erprobung dieser L-festen Papiere und Gewebe wird z.Zt. in grösserem Umfange durchgeführt.-

Unsere Feststellung, daß die Einführung von Urethangruppen den Stoffen eine hohe Wasserfestigkeit verleiht und daß ausserdem die Molekülverknupfung mittels Diisocyanaten ein äußerst mildes Aufbauprinzip darstellt, war fur uns die Veranlassung, unter diesen Gesichtspunkten das so wichtige und schon so oft bearbeitete Problem der Leinölveredlung in Angriff zu nehmen.-

Wir haben einfach Leinol mit der berechneten Menge Glycerin oder Trimethyloläthan zu dem Diglycerid umgeestert und dieses durch Zugabe von 1/2 Mol Chlorphenylendiisocyanat zu einem Molekül vereinigt, das nun 4 trocknende Fettsäurereste enthält.

Formel



Man kann auf diese Weise, je nach dem Grad der Umesterung, Oele mit beliebiger Viskosität herstellen, die nicht wie Leinöl-Standöl und auch gewisse Alkydale den starken thermischen Eingriff des Verkochens bis zu 28o° durchgemacht haben.-

Ein so erhaltenes modifiziertes Leinöl übertrifft das Leinöl-Standöl ganz wesentlich und besitzt nach dem Urteil der Uerdinger Alkydalabteilung Eigenschaften, ähnlich denen des höchstwertigsten Alkydal L extra, vereinigt darüber hinaus in sich sogar die Spitzeneigenschaften aller Alkydale. Vor Alkydal L extra besitzt es u.a. den Vorzug des noch rascheren An- und Durchtrocknens, der höheren Filmelastizität, des schnelleren Erreichens der Wasserfestigkeit, der höheren Verträglichkeit und des nicht Nachdickens mit basischen Pigmenten.-
Nachteilig ist nur seine etwas geringere Lichtechtheit.-

<u>Tabelle</u>

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[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]
[illegible]		[illegible]	[illegible]
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[illegible]	[illegible]	[illegible]	[illegible]

Sobald wieder in größeren Mengen Leinöl zur Verfügung steht, wird Uerdingen die Fabrikation des Urethan-Leinöles im großen Maßstabe aufnehmen, dessen Gestehpreis etwa gleich dem von Alkydal L extra ist.-

Mit diesen Diisocyanatleinölen ergeben sich noch eine Reihe weiterer interessanter Anwendungsmöglichkeiten auf dem Gebiete des Rostschutzes, der Herstellung von Oelseide, Elektroisolierlacken, Spachtelmassen für den Flugzeugbau usw., ja es gelingt sogar in gleicher Weise schlecht trocknende Oele wie Tran, Sardinenöl in rasch- und durchtrocknende umzuwandeln. (Anm. J.67 805 u. J. 68 374).-

Für die Herstellung neuartiger Pressmassen mischt man das Diisocyanat mit der Polyoxyverbindung etwa im molaren Verhältnis der reaktionsfähigen Gruppen, gibt ausserdem noch größere Mengen Füllstoff, wie z.B. Holzmehl usw., zu und lässt die Addition der beiden Komponenten unter Druck und Hitze, ähnlich den Fertigungen aus Bakelit- und Harnstoffpressmassen, vor sich gehen. Unbequem ist auch hier die begrenzte Haltbarkeit der Diisocyanat-Polyalkohol-Gemische. Bei unvorsichtigem Arbeiten reagieren diese schon auf der Walze beim Vermischen miteinander. Man ist daher praktisch nur auf die Verwendung der langsam reagierenden und hochschmelzenden Diisocyanate aus Dianisidin und aus Di-p-xylylidinmethan angewiesen, mit denen man recht beachtliche Resultate in Verbindung mit z.B. einem hydroxylgruppenreichen Polyester aus Adipinsäure und Trimethyloläthan, ähnlich wie er bei den Lackansätzen Verwendung findet, erhält. Bei Presstemperaturen von ca. 140°-160° und einer Pressdauer von 5-10 Min. erhält man daraus Presslinge, die bei höherer Temperatur zwar noch etwas thermoplastischer als ausgehärtete Phenoplaste, dafür aber diesen im wesentlichen Eigenschaften überlegen sind. Ihre Hauptvorzüge sind :

1.) Eine sehr hohe Alkalibeständigkeit,
2.) hoher elektrischer Widerstand von ca. 3-5 Mill. Megohm gegenüber 20 000 Megohm bei Bakelit,
3.) hohe Kriechstromfestigkeit, auch im feuchten Zustand,
4.) wesentlich leichtere Fliessbarkeit als die Bakelitmassen, was nach Angabe von Troisdorf die Fertigung von Presslingen bis zum 3fachen Gewicht der bis jetzt herstellbaren Phenol-

[redacted]

Formaldehyd-Presskörper gestatten wird.

Pressmassen aus 1 Teil [illegible] + 1 Teil [illegible]		Schlagbiegefestigkeit in cmkg/cm²	Biegefestigkeit in kg/cm²	Kugeldruckhärte in kg/cm² bei 1[illegible]	bei [illegible]	Martens Grad.
3 Mol Adipinsaure [illegible] Mol Trimethylolpropan	[illegible] 12 D-[illegible]in	1[illegible]	26[illegible]	17	4[illegible]	2[illegible]°C
	[illegible],6 Hexamethylendiamin	1[illegible]	34[illegible]	58[illegible]	[illegible]	[illegible]
	m-Toluylendiamin	12,[illegible]	911	1215	117[illegible]	6[illegible]°C
2,5 mol Adipinsaure 0,5 mol Phthalsaure 4,1 mol trimethylol propan	Dianisidin	13,5	1367	1590	1530	74°C
3 mol-Adipinsaure 4.2 mol 1,2,4 tri-oxybutan	Dianisidin	14,5	1170	1380	1280	55°C
3 mol-thiodipropionsaure 4 mol trimethylolpropan	m-Toluylendiamin	13,1-	1110	1580	1520	50°C
Phenoplast Typ-S		6	700	1300	-	125°C
Schnitzel Bakelit Typ-Ts		12	600	1300	-	125°C

5.) Die wichtigste Eigenschaft der neuen Materialien aber ist ihre hohe Elastizität, die sich in der erhöhten Schlagbiegefestigkeit äußert. Damit dürfte das wichtige Problem der Schaffung des sogenannten "elastischen Bakelits" gelöst sein. Aehnlich wie auf dem Lackgebiet hat man auch hier die Möglichkeit, durch Verwendung vorwiegend aliphatischer Komponenten weiche und hochelastische Materialien und unter Heranziehung von vorwiegend aromatischen Ausgangsmaterialien härtere und sprödere Presslinge zu erzeugen. Sogar eine erhebliche Vereinfachung des Hitze-Druckfertigungs-Verfahrens scheint möglich zu sein: Sie besteht, ähnlich dem Brennen von Porzellan, darin, daß man die Pressmischungen kalt verformt und dann ohne Druck im Ofen "ausbackt". Die Vernetzung verläuft derart schnell, daß keine Deformation und Maßänderung eintritt. (Anm.J. 69 444.)-

Derartig stark vernetzte Polyurethane werden z.Zt. in erster Linie Verwendung zur Herstellung tragender Konstruktionsteile für Flugzeuge finden und die Fertigung von bestimmten großen Spezialkörpern gestatten, bei denen Metall nicht verwendet werden kann und Bakelit auf Grund seiner geringeren Festigkeit und Sprödigkeit nicht genügt. Auch auf dem Gebiet der Fernmeldetechnik werden sich neue interessante Anwendungsmöglichkeiten ergeben.
Da die neuen Pressmassen ebenfalls eine ausgezeichnete Haftfestigkeit auf den sie umhüllender Materialien besitzen, eignen sie sich nach Befunden von Troisdorf unter vielen anderen auch ausgezeichnet zur Herstellung von hochwertigen Schleifscheiben, ein großes und wichtiges Anwendungsgebiet, auf dem z.Zt. noch die Bakelitgesellschaft mit ihren Formaldehydpressmassen unter Zusatz von Furfurolderivaten ein Monopol besitzt.-

Aus der großen Zahl der billig zur Verfügung stehenden Polyoxyverbindungen haben wir auch die Vernetzung des Cellits eingehender untersucht, der sich mit Diisocyanaten ebenfalls zu unschmelzbaren und heiss aus der Form ausfahrbaren Presslingen verarbeiten lässt. Auch hier wird sich ein bedeutendes Anwendungsgebiet eröffnen.-

An dieser Stelle sei eingeschaltet, daß man mit Hilfe der Diisocyanate auch die unlösliche und unschmelzbare Acetatseide herstellen kann. Da Cellit aus alkohol-acetonischer Lösung versponnen wird, geht man zweckmässig von den bereits bei den Lacken erwähnten Abspaltern aus, die beim Erhitzen des Fadens auf ca. 130° in die Diisocyanate übergehen und dann die langen Celluloseketten völlig vernetzen. Das Verfahren befindet sich z.Zt. bei der Aceta, mit der die Versuche gemeinsam durchgeführt wurden.

in Durchprüfung (Anm. J.67 163).-

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Außer mit den reaktionsfähigen Wasserstoffatomen der Hydroxyl- und Aminogruppen reagiert die Isocyanatgruppe auch noch, wie Wurtz ebenfalls schon im Jahre 1848 gefunden hat, mit der Carboxylgruppe, z.B.

$$CH_3.COOH + O=C=N.C_2H_5 \longrightarrow CH_3.CO.NH.C_2H_5 + CO_2$$

wobei unter Abspaltung von Kohlensäure das Säureamid entsteht. Diese Reaktion lässt sich nun zur Herstellung neuartiger und hochfester Schaumstoffe ausnutzen. Bringt man beispielsweise einen Polyester aus einer Dicarbonsäure + einem 3-wertigen Alkohol, der sowohl noch freie Hydroxyl- als auch Carboxyl-Gruppen enthält, mit einem Diisocyanat zusammen, so tritt bereits in der honigartigen Masse bei 50° eine Reaktion unter Entstehung von Urethan- und Carbonamid-Brücken bei gleichzeitiger Kohlensäureabspaltung ein. Dadurch wird die zähe Masse wie ein Kuchenteig aufgetrieben und erhärtet unter der weiter fortschreitenden Vernetzung immer mehr und mehr. Man hat es so in der Hand, Schaumstoffe mit sehr hohen Festigkeiten und jedem gewünschten Elastizitätsgrad herzustellen. Ein Material, das beispielsweise eine Druckfestigkeit von ca. 10 kg/cm³ bei einer genügenden Wärmebeständigkeit bis zu 100° besitzt, wird hergestellt aus : Toluylendiisocyanat + einem Polyester aus Oxalsäure, Adipinsäure und Trimethyloläthan, spez. Gew.: unter 0,1. (Anm.J. 69 394).-

Für derartige Leichtstoffe besitzt heute die Luftwaffe zur Herstellung von unsinkbaren Flugzeugteilen das allergrößte

Interesse. Auf Grund seiner hohen Festigkeit kann der Schaumstoff gleichzeitig auch als tragendes Konstruktionsmaterial mit benutzt werden. Er ist hierin dem von den Amerikanern verwendeten Balsa-Holz oder gar den Iporitmassen bei weitem überlegen. Auch zur Kälteisolation von Behältern ist das neue Schaummaterial gut brauchbar.-

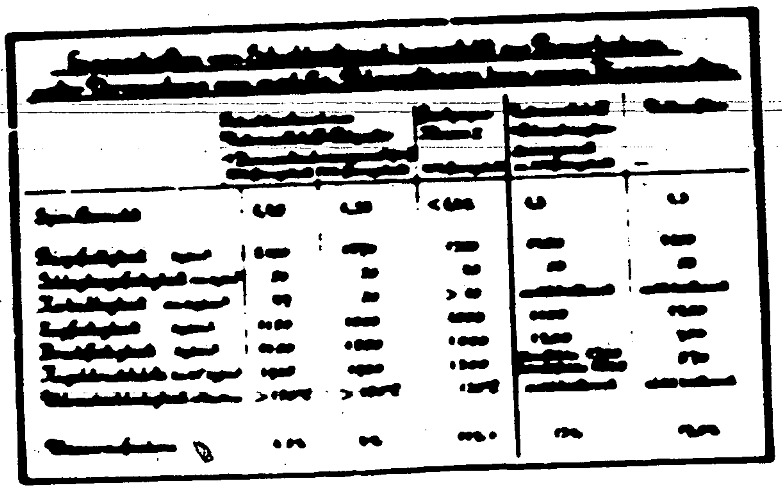
Als wir nun auf dem Kautschukgebiet versuchten, die Vulkanisation des Bunas mit Schwefel durch die Addition von Diisocyanaten an hydroxylgruppenhaltige Bunamischpolymerisate bezw. OH-Gruppen enthaltende Polyisobutylene zu ersetzen, machten wir die interessante Feststellung, daß bereits auch Buna S mit Diisocyanaten einen ausgesprochenen Vulkanisationseffekt ergibt. Ob dafür der geringe Sauerstoffgehalt des Buna oder reaktionsfähige Doppelbindungen bezw. CH_2-Gruppen verantwortlich zu machen sind, konnte noch nicht geklärt werden. (Fumarsäureester reagieren jedenfalls mit Isocyanaten !) Wir machten aber bei dieser Gelegenheit weiterhin die wertvolle Beobachtung, daß derartige "Vulkanisate" ausserordentlich fest an den Metallteilen der Vulkanisierpresse hafteten. Die praktische Auswertung dieses Phänomens bescherte uns nun das schon lange gesuchte Haftmittel für Buna auf beliebigen Unterlagen. Wie die eingehenden Arbeiten unseres Kautschuk-Laboratoriums ergaben, lassen sich mit Hülfe von Diisocyanaten temperaturbeständige Haftungen von normalen Buna-Schwefelmischungen auf Eisen, Leichtmetallen, Porzellan usw. mit Festigkeiten bis zu 80 kg/cm² erzielen (d.h. der Buna reißt in sich und nicht an der Klebestelle !) Besonders bewährt haben sich hierfür die Diisocyanate des m-Toluylendiamins und des Hexamethylendiamins, die als Vulkollan T bzw. H bereits im Handel sind. Nur mit ihrer Hülfe ist es heute beispielsweise ohne die Mitverwendung von Naturkautschuk möglich, die Gleiskettenpolster für Tanks und die hochwertige Verklebung von gummierten Stoffen durchzuführen. In Leverkusen wird z.Zt. sehr intensiv an dem Problem gearbeitet, mit Hülfe dieser Vulkollane einen Reifen aus Metallcordfäden und Kautschuk aufzubauen, was bisher hauptsächlich wegen der geringen Haftfestigkeit zwischen Gummi und Metall nicht möglich war. Gelingt die Lösung dieses wichtigen Problems, so wäre damit der hochwärmebeständige und vor allen Dingen der beliebig oft neu protektierbare Reifen, z.B. für den Volkswagen, geschaffen.-

Das gute Haftvermögen von Buna-Diisocyanatgemischen gestattet auch die Herstellung eines von der Gothaer Waggonfabrik vorgeschlagenen neuen Konstruktionsmaterials für Flugzeuge, das aus einer verschweißten dünnen Platte aus Vulkanfiber und Leichtmetallblech besteht. Die so hergestellte Verklebung reisst eher im Vulkanfiber bzw. im Metall als an den Verklebungsstellen. Dieses Material, das also außen aus Leichtmetall und innen aus Cellulose besteht, gestattet nun, ein Metallflugzeug nach der Holzbauweise herzustellen !! Dadurch würden bei dem Bau eines schweren Bombers etwa 2/3 der bisher erforderlichen Arbeitsstunden eingespart werden. Gleichzeitig weist der neue Werkstoff eine höhere Beschußsicherheit als das Leichtmetallblech ohne Unterlage auf.- Nach dem Kriege wird dieses Konstruktionsmaterial auch im Karosseriebau Verwendung finden.- Auch aus Vulkanfiber mit Bunaüberzug lässt sich ein interessanter Werkstoff aufbauen, der zur Herstellung von Tropenkoffern Verwendung finden soll.-

Weitere wichtige Anwendung finden die Buna-Isocyanathaftungen z.B. auf dem Gebiet der neuartigen Bunafederkonstruktionen.-

Dieser Erfolg auf dem Gebiet der Bunahaftung regte natürlich auch zu Versuchen an, die Diisocyanate ganz allgemein auf ihre Eignung als Klebstoffe durchzuprufen. Dabei stellte sich nun heraus, daß sich mit ihrer Hülfe bisher fur unlösbar gehaltene Klebprobleme lösen lassen. So gelingt es beispielsweise schon in der Kälte, Oppanolfolie mit Eisen oder Holz unter Mitverwendung eines Polyesters als Bindemittel festhaftend zu verkleben und die Verschweissung von dünnen Vulkanfiberfolien zu dicken Platten durchzuführen, die den sonst nur in mehrjährigem Arbeitsprozess herstellbaren dicken Vulkanfiberplatten durchaus entsprechen.-

Die Verklebungen von Papierbahnen mit Diisocyanaten allein oder zusammen mit einem Polyalkohol ergeben ein Schichtmaterial, das in all seinen Eigenschaften dem Vulkanfiber durchaus ebenbürtig ist.-



Ja es gelingt sogar, Metall auf Metall sehr fest aufzukleben, was wiederum für die Serienherstellung von Flugzeugen von großer Bedeutung ist.-

[illegible]		
[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	"
[illegible]	[illegible]	"
[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	"
[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]

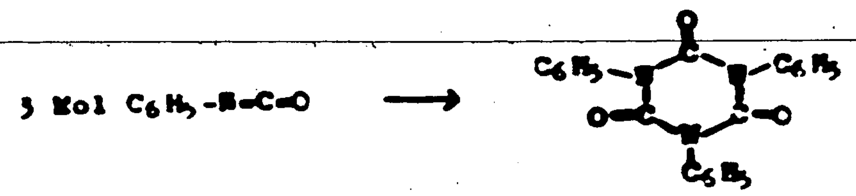
[illegible]

Den Chemismus dieses eigenartigen Klebeeffektes erklären wir uns so, daß die Diisocyanate

1.) auch mit den auf Metalloberflächen haftenden Oxydhydratschichten reagieren, dadurch blanke Oberflächen schaffen, an denen die Harnstoffgruppen mit den Restvalenzen des Metallgitters möglicherweise eine chemische, zumindestens eine Nebenvalenz-Bindung eingehen,

2.) daß sie in den allermeisten organischen Stoffen löslich sind und daß sie

3.) unter der Einwirkung von Metall- besonders Eisen-Verbindungen oder basischen Stoffen wie Phenolaten und Pyridin leicht zu hochmolekularen Stoffen polymerisieren, wobei viele untereinander verknüpfte und stark vernetzte Triazinringe entstehen. Bereits das monofunktionelle Phenylisocyanat geht ja leicht in das entsprechende trimere Produkt über.-



Mit Hilfe der Diisocyanate konnten wir auch das Problem der Herstellung eines Animalisiermittels für Kupferseide befriedigend losen. Auf Grund eingehender Vorarbeiten sind wir zu der Erkenntnis gekommen, daß ein Animalisiermittel, das Cellulosefasern mittels saurer Farbstoffe tongleich mit Wolle anzufärben gestattet, folgende Eigenschaften besitzen muß :

1.) Sehr hohe Molekülgröße mit bereits ausgesprochenem Absorptionsvermögen.

2.) Der für das Säurebindevermögen verantwortliche basische Stickstoff darf nicht mehr als etwa 3% im Molekül ausmachen.

3.) Vollige Unlöslichkeit aller Salze auch in kochendem Wasser.

4.) Völlige Farblosigkeit, beim Belichten darf keine Bräunung auftreten, und die Lichtechtheit der sauren Farbstoffe darf nicht beeinträchtigt werden.

5.) Das Animalisiermittel muss in möglichst feiner Verteilung vorliegen.

Wir haben daraufhin ein Pigment herausgearbeitet, daß aus einem basischen Polyharnstoff besteht, der durch Mischaddition von Chlorphenylendiisocyanat + γ-γ'-Di(amidopropyl)-methylamin + beliebigen Diaminen entstanden ist (Amm.J. 64 249).-

Mit unserem Persistolsalz A (Zirkonoxychlorid) + Persistolgrund B (Paraffinemulsion) oder mit dem aus beiden hergestellten Einbadprodukt Persistol E wird auf Textilmaterialien eine bemerkenswert gut waschechte wasserabstoßende Ausrüstung erzielt, jedoch gelingt es auf diese Weise nicht, auch einen gegen Benzinwäsche beständigen Hydrophobiereffekt zu erzielen.-

Die Diisocyanate gaben uns nun die Möglichkeit, sowohl hydrophobe als auch gleichzeitig benzinunlösliche Wachse herstellen. Eine sich in Vorbereitung befindliche, befriedigend wasch- und benzinfeste Persistolgrundierung, die mit Zirkonoxychlorid und etwas Kaurit zusammen angewandt wird, enthält ein Wachs, das aus 1 Mol 1.6-Hexandiisocyanat + 2 Mol eines Gemische höherer Fettalkohole (C_{12}-C_{18}) hergestellt wird (J.68 271. J. 68 279. J. 7o 125).-

Die zur Herstellung der Polyurethane notwendigen Ausgangsmaterialien sind Diamine, Phosgen, Glykole und Polyoxyverbindungen.-

Zur Herstellung der linearen Polyurethane werden in erster Linie das 1.4-Butylenglykol und das Methyl-1,6-hexandiol verwandt. 1.4-Butandiol ist heute nach der Reppe-Synthese aus Formaldehyd und Acetylen sehr billig und großtechnisch zugänglich. Das Methylhexandiol wird durch Hydrierung eines Gemisches der Ester aus Rohmethyladipinsaure hergestellt, wie sie in Leuna bei der Oxydation des Cyclohexanol-Methylhexanol-Gemisches anfallt. Das Dimethyl-1.3-propandiol ist aus Isobutyraldehyd + Formaldehyd und anschliessender Hydrierung technisch ebenfalls leicht zugänglich. Die Einführung weiterer Methylgruppen oder größerer Seitenketten ergibt Linearpolymere, deren Festigkeitseigenschaften und Schmelzpunkte schon sehr stark abfallen.-

Die Ausgangsmaterialien fur die Diisocyanate sind die entsprechenden aliphatischen und aromatischen Diamine, die mit Phosgen in die Diisocyanate

$$COCl_2 + NH_2-R-NH_2 + COCl_2 \longrightarrow O=C=N - R - N=C=O + 4\ HCl$$

ubergeführt werden. Von den aliphatischen gradkettigen Diaminen ist das 1.6-Hexamethylendiamin nach bekannten Verfahren durch Hydrieren von Adipinsauredinitril gut zugänglich. Wir sind jedoch bestrebt, von dem 1.4-Diaminobutan auszugehen, da man dasselbe billiger aus Acetylen und HCN, also unabhangig von der Phenol- und Benzolbasis darstellen kann. Wir haben ja gefunden, daß man Acrylnitril direkt aus Acetylen und Blausäure mit Hilfe von Kupferchlorid-Katalysatoren sehr billig herstellen kann und dass dieses in Gegenwart alkalischer Katalysatoren glatt ein weiteres Mol HCN addiert.-

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[redacted]

Das so entstandene Bernsteinsäuredinitril lässt sich nun unter sehr milden Bedingungen zum 1.4-Diaminobutan hydrieren.-

[illegible]

$$CH{\equiv}CH + HCN \longrightarrow CH_2{=}CH{\cdot}CN \longrightarrow + HCN \longrightarrow$$

$$NC{\cdot}CH_2{\cdot}CH_2CN \xrightarrow[+8H]{} NH_2CH_2CH_2CH_2CH_2NH_2 \longrightarrow$$

$$+ 2COCl_2 \longrightarrow O{=}C{=}N\,CH_2CH_2CH_2CH_2{\cdot}N{=}C{=}O + 4HCl$$

Auf die Herstellung der aromatischen Diamine einzugehen, erübrigt sich, da dieselben ja alt bekannte Farbstoffzwischenprodukte darstellen.-

Für die Ueberführung der aliphatischen Diamine in die Diisocyanate stehen uns verschiedene Varianten der Phosgeneinwirkung zur Verfügung: einmal kann man diskontinuierlich und kontinuierlich das Chlorhydrat der Basen in Dichlorbenzolsuspension mit einer Ausbeute von über 80% der Theorie an reinstem Diisocyanat phosgenieren. Im Betrieb werden wir aber so arbeiten, daß wir die freie Base in vorgelegtes Dichlorbenzol-Phosgen eintragen, wobei wahrscheinlich zunächst das salzsaure Salz des Aminocarbaminsäurechlorids

$$HCl.NH_2(CH_2)_6.NH.CO.Cl$$

entsteht, das sich ohne Schwierigkeiten weiterphosgenieren läßt. Die Reinherstellung der Diisocyanate, die ja sehr empfindliche und leicht polymerisierbare Körper sind, hat anfangs sehr große Schwierigkeiten bereitet.-

Die Ueberführung der aromatischen Diamine in die Diisocyanate gelingt sehr leicht. Die niederen Glieder sind noch destillierbar, während die Diisocyanate mit 2 Benzolkernen im Großen nicht mehr destilliert werden konnen, sich aber in einigen Fällen praktisch quantitativ nach der Phosgenierung aus dem Chlorbenzol abscheiden.-

Wie ich schon erwähnte, werden die Linearpolyurethane etwa zu dem gleichen Preis wie die Polyamide einstehen; bei dem Polyurethanleder, das im Schmelzfluss hergestellt wird, glauben wir sogar die Gestehpreise der mitkonkurrierenden Polyamidmarken unterschreiten zu können. Die Gestehpreise der aromatischen Diisocyanate werden sich zwischen RM 1.8o - 2.3o bewegen, sodaß sich für die Herstellung der hochwertigen Lacke und Pressmassen, von denen ja nur ein Bruchteil aus den Diisocyanaten besteht, gut tragbare Einstandspreise ergeben werden.-

Ich habe Ihnen nun in großen Umrissen die neuen und breiten Anwendungsmöglichkeiten der Diisocyanate aufgezeigt.-
Wenn wir daher heute um die Genehmigung einer Fabrikationsanlage zur Herstellung von zunächst 2oo Moto aliphatischer und 1oo Moto aromatischer Diisocyanate nachsuchen, so dürfte dieser erste Ausbau durch die überraschend vielseitigen Anwendungsgebiete durchaus gerechtfertigt sein und auch nach dem Kriege einen wirklichen Bedürfnis entsprechen.-

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CNO ltr. Op-23-PT,
Serial 327P23,
dated 22 October 1945

80324

TECHNICAL REPORT No. 106-45

THE PREPARATION OF FORMAMIDE AS AN INTERMEDIATE FOR ACRYLONITRIL PRODUCTION AND ACRYLONITRIL FROM ACETYLENE

JUNE 1945

U·S·NAVAL·TECHNICAL·MISSION·IN·EUROPE

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Serial: 490

20 June 1945

[redacted]

From: Chief, U. S. Naval Technical Mission in Europe.
To : Chief of Naval Operations (OP-16-PT).

Subject: U. S. Naval Technical Mission in Europe Technical Report No. 106-45, The Preparation of Formamide as an Intermediate for Acrylonitril Production and Acrylonitril from Acetylene - Forwarding of.

Enclosure: (A) (HW) Copies of subject report.

1. Enclosure (A) is forwarded herewith.

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H. A. SCHADE.

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TECHNICAL REPORT No. 106-45

THE PREPARATION OF FORMAMIDE AS AN INTERMEDIATE FOR ACRYLONITRIL PRODUCTION AND ACRYLONITRIL FROM ACETYLENE

JUNE 1945

U. S. NAVAL TECHNICAL MISSION IN EUROPE

80327

[redacted]

THE PREPARATION OF FORMAMIDE AS AN INTERMEDIATE FOR ACRYLONITRIL PRODUCTION AND ACRYLONITRIL FROM ACETYLENE

1. Summary.

The following information was obtained during an interrogation of Dr. Göggel of the I.G. Farbenindustrie at the Ludwigshafen Plant on 28 May 1945 and interrogation of Dr. Bauman of the I.G. Farbenindustrie Plant at Hüls on 24 May 1945. The products are not novel nor are their end uses. Methods analogous to these, with the exception of the synthesis of formamide, are used in the United States with comparable or better yields. The disclosure here is not intended to suggest that this path for synthesis is better in any way; but is simply to indicate the methods used in Germany. The application to any war effort is remote since these are established products in the United States. Formamide is an intermediate for the preparation of hydrogen cyanide. This compound in turn reacts with ethylene oxide to give ethylene cyanohydrin which is dehydrated to acrylonitril. The only novel part of the synthesis is the production of methyl formate by the addition of carbon monoxide to methanol. The synthesis used at the Hüls plant is the direct addition of hydrogen cyanide to acetylene which gives acrylonitril.

2. Details.

(a) Methyl formate is produced at Ludwigshafen by the addition of carbon monoxide to methanol. A solution of one percent sodium methylate in methanol is used as catalyst. $CH_3OH + CO\ CH_3ONa;\ HC = O - OCH_3$. To this solution, contained in a pressure autoclave, of steel resistant to carbon monoxide attack, carbon monoxide is slowly added. The heat of reaction is large and cooling by means of a brine jacket is used. Carbon monoxide is added up to an ultimate pressure of 200 atmospheres. The temperature is allowed to rise slowly from 30 degrees to 110 degrees centigrade. The reaction is terminated when there is no further absorption of carbon monoxide as indicated by a drop in the pressure on the autoclave. The operation is entirely batch wise. It is imperative that the entering carbon monoxide be dry and free of carbon dioxide. Either of these impurities would attack the catalyst by hydrolysis in the case of water or neutralization to form sodium carbonate in the case of carbon dioxide,

Correct to:

$$CH_3OH + CO = H-\overset{\overset{O}{\|}}{C}-OCH_3$$

(CH_3ONa)

[redacted]

2. Details (a) (Cont'd.)

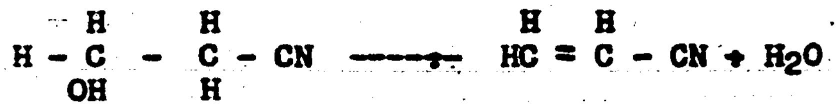
thus precluding further reaction. The crude reaction mixture from this step is subjected to distillation to separate the methyl formate and methanol from the sodium methylate. No attempt is made to separate the alcohol and ester. The yield in this step is approximately 70 percent.

(b) The above mixture of methanol and methal formate is used for the preparation of formamide by the addition of aqueous ammonia. This reaction is quantitive and the products are separated by vacuum distillation. The formamide is recovered in a high state of purity by distillation at 10 to 15 millimeters of mercury absolute pressure after removal of the by-product methanol and water. The formamide is catalytically dehydrated in a vapor phase reaction over activated alumina to yield hydrogen cyanide. The yield in this step is 80 to 90 percent.

(c) Acrylonitril is prepared by the addition of hydrogen cyanide to ethylene oxide to give ethylene cyanohydrin:

$$H_2C\underset{O}{-}CH_2 + HCN \longrightarrow H-\overset{H}{\underset{OH}{C}}-\overset{H}{\underset{H}{C}}-CN$$

(d) The cyanohydrin is dehydrated to acrylonitril according to the following equation:



$$H-\overset{H}{\underset{OH}{C}}-\overset{H}{\underset{H}{C}}-CN \longrightarrow \overset{H}{HC}=\overset{H}{C}-CN+H_2O$$

in a liquid phase batch reaction using 10 to 20 percent anhydrous magnesium carbonate as catalyst. The apparatus is an agitated autoclave to keep the catalyst in suspension and is equipped for removal of the acrylonitril as vapor as rapidly as it is formed. The dehydration starts at about 150 degrees centigrade and the reaction is run to a maximum kettle temperature of the residues of 300 degrees centigrade. The yield from a charge of 200 kilograms of cyanohydrin is about 100 kilograms of acrylonitril. This is 65 to 70 percent of the theoretical yield. The residues, a heavy tar containing the magnesium carbonate are discarded.

(e) Acrylonitril is produced on a very small scale at the Hüls plant

[redacted]

2. Details (e) (Cont'd.)

by the direct addition of hydrogen cyanide to acetylene. This reaction takes place in aqueous medium in the presence of a monovalent copper salt catalyst described by Nieuland in the United States for general reactions of acetylene, especially the dimerization of acetylene to vinylacetylene. The acrylonitril is isolated continuously from the aqueous reaction medium by distillation.

Prepared by:

F.H. ROBERTS,
Technician.

py No. 10.

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Unclassified by
CNO ltr. Op-23-PT,
Serial 327P23,
dated 22 October, 1945.

80330

TECHNICAL REPORT No. 107-45

SYNTHETIC LUBRICATING OILS

JUNE 1945

U·S·NAVAL·TECHNICAL·MISSION·IN·EUROPE

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U. S. NAVAL TECHNICAL MISSION IN EUROPE
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File: A9-16(3)(10/Ms)

Serial: 491

20 June 1945

[redacted]

From: Chief, U. S. Naval Technical Mission in Europe.
To : Chief of Naval Operations (OP-16-PT).

Subject: U. S. Naval Technical Mission in Europe Technical Report No. 107-45, Synthetic Lubricating Oils - Forwarding of.

Enclosure: (A) (HW) Copies of subject report.

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H. A. SCHADE.

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TECHNICAL REPORT No. 107-45

SYNTHETIC LUBRICATING OILS

JUNE 1945

U. S. NAVAL TECHNICAL MISSION IN EUROPE

[redacted] 80333

SYNTHETIC LUBRICATING OILS

1. Summary.

(a) The following information was obtained during an interrogation of Mr. Immhausen, owner, and Dr. Rossow, Chief Chemist, of the Deutsche Fettsaurewerke at Witten on 23 May 1945. This company was requested by the German Navy to prepare a substitute for Camel-Hoof oil, which was being used as a torpedo lubricant. The objection to Camel-Hoof oil was two-fold. Firstly because it was insoluble in water it left an oil streak, and secondly it possessed such a high pour point that it was unsatisfactory for cold weather or arctic operations. To overcome the latter of the two objections the Camel-Hoof oil was diluted with a light mineral oil or rape seed oil. This expedient lowered the pour point at the expense of its lubricating ability. A substitute was made which was simply a fatty acid salt of triethanolamine. The acid used was a mixture of C_6 to C_9 fatty acids of unknown composition. This salt was used in 20 to 40 percent by weight in some water soluble medium such as glycol, diglycol or glycerine. The exact composition depended upon the desired viscosity for a particular use. It is claimed that these compositions can also be used at high temperatures. No additives or stabilizers were ever used in these compositions.

(b) In addition to the above compound the Deutsche Fettsaurewerke was also working on an additive for mineral oil lubricants. The purpose of this additive, used to about 10 percent by weight of the oil, was to raise the viscosity index and lower the pour point temperature of the mineral oil. This additive was made by the esterification of pentaerythritol with a mixture of fatty acids from C_6 to C_{10} molecular weight. The composition of the acid mixture was not known. This ester additive was not used commercially. It was, at the time of the interview, only a laboratory curiosity. For this reason no details of preparation had been decided upon. The technique used in the esterification were standard. A sample of the water soluble lubricating oil for torpedoes was obtained and forwarded to Naval Research Laboratories, Anacostia Station, Attention of Dr. Daniel Fore. This shipment was made on consignment Tag No. 4577.

2. Conclusions and Recommendations.

The claim that the triethanolamine salts of fatty acids can

[redacted]

2. Conclusions and Recommendations (Cont'd.)

be used at high temperatures as a general lubricant would appear to be too broad. The instability of these compounds both to heat and oxidation would indicate that considerably more laboratory work and testing would have to be done before justifiable adoption. In addition to this objection it would appear that any copper or bronze present in the lubricated parts would be subject to preferential corrosion by the amine.

3. Details.

(a) The triethanolamine salt of the C_6 to C_9 fatty acids is made by addition of stoichiometric quantities of amine to acid mixture at room temperature. The reaction, one of neutralization, is instantaneous. The triethanolamine used in the preparation was commercial grade material purchased from Ridael de Haen or Schering-Kahlbaum, both German producers.

(b) The fatty acid esters of pentaerythritol were prepared in the laboratory both with and without a catalyst of sulfuric acid. Preparations were made using an excess of the acid as the agent for removal of by-product water and also experiments were made using totuene as drying agent. The products were the same in either case.

Prepared by:

F.H. ROBERTS,
Technician.

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80335

TECHNICAL REPORT No. 108-45

SYNTHESIS OF ACETONE

JUNE 1945

U·S·NAVAL·TECHNICAL·MISSION·IN·EUROPE

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U. S. NAVAL TECHNICAL MISSION IN EUROPE
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File: A9-16(3)(10/Ms)

Serial: 492

20 June 1945

[redacted]:

From: Chief, U. S. Naval Technical Mission in Europe.
To : Chief of Naval Operations (OP-16-PT).

Subject: U. S. Naval Technical Mission in Europe Technical Report No. 108-45, Synthesis of Acetone - Forwarding of.

Enclosure: (A) (HW) Copies of subject report.

1. Enclosure (A) is forwarded herewith.

H. A. SCHADE.

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[redacted]

TECHNICAL REPORT No. 108-45

SYNTHESIS OF ACETONE

JUNE 1945

U. S. NAVAL TECHNICAL MISSION IN EUROPE

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80338

[redacted]

SYNTHESIS OF ACETONE

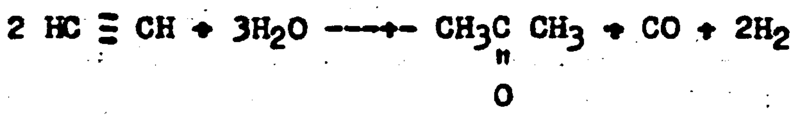
1. Summary.

(a) The following information was obtained during an interrogation of Dr. Sachsee of the I.G. Farbenindustrie Plant at Ludwigshafen, 28 May 1945. The synthesis of acetone from acetylene described here would not appear to be of particular interest to the Navy for use in any war effort, nor would it appear to be of any immediate interest to American industry in view of established methods utilizing raw materials more abundant and less costly than acetylene. It was, however, used on a sufficiently large scale in Germany to merit some comment and the chemistry involved is sufficiently novel that the information should be passed on to interested producers of acetone. The production of this commodity at the Ludwigshafen plant was 400 tons per month.

(b) The raw materials used are acetylene and water. These are passed in vapor phase over a catalyst of pure zinc oxide. Yields and efficiencies to acetone of 80 to 90 percent of the theoretical are claimed for the process. By-products of higher ketones and acetaldehyde are formed which if recovered would raise the efficiency of the consumed acetylene. The methods of operation, however, at the present time made no attempt to recover the by-products.

2. Details.

(a) Acet~~one~~ylene and water react according to the following scheme:



$$2\ HC \equiv CH + 3H_2O \longrightarrow CH_3\underset{\underset{O}{\|}}{C}CH_3 + CO + 2H_2$$

(b) The conditions for the reaction are as follows:

Pressure .... 1 atmosphere.
Temperature .... 400° Centigrade.
Catalyst .... Zinc oxide - pelleted.
Contact time .... Approximately 2 seconds.

80339

[redacted]

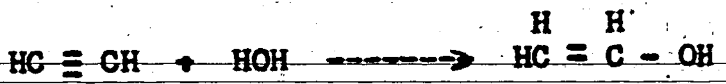
2. Details (Cont'd.)

(c) The converter is ordinary fabricating steel. The feed gas composition for the conversion step is as follows:

Acetylene	10 percent
CO	25 percent
H_2O	55 percent
CO_2	3 percent
N_2	5 percent

The effluent gas from the converters is quenched with water in counter current scrubbers and the product, acetone, from these absorbing towers is recovered as a 3 percent aqueous solution. This solution is charged continuously to stills for recovery of the acetone. Several mechanisms were offered for elucidation of the simple equation shown above. These are given for consideration only and not as a factual representation of the reaction:

(1) a.

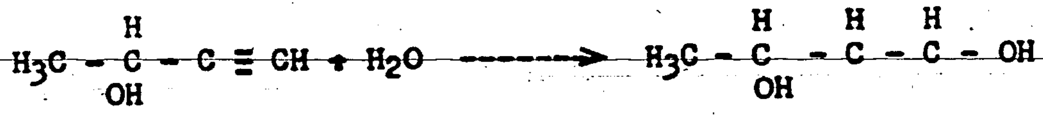


$$HC \equiv CH + HOH \longrightarrow \overset{H}{HC} = \overset{H}{C} - OH$$

b.

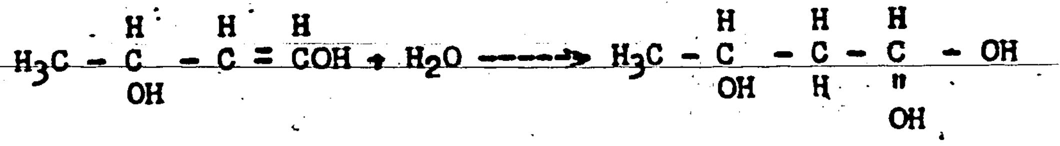
$$\overset{H}{HC} = \overset{H}{C} - OH + HC \equiv CH \longrightarrow \underset{H}{\overset{H}{HC}} - \underset{OH}{\overset{H}{C}} - C \equiv CH$$

c.



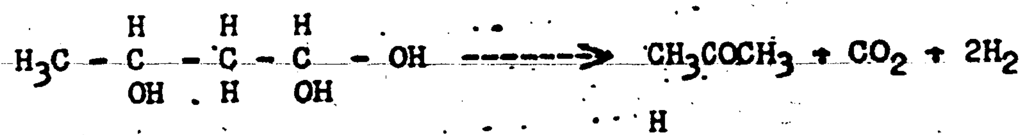
$$H_3C - \underset{OH}{\overset{H}{C}} - C \equiv CH + H_2O \longrightarrow H_3C - \underset{OH}{\overset{H}{C}} - \overset{H}{C} - \overset{H}{C} - OH$$

d.



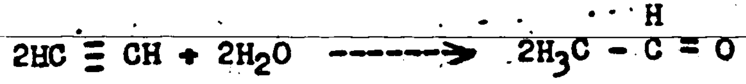
$$H_3C - \underset{OH}{\overset{H}{C}} - \overset{H}{C} = \overset{H}{C}OH + H_2O \longrightarrow H_3C - \underset{OH}{\overset{H}{C}} - \underset{H}{\overset{H}{C}} - \underset{OH}{\overset{H}{C}} - OH$$

e.



$$H_3C - \underset{OH}{\overset{H}{C}} - \underset{H}{\overset{H}{C}} - \underset{OH}{\overset{H}{C}} - OH \longrightarrow CH_3COCH_3 + CO_2 + 2H_2$$

(2) a.



$$2HC \equiv CH + 2H_2O \longrightarrow 2H_3C - \overset{H}{C} = O$$

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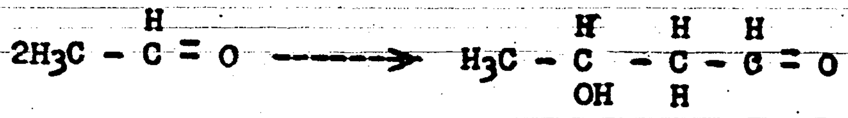
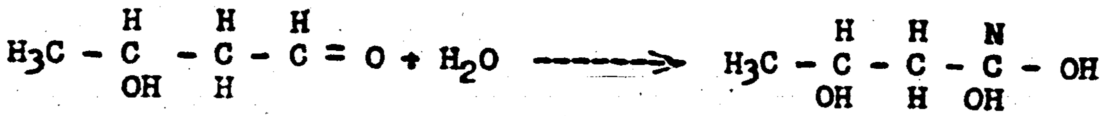
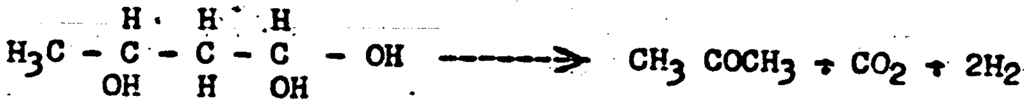
2. Details (c) (2) (Cont'd.)

b.


$$2H_3C-\overset{H}{C}=O \longrightarrow H_3C-\overset{H}{\underset{OH}{C}}-\overset{H}{\underset{H}{C}}-\overset{H}{C}=O$$

c.


$$H_3C-\overset{H}{\underset{OH}{C}}-\overset{H}{\underset{H}{C}}-\overset{H}{C}=O+H_2O \longrightarrow H_3C-\overset{H}{\underset{OH}{C}}-\overset{H}{\underset{H}{C}}-\overset{N}{\underset{OH}{C}}-OH$$

d.


$$H_3C-\overset{H}{\underset{OH}{C}}-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{OH}{C}}-OH \longrightarrow CH_3\,COCH_3+CO_2+2H_2$$

Prepared by:

F.H. ROBERTS,
Technician.

5

No. 14.

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Unclassified by
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dated 22 October, 1945

80341

TECHNICAL REPORT No. 110-45

WARTIME RESEARCH ON SYNTHETIC FUELS BY THE KAISER WILHELM INSTITUT FUR KOHLENFORSCHUNG

June 1945

U·S·NAVAL·TECHNICAL·MISSION·IN·EUROPE

350

U. S. NAVAL TECHNICAL MISSION IN EUROPE
c/o Fleet Post Office,
New York, N.Y.

80342

File: A9-16(3)(10/Ms)

Serial: 509

25 June 1945

[redacted]

From: Chief, U. S. Naval Technical Mission in Europe.
To : Chief of Naval Operations (OP-16-PT).

Subject: U. S. Naval Technical Mission in Europe Technical Report No. 110-45, Wartime Research on Synthetic Fuels by the Kaiser Wilhelm Institut für Kohlenforschung - Forwarding of.

Enclosure: (A) (HW) Copies of subject report.

1. Enclosure (A) is forwarded herewith.

HARRY D. HOFFMAN,
Captain, USN,
Acting.

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80343

TECHNICAL REPORT No. 110-45

WARTIME RESEARCH ON SYNTHETIC FUELS BY THE KAISER WILHELM INSTITUT FUR KOHLENFORSCHUNG

SUMMARY

Wartime research by the Kaiser Wilhelm Institut fur Kohlenforschung on the Fischer-Tropsch synthesis has been primarily directed along the line of iso-paraffin synthesis. Good yields of iso-paraffins have been obtained using the normal synthesis gas at three hundred (300) atmosphere pressure and four hundred twenty (420) to four hundred fifty (450) degrees centigrade over an alumina-thoria catalyst. Zinc oxide-alumina has also been used successfully. About one hundred twenty (120) to one hundred thirty (130) grams per cubic meter of synthesis gas have been obtained as liquid products of over ninety (90) percent iso-paraffins.

Synthesis of aromatics has been studied, using thirty (30) atmosphere pressure and five hundred (500) degrees centigrade. However, very poor yields and napthene side reactions do not make this process look promising. Further work was abandoned by KWI for the duration of the war.

Fischer-Tropsch synthesis using iron catalysts was studied, but inferior operations resulting from this catalyst made it only desirable as a wartime substitute for scarce chromium.

June 1945

U. S. NAVAL TECHNICAL MISSION IN EUROPE

80344

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WARTIME RESEARCH ON SYNTHETIC FUELS BY THE KAISER WILHELM INSTITUT FUR KOHLENFORSCHUNG

1. DETAILS OF RESEARCH

(a) Iso-Paraffin Synthesis

(1) Operating conditions for the synthesis of iso-paraffins have been found to lie in the range of three hundred (300) atmospheres pressure and four hundred twenty (420) to four hundred fifty (450) degrees centigrade. For pressure under three hundred (300) atmospheres the yield falls off rather sharply, although a very slow reaction will take place at thirty (30) atmospheres or over. Higher pressures than three hundred (300) atmospheres give increasingly greater percentages of oxygenated products, until at one thousand (1000) atmospheres the principal product is dimethyl ether. Similarly, lower operating temperatures give slower reaction rates, more unsaturated compounds, a very high percentage of alcohols, and less carbon formation on the catalyst. For temepratures slightly greater than four hundred fifty (450) degrees centigrade, the products become principally napthenic, and carbon deposition becomes excessive. Instantaneous reaction rates, however, are increased.

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840°F

(2) It has been found that the best synthesis gas has a CO/H_2 ration of 1.2 volumes of CO to one (1) of H_2. Increasing the hydrogen increases methane formation; decreasing the hydrogen lowers the overall yield.

(3) The best catalyst found for this synthesis has been an aluminathoria co-precipitated one, although $ZnO-Al_2O_3$ appears to be nearly as good and much cheaper. Using either of these materials it was found necessary to burn off the carbon deposits about every two weeks of steady operation. This was accomplished with air at the temperature of the synthesis (450 degrees centigrade). Catalysts so treated have been used continuously for over six (6) months without appreciable decline in activity. Their heat sensitivity is also quite good, as they have been held for prolonged periods at eight hundred (800) degrees centigrade without damage.

80346

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1. DETAILS OF RESEARCH (a)(cont'd).

(4) Heat evolution during synthesis is approximately the same as with the normal synthesis, i.e. one-fifth (1/5) of the heat of combusion of the products. Since it is possible to work in a twenty (20) to thirty (30) degree centigrade temperature range, this lessens the problem of very close temperature control normally encountered in this process. Another advantage is found in the fact that sulphur does not seem to be nearly as deleterious as in former syntheses, although the upper allowable limit has not yet been determined.

(5) Gas velocities have been fairly accurately studied, and it was determined that twenty (20) cubic centimeters of a two (2) to four (4) millimeter catalyst were necessary for each ten (10) liters of synthesis gas per hour. Any increase above this velocity gave sharp decreases in yield and also tended to form increasing amounts of alcohols.

(6) Product yields are as follows from a $ZnO-Al_2O_3$ catalyst using a CO/H_2 ratio of 1, at three hundred (300) atmospheres and four hundred fifty (450) degrees centigrade:

		wt %
Total yield of C_3 and higher	120 - 130 gm./m^3	17.9 - 19.4
C_3	20 gm./m^3	3.0 - 3.0
C_4 (90% isobutane)	50 - 80 gm./m^3	7.5 - 11.9
C_5 and higher (over 97% iso)	30 - 60 gm./m^3	4.5 9.0

CO = 28
H_2 = 2
15
$15 \times \frac{1000}{22.4} = 670$ gm/m^3

(7) A comparison of the two (2) catalysts shows that for a thoria-alumina catalyst (1:4 by weight) the best yields of all are obtained. Higher gas velocities can be used, and there is little tendency to form alcohols. However, there is a greater tendency to form carbon on the catalyst, meaning shorter burn-off times. Experiments have varied the ratio of the two materials in the catalyst from twenty (20) to forty (40) percent Al_2O_3, with very little change in overall yields. However, increased alumina does increase methane formation somewhat. The addition of one-half (½) to one (1) percent K_2CO_3 to the catalyst will give a slight increase in yield.

80347

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1. DETAILS OF RESEARCH (a) (cont'd).

(8) On the other hand the $\overset{ZnO}{\text{AnO}}$-$Al_2O_3$ catalyst (1:1 by weight) is believed to carry more promise as a commercial catalyst because of its cheapness. It does give slightly less yield than the thoria type, and produces about ten (10) percent alcohols. There is less tendency to form carbon deposits on the catalyst. The same tendency holds true as with thoria catalysts, ie., higher alumina content promotes methane formation. However, experiments have been made over a range of Al_2O_3 content from 2:1 to 1:2 without much change in results. Additions of K_2CO_3 do not appear to give any advantage.

(9) The thoria type catalyst was prepared by using two (2) liters of thorium and aluminum nitrates at their boiling point and in the right proportion to give a 1:4 weight ratio of thoria to alumina. This was added one (1) liter of a boiling Na_2CO_3 solution of proper strength to give one hundred (100) grams of dry co-ppt., in stoiciometric amounts. More dilute solutions gave greater density catalysts. The resultant precipitate was washed, dried, and sized to two (2) to four (4) millimeters.

(10) The same method was used for preparing the ZnO type catalysts, except it was found that the addition of the nitrate solution to the soda solution instead of the normal method gave increased liquid hydrocarbon yields.

(11) An alternate method for preparing thoria catalysts, and the one which gave the best yields, was to make sodium aluminate and then precipitate with sulphuric acid. Thorium hydroxide precipitate was also made, and these two ppts., were washed separately and mixed while wet. They were then air dried at one hundred (100) degrees centigrade and ground to normal size.

(b) Aromatic Synthesis

(1) Aromatics were successfully synthesized by the use of Cr, Mo, Th oxides as catalysts. Five (5) to ten (10) percent K_2CO_3 was added to reduce carbon formation. It also reduced activity. A CO/H_2 ration of 1:1 was used, at thirty (30) atmospheres and five hundred (500) degrees centigrade. Any higher temperature or pressure gave excessive carbon formation on the catalyst, while

[redacted]

1. **DETAIL OF RESEARCH** (b)(cont'd)

lower temperatures gave no aromatics, and reduced the reaction rate. Lower pressure similarly reduced the reaction rate.

(2) The yields were very poor, being only about eight (8) to ten (10) $gm./m^3$ of liquids which were about fifty (50) percent aromatics and fifty (50) percent napthenes. There was lots of methane formed, and much unconverted gas. The aromatics were principally toluene, xylene, and alkyl benzenes. The napthenes were a grand mixture not yet identified.

(3) Because of the poor yields and the excessive carbon formation when working at such high temperatures, the KWI staff had temporarily abandoned this line of research to concentrate on more productive wartime work.

(c) Iron Catalyst Synthesis

(1) The entire staff of the KWI was quite emphatic in stating that the use of iron catalysts in Fischer-Tropsch synthesis was considered only as a wartime necessity because of the shortage of chromium. Cobalt catalysts were stated to be definitely superior, cleaner to use, and capable of operating at lower temperatures. They did not know of a single instance where iron catalysts were actually used in commercial installations, although it had been planned in the event that chromium became unobtainable.

(2) Iron catalysts are prepared by precipitation from its nitrate with soda solution, drying at one hundred ten (110) degrees centigrade, grinding and sizing, and then treatment with 1:1 CO/H_2 gas at reduced pressures (from 0.1 to 1 atmosphere) and two hundred forty (240) to three hundred twenty (320) degrees centigrade. This treatment forms an iron carbide on the catalyst surface, and is continued until a sharp drop in CO_2 content of the exhaust gas indicates cessation of carbide formation. It is generally used in sizes ranging two (2) to five (5) millimeters.

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2. CONCLUSIONS AND RECOMMENDATIONS

The development of the Fischer-Tropsch process as a producer of iso-paraffins, and thus a source of high quality aviation and automotive fuels, opens the way for it to become the most versatile of all synthetic fuel processes. It would then be capable of producing products which range all the way from high quality diesel fuels and lubricants to excellent aviation gasoline. No other process could make such a claim. It is therefore recommended that this information be made available to all interested agencies, and that the work of Dr. Pichler and Dr. Koch of KWI, which is still continuing at the Institute, be closely followed in order to keep American technology as well informed as possible.

3. DETAILS OF SHIPMENTS

Small samples of the thoria-alumina and the $ZnO-Al_2O_3$ catalysts used in iso-paraffin synthesis are being forwarded to Bureau of Ships (Code 341) on Consignment Tag No. 3655. Under the same consignment is also being shipped small samples of n-octane, n-nonane, and n-decane for use in the standardization of mass spectrographic analysis procedure.

Prepared by:

D. R. DEWEY,
Lieut. (jg), USNR

No. 11.

CODE 341 - FILE COPY

U·S·NAVAL·TECHNICAL·MISSION·IN·EUROPE

Unclassified by
CNO ltr. Op-23-PT,
Serial 327P23,
dated 22 October 1945

80350

TECHNICAL REPORT No. 111-45

PREPARATION OF "ALKAZID" M AND DIK

JUNE 1945

U·S·NAVAL·TECHNICAL·MISSION·IN·EUROPE

cc/cy filed in BuShips file

QC/NTME Serial 6280337

U. S. NAVAL TECHNICAL MISSION IN EUROPE
c/o Fleet Post Office,
New York, N.Y.

80351

File: A9-16(3)(10/Ms)

Serial: 502

22 June 1945

[redacted]

From: Chief, U. S. Naval Technical Mission in Europe.
To : Chief of Naval Operations (OP-16-PT).

Subject: U. S. Naval Technical Mission in Europe Technical Report No. 111-45, Preparation of Alkazid M and DIK - Forwarding of.

Enclosure: (A) (HW) Copies of subject report.

1. Enclosure (A) is forwarded herewith.

HARRY D. HOFFMAN,
Captain, USN,
Acting.

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TECHNICAL REPORT No. 111-45

PREPARATION OF "ALKAZID" M AND DIK

SUMMARY

The following information was obtained during interogation of Dr. Pfhanmuller of the I.G. Farbenindustrie Plant at Ludwingshafen on 28 May 1945. Alkazid M and Alkazid DIK are trade names for alkaline agents used to remove carbon dioxide and hydrogen sulfide from manufactured gases, either coke-oven gas or water gas. The M product will absorb hydrogen sulfide and carbon dioxide, the DIK product is used primarily for hydrogen sulfide removal after carbon dioxide has been swept out. The DIK compound, however, will also absorb carbon dioxide,

These alkaline agents are complex condensation products of aldehydes with alkylamines and hydrocyanic acid. The M compound is synthesized from acetaldehyde and methylamine, the DIK compound from formaldehyde and dimethylamine. These agents will absorbe about seventy cubic (70) centimeters of the respective gases per cubic centimeter of thirty (30) percent solution in water. The alkazids are capable of regeneration upon reaching the saturation point by simply heating to one hundred (100) degrees centigrade and dispelling the carbon dioxide or hydrogen sulfide.

JUNE 1945

U.S. NAVAL TECHNICAL MISSION IN EUROPE

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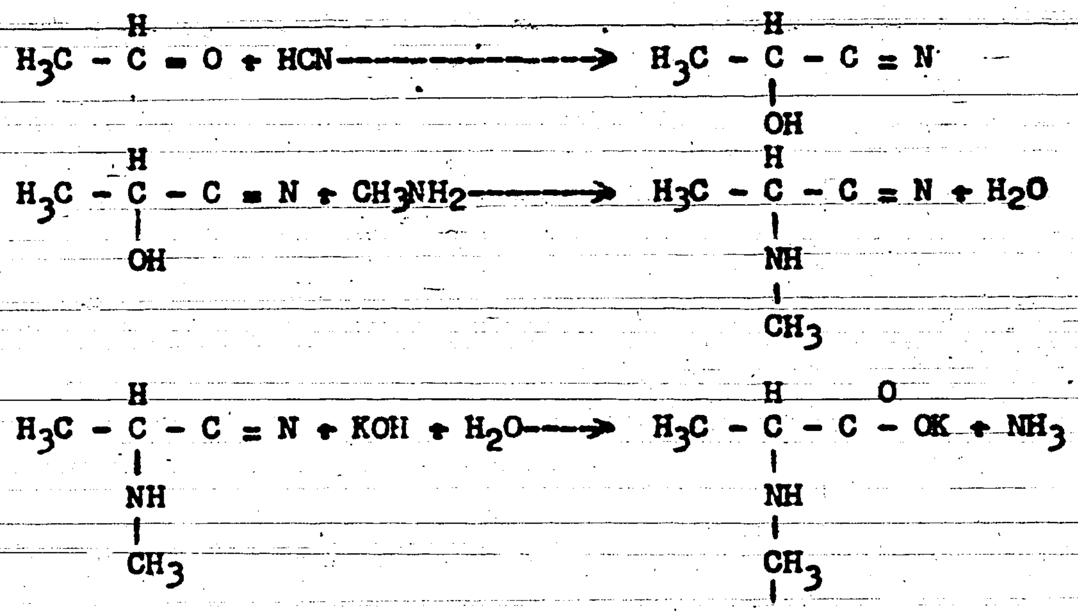
80354 [redacted]

PREPARATION OF "ALKAZID" M AND DIK

1. Details

(a). Attached to this report are detailed operating instructions for the preparation of the alkazids. These insstructions are briefly reviewed here with a schematic presentation of the chemistry involved. For the M compound (potassium N-methylalanin) acetaldehyde, methylamine and hydrogen cyanide are used according to the following scheme:



(1). $H_3C - \overset{H}{C} = O + HCN \longrightarrow H_3C - \underset{OH}{\overset{H}{C}} - C = N$

(2). $H_3C - \underset{OH}{\overset{H}{C}} - C = N + CH_3NH_2 \longrightarrow H_3C - \underset{\underset{CH_3}{NH}}{\overset{H}{C}} - C = N + H_2O$

(3). $H_3C - \underset{\underset{CH_3}{NH}}{\overset{H}{C}} - C = N + KOH + H_2O \longrightarrow H_3C - \underset{\underset{CH_3}{NH}}{\overset{H}{C}} - \overset{O}{C} - OK + NH_3$

ALKAZID - M

For the DIK compound (potassium N - dimethyl glycine) formaldehyde, dimethylamine and hydrogen cyanide are used in a manner analogous to the above scheme.

(b) An iron autoclave equipped with an agitator and brine cooled coil and jacket is charged with a thirty-five (35) percent aqueous solution of the amine. The temperature is adjusted to fifteen (15) to eighteen (18) degrees centigrade and

[redacted]

1. Details (b) (cont'd)

maintained there during the slow simultaneous addition of hydrogen cyanide and the aldehyde. The completion of the reaction is determinded by titration with aqueous silver nitrate solution for free hydrogen cyanide. The nitril thus formed in equations (1) and (2) above is hydrolyzed by the addition of potassium hydroide solution and heating to one hundred and ten (110) degrees centigrade. The concentration of the product is adjusted by distillation under vacuum to remove water and adjust the specific gravity to 1.18 to 1.20 which corresponds to approximately a thirty (30) percent solution.

Prepared by:
F. H. ROBERTS,
Technician

[illegible] 15.3.44 [illegible]

[illegible]-Kohle).

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[illegible] Ltr. Inhalt mit Kühlschlange [illegible] Ltr/Minute, werden zu 200 kg [illegible] bei 15-18° pro Stunde [illegible] 30-35 Vol.%iger Lösung ent- [illegible] in 6 kg H_2O vorgelegt. [illegible] bei 15-18° [illegible] und 30 kg Acetaldehyd pro Stunde [illegible] 2 kg Kalk zu. In etwa [illegible] berechnete theoretische [illegible] %iger Lösung) und die ebenso [illegible] Menge Acetaldehyd (300 kg). [illegible] anschließend zur Acetaldehyd-Ein- [illegible] Zur Kühlung dient Sole aus einer [illegible] 000 WE/Std. von + 5° Temperatur. [illegible] des Acetaldehyd-Zulaufs wird noch 1 Stunde bei [illegible] dabei zu beachten ist, daß die Temperatur nicht [illegible] soll zum Schluß einen Aldehydgehalt [illegible] 3,2 [illegible] kg für 5 ccm Lösung [illegible] wenn er höher ist, wird die entsprechende [illegible] zugesetzt. Fehler entstehen, wenn die Tempera- [illegible] eingehalten wird.

[illegible]

[illegible] mit Dampf- [illegible] spezifischen Gewicht [illegible] 70-75 % d.Th.).

4. [illegible]
[illegible] 3. werden nach Zusatz von 15 kg CaO in einem Rührbe- [illegible] von 10 cbm Inhalt mit Heizschlange auf 105-110° erhitzt. Dann [illegible] 3-4 Stunden bei 110° Dampf oder N_2 durchgeleitet. Durch häufige Probenahme ist festzustellen, daß kein Eisen in Lösung geht, in welchem Falle das Abdampfen sofort zu unterbrechen ist.

Analyse:
Nach 3-4 Stunden Abdampfzeit. Es werden aus einer filtrierten Probe von 1 kg im Glaskolben 750 ccm abdestilliert, die Lösung dann auf 1 Ltr. aufgefüllt und mit n/1 HCl gegen Methylorange titriert. Der Verbrauch soll nicht über 20-30 ccm n/1 HCl pro kg betragen.

5. Aufarbeitung.
Aus der [illegible] anfallenden, auf 25° abgekühlten ca. 3,5 cbm Lösung wird der Kalk durch Einleiten von ca. 30 kg CO_2 ausgefällt, eine Lösung von 35 kg [illegible] vom spez.Gew. 1,362 in 70 kg Wasser und [illegible] 25 kg verbrannten Carboraffin zugesetzt, [illegible] Stunden bei 50-60° gerührt, in einem gummierten Rührbehälter [illegible] ca. 100 kg CO_2 eingeleitet bis zur erhalten-

---

+) Carboraffin [illegible] die schwimmenden Bestandteil.

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alkalischen Reaktion gegen [illegible]papier, dann mit 35 kg [illegible] Carboraffin [illegible] 14 Stunden gerührt, auf ein [illegible] von 1,2 eingestellt und filtriert. (Der Filterrückstand wird wie oben beschrieben einer folgenden Partie als verbrauchtes Carboraffin zugesetzt.)

Fehler: Lauge schäumt. Dann nochmals mit Carboraffin behandel

6. **Produktion** beträgt 3,5 - 4,5 tato.

7. **Analysen** werden wie bei Dik - Lauge D ausgeführt.
Absorptionswert: 70 - 72 ccm CO_2 / 1 ccm Lauge von d = 1,18.
Bei graphischer Darstellung entsteht eine steile Kurve gegen CO_2

Der Korrosionswert soll konstante Werte oder eine geri[illegible]ch zunahme ergeben.

Der Abdampfwert beträgt 20-30 ccm n/1 HCl pro kg.

Freie Blausäure wird wie bei Dik - D - Lauge bestimmt.

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UNCLASSIFIED BY
CNO ltr. Op-23-PT,
Serial 327P23,
dated 22 October, 1945.

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TECHNICAL REPORT No. 115-45

THE ARC PROCESS FOR ACETYLENE PRODUCTION

JUNE 1945

U·S·NAVAL·TECHNICAL·MISSION·IN·EUROPE

U. S. NAVAL TECHNICAL MISSION IN EUROPE
c/o Fleet Post Office,
New York, N. Y.

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File: A9-16(3)(10/Ms)

Serial: 619

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by CNO ltr. OP23 PT.
Serial 327P23 of 23 Oct, 1945

~~RESTRICTED~~

16 July 1945.

From: Chief, U. S. Naval Technical Mission in Europe.
To : Chief of Naval Operations (OP-16-PT).

Subject: U. S. Naval Technical Mission in Europe Technical Report No. 115-45, The Arc Process for Acetylene Production - Forwarding of.

Enclosure: (A) (HW) Copies of subject report.

1. Enclosure (A) is forwarded herewith.

Harry D. Hoffman
HARRY D. HOFFMAN,
Captain, USN,
Acting.
Acting

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TECHNICAL REPORT No. 115-45

THE ARC PROCESS FOR ACETYLENE PRODUCTION

SUMMARY

The "Chemische Werke, Huls", of I.G. Farbenindustrie, in the Ruhr area has been the first successful commercial producer of acetylene by electro-thermal cracking of hydrocarbons in natural and refinery tail gases. The total production of acetylene in this plant has been approximately 200 metric tons per day (97 percent C_2H_2), for further use in synthetic rubber manufacture. The plant is virtually undamaged, and technical information was obtained from Dr. Baumann, chief chemist, who has currently assumed direction of the works.

In that the overall electric power requirements of this process are estimated to be approximately the same as for the carbide process, and in that other factors such as the costs and availabilities of different types of plant equipment, various raw materials and by-products, etc., differ from American industrial economy, it is considered that further detailed economic studies of the process might be desirable on a long-range commercial basis.

JUNE 1945

U. S. NAVAL TECHNICAL MISSION IN EUROPE

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THE ARC PROCESS FOR ACETYLENE PRODUCTION

1. Introduction.

(a) The synthetic rubber plant of I.G. Farbenindustrie at Huls, Germany, has what is believed to be the first successful commercial plant in existence for the production of acetylene by the thermal cracking of low molecular weight hydrocarbons. The plant produced around 200 metric tons per day of a 97 percent acetylene for subsequent use in other parts of the plant in the manufacture of acetaldehyde, aldol, buylene glycol, and butadiene. By-products of the acetylene production were hydrogen, carbon black, and some small amounts of ethylene. The plant is at present time intact and capable of immediate operation as soon as raw materials are supplied. Dr. Baumann, former chief chemist of the plant, has assumed direction of the entire works.

(b) The process in brief consists of high temperature, normal pressure cracking of natural gas using an electric arc, and the subsequent purification of the acetylene by scrubbing it from the gas stream with water at 18 atmospheres. Hydrogen and ethylene are removed from the tail gases by low temperature liquefaction and fractionation, and the remaining gases are recycled to the arc. Carbon black formed in the arc is removed by water sprays, cyclones and bag filters, and is used in the compounding of synthetic rubbers.

(c) The plant formerly operated on a refinery tail gas consisting largely of C_2 and C_3 hydrocarbons. At that time the yields were much superior to the present methane feed stock. However, subsequent bombings so destroyed surrounding refineries that the acetylene plant was forced to the use of natural gas. In the following sections of this report an attempt will be made to describe in detail the operating conditions and equipment used when operating on natural gas, and to point out what differences were encountered when using the refinery tail gas.

2. Arc Converters.

(a) The plant had seventeen (17) pairs of high temperature arc converters for the thermal cracking step. Only ten (10) pairs of these were ever used because of bottlenecks further along the process, and because

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2. Arc Converters (a) (Cont'd.)

of power shortages in the area. Each converter pair was equipped with its own rectifiers, coolers, and minor appurtenances. One converter was operated while the other was shut down for repair or overhaul.

(b) Feed to each arc converter wab 2800 m3/hour of a mixed gas consisting of 50 percent by volume natural gas, and 50 percent by volume recycle gas. The natural gas contained about 92 percent volume methane, 5 percent nitrogen, and 3 percent carbon monoxide. There was about 10 grams of sulfur per cubic meter present in the form of hydrogen sulfide. The recycle gas contained about 85 percent methane, and the balance hydrogen, nitrogen and heavier hydrocarbons. The gas was fed to the arc at normal temperature and around 1.8 - 1.5 atmospheres pressure.

(c) Each arc was powered by a mercury vapor rectifier system operting on 6000 volts three-phase line power. Where at all possible, two rectifiers operated in series, each giving 1000 amperes at 3500 volts, and rectifying from a twelve phase secondary for smooth rectification. This gave a 7,000 volt, 1,000 amperes feed to the arc. Because of the shortage of rectifiers, some of the arcs were forced to use a single one with 7,000 volt output. This was found to be quite unsatisfactory, and there was continual trouble with backfires, etc. Figure 1 shows the electrical hookup of the rectifiers when working in series for one pair of arcs. The rectifiers were made by Brown-Boveri Company.

(d) The arc converter proper is shown in Figure 2. Feed gas enters the distributing ring tangentially near the top of the apparatus. It then flows through slots in the annular distributor and swirls down through the arc tube. On leaving the tube it is immediately quenched with a water spray in the bottom section. The distributing ring, arc tube, and spray section are all made of ordinary steel. They are grounded, as is one side of the rectifier output, and water jacketed for proper cooling.

(e) The upper electrode is made of copper and separated from the converter proper by a porcelain insulator. It is water jacketed to prevent local overheating. A pneumatic operated steel shortingrod starts the arc, and is withdrawn automatically when the right current is flowing.

(f) Control of the arc synthesis is affected by control of the power factor. At the design current and voltage, the feed gas flow is in-

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2. Arc Converters (f) (Cont'd.)

creased until the power factor is 0.7 to 0.75. Under these conditions the arc flame extends the full one meter length of the arc tube. Higher powerfactors cause the arc to go out; lower ones give lower conversion. The arc tube proper, or the center one (1) meter section of the apparatus, has a life of about 250 hours. At the end of this time the internal diameter is so enlarged as to prevent further satisfactory operation. This tube can readily be replaced by disconnecting flanges at either end and springing down the lower section through its bellows expansion joint. During this time the other arc of the pair is in operation, thus avoiding the necessity for shutting down the synthesis.

(g) Mean gas temperature in the arc is estimated as 1,600 degrees centigrade. Temperatures nearer 1,300 would be preferable, but are difficult to obtain in the apparatus without seriously affecting its operation. The exit gas from the apparatus, after quenching with water, has the approximate composition (carbon black free) as given below:

C_2H_2	13% by volume
H_2	52%
C_2H_4	1%
sat. HC's (mostly methane)	25%
CO	2%
N_2	7%

In addition about 3 percent of the hydrocarbon input is converted to carbon black and leaves the arc entrained in the gas stream.

(h) When operating on refinery tail gases it was found that the exit acetylene concentration was much higher and hydrogen also up accordingly. Saturated hydrocarbons took care of this increase by being correspondingly lower. This means that when operating on natural gas the yield was 50 percent of theoretical, while on refinery gases it was stated to be even better. No figure was given to indicate the magnitude of the improvement.

3. Preliminary Purification.

(a) The plant had a rather elaborate preliminary purification plant which was admittedly not all necessary for acetylene production. However,

[redacted]

3. Preliminary Purification (a) (Cont'd.)

the management stated that in view of the fact that the entire process was built hurriedly during the war without all necessary piloting, and in view of war-time shortages of certain materials such as HCN, the elaborate system was installed. This seems entirely reasonable, and experience has shown the lack of necessity for many of the items.

(b) In Figure 3 is shown a process flow diagram of the preliminary purification, including the carbon black plant. Gas from the arc, which has been cooled to 150 degrees centigrade by the water quench, is passed down through a water seal to four (4) cyclones, two (2) operating in series, two (2) in parallel. High density carbon black is removed here, and sent through a series of hoppers and conveyors to an air classifying tower. Oversize material is removed, and the remaining black is tumbled in drums to increase its packed density for shipping. It is then bagged and shipped to rubber plants throughout Germany.

(c) The gas from the cyclones is then cooled to 70 degrees centigrade in a spray cooling tower, where low density carbon black is removed as a slurry in the spent cooling water. This black is then settled in a Dorr classifier, filtered in a vacuum filter, dried, and bagged. It is used in mixture with the other black in rubber goods manufacture.

(d) For final cleanup the last traces of black are removed in eight (8) bag filter towers. These towers are heated slightly with steam to prevent the saturated entering gas from wetting the bags and ruining their efficiency.

(e) So far the system described has applied to each pair of arc converters. At this point however the gas streams from all converge in a common header, and goes to two (2) water spray coolers operating in parallel. It is cooled to 25 degrees centigrade with a minimum of water so as to prevent the solution of much of the HCN present. The gas then passes to two (2) oil scrubbers operating in parallel, using revolving trays. Here the benzene and higher hydrocarbons are removed. The wash oil used was a light tar oil, although an aliphatic oil was preferable but not obtainable. The scrubber bottoms were heated to 70 degrees centigrade and stripped in two (2) parallel towers using CO from subsequent purification steps. These towers were operated under 600 millimeters vacuum, and the overhead from them was water-washed and sent to the boiler house for fuel.

3. Preliminary Purification (3) (Cont'd.)

The stripper bottoms were in main recycled to the oil scrubbers, but a small part was continuously withdrawn and distilled in one (1) of four (4) tar stills. Here the heavier hydrocarbons and sludges were removed from the system, and fresh wash oil returned.

(f) The main process gas is next passed through two water scrubbers in parallel, where HCN is removed. The bottoms from these scrubbers, along with the water from the previous water spray after the carbon black cyclones, are sent to two (2) vacuum stills for HCN recovery. Bottoms from these stills are aerated in a cooling tower and returned to the system. HCN overhead, still in crude form, is worked up in a small batch still. Much trouble was encountered in this recovery because of the presence of higher acetylenes in the HCN cut. Nevertheless HCN was recovered and used elsewhere for acrylonitrile production.

(g) The gas stream was finally sent to six (6) large "Luxmasse" or iron oxide towers where sulphur was removed. These are similar to towers used in the U.S. manufactured gas industry. The gas is now ready for acetylene recovery.

4. Acetylene Recovery.

(a) In Figure 4 is shown the acetylene recovery system. Raw gas from desulfurization is combined with recycle gas from the recovery system and compressed in four (4) stages to 18 atmospheres. Four stages were deemed necessary to prevent local interstage overheating of the high pressure acetylene-containing gas. There were six (6) complete acetylene recovery units similar to the one herein described, all operating in parallel.

(b) The high pressure gas was scrubbed in a 66 perforated-tray tower with pure water, and the overhead gas from the tower contained less than 0.1 percent acetylene. Its composition was approximately as follows:

25%	CH
55%	H_2
1%	C_2H_4
4%	CO

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4. Acetylene Recovery (b) (Cont'd.)

10%	N_2
4%	C_2H_6 and higher
1%	O_2

This gas is sent to units for hydrogen and ethylene recovery which are described later.

(c) The acetylene containing water is expanded to 2 atmospheres through a turbine, and flashed in a vessel. The off-gas, containing 45 percent acetylene, is recycled to the compressor mentioned above. The water is then flashed to one atmosphere and a 92 percent acetylene off-gas obtained. It is further flashed to 0.15 and then 0.05 atmospheres, using suitable vacuum pumps, and these gas streams combined with the one atmosphere flash to give a 96 percent acetylene, containing N_2, CO_2, CH_4, C_2H_4, H_2, and small amounts of higher acetylenes. Before acetaldehyde synthesis it was necessary to remove the higher acetylenes, which was done in one of two (2) fashions and will be described below. The water from the last flash is pumped to one atmosphere, stripped with gas being recycled to the arc, and aerated in a cooling tower to remove last traces of acetylene before returning to the water scrubber. Summer water temperatures into the top of the scrubber never exceeded 26 degrees centigrade.

5. Acetylene Purification.

(a) Removal of higher acetylenes was accomplished in one of two (2) ways. The first method made no attempt to recover this material, but was much cheaper to build and operate. The second attempted recovery for further synthesis, but was quite expensive to build and operate.

(b) In Figure 5 is shown the first or oil scrubbing method. Here a light wash oil of unknown composition (stated to be aliphatic) was used to scrub out the higher acetylenes. This oil was then stripped with recycle gas to the arc, first of acetylene in the upper section of the column, then of higher acetylenes in the lower. However, the selective stripping proved unworkable, and the column was finally run as a single stripper. The off-gas from the oil scrubber, containing about 97 percent acetylene, was considered purified material and sent to the acetaldehyde synthesis unit. It was essentially free of all higher acetylenes.

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5. Acetylene Purification (Cont'd.)

(c) In Figure 6 is shown the second or liquefaction method of higher acetylene removal. Here the raw acetylene gas is first cooled in a water scrubber and then the higher acetylenes condensed by cascade refrigeration to -78 degrees centigrade using ammonia and ethylene. Counter current heat exchangers assure maximum recovery of refrigeration from the purified acetylene. The condensed higher acetylenes are quickly flashed in a stripper by the use of warm recycle gas. It is imperative that the warming up and vaporization of the higher acetylenes is accomplished rapidly to minimize the explosion hazards.

(d) Some small amounts of aromatics, particularly benzene, condense from the gas stream when it is cooled to about -10 degrees centigrade. These are steam distilled, decanted, and used as fuel.

(e) It has been found that the use of methanol as a diluent for the liquified higher acetylenes greatly decreases the hazard of explosion. Therefore, the entire system is properly protected with methanol flushing lines to enable quick dilution in the event of trouble.

6. Hydrogen Recovery.

(a) The off-gas from the acetylene purification contains a number of valuable constituents which are recovered before recycling the remainder to the arc. The two (2) principal ones are hydrogen and ethylene. The gas, whose composition has been given in former sections, is first treated for hydrogen recovery in a Linde designed liquefaction plant. Figure 7 shows the flow sheet of the apparatus. In it five (5) cuts are made on the gas; a hydrogen cut, a $CO-N_2$ cut, an ethylene or C_2 cut, a CH_4 cut, and a C_3 cut. The last two (2) are combined within the apparatus and furnish the major source of recycle gas for the arc. The hydrogen cut is used for hydrogenation within the plant, the $CO-N_2$ cut for inert stripping, and the C_2 cut is further processed for ethylene.

(b) The off-gas is first compressed to 16 atmospheres and cooled by counter current exchange with the product streams to -15 degrees centigrade. It is then cooled with ammonia refrigeration to -50 degrees centigrade. Further heat exchange with the cold product gases condenses the C_3 cut, which is caught in a trap, flashed to one atmosphere, and joins

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6. Hydrogen Recovery (b) (Cont'd.)

the CH_4 stream as the recycle gas cut. This stream returns through the two (2) previously mentioned exchangers, and goes to the arc.

(c) The off-gas, now at -70 degrees centigrade, is further cooled to -140 degrees centigrade by counter current exchange with product gases and sent to a condenser. Here the C_2 cut is liquified by condensing with the cold hydrogen cut and a medium pressure outside nitrogen refrigeration coil. The nitrogen has been previously compressed to 200 atmospheres and condensed by exchange with one of several of the cold gas streams; i.e., cold medium pressure gaseous nitrogen, cold methane, cold atmospheric pressure nitrogen, and cold high vacuum nitrogen. The C_2 cut is flashed to one atmosphere and sent to the ethylene recovery plant through the previously mentioned exchangers.

(d) The off-gas, now free of C_2 and higher, and at -145 degrees centigrade, is further cooled to -170 degrees centigrade with the H_2, $CO-N_2$, and CH_4 streams. The CH_4 cut is then condensed with a one atmosphere outside nitrogen cooling cycle, and is flashed to one atmosphere and returned through suitable exchangers as shown to the arc, mixed with the C_3 cut just before the C_3 condensing exchanger. The remaining off-gas, now at -185 degrees centigrade, is sent to the base of a double rectification column.

(e) The bottom or high pressure part of the column condenses and removes the $CO-N_2$ cut as bottoms. Liquid nitrogen at one atmosphere is used as reflux for this section, and a liquid hydrogen evaporator at the bottom adds additional cooling. The $CO-N_2$ cut is evaporated by liquifying medium pressure nitrogen and cooling atmospheric pressure nitrogen, and is then sent back through the counter current exchangers mentioned before and used as an inert stripping gas.

(f) The hydrogen cut is liquified in the condenser side of the upper column by using boiling liquid nitrogen at 0.1 atmosphere absolute pressure. It is evaporated in the lower section and returns through the exchangers previously mentioned. Temperature of liquefaction is about -212 degrees centigrade. This hydrogen is used in other sections of the plant for various hydrogenation processes.

(g) The hydrogen cut contains about 2 to 3 percent N_2, and the re-

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6. Hydrogen Recovery (g) (Cont'd.)

mainder H_2. The CO-N_2 cut contains about 15 percent CO, 70 percent N_2, and 15 percent CH_4. The recycle gas cut contains about 85 percent CH_4, with the rest C_3's.

7. Ethylene Recovery.

(a) The ethylene recovery system is shown in Figure 8. It is a Linde designed liquefaction system for fractionation of the C_2 cut. The feed gas contains about 15 to 25 percent ethylene, and the purified ethylene product contains over 98 percent C_2H_4. The other cut, containing principally ethane diluted with some methane, is combined with the recycle gas from the hydrogen recovery unit and recycled to the arc.

(b) The feed gas is first compressed to 30 atmospheres and cooled to -35 degrees centigrade by ammonia refrigeration. It is then cooled to -55 degrees centigrade by exchange with cold CH_4 cut, to -95 degrees centigrade in the reboiler coil of the methane column, to -105 degrees centigrade by exchange with the C_2 intermediate fraction, and the CH_4 cut, and is then flashed to one atmosphere and -140 degrees centigrade and put into the top of the methane column.

(c) The methane gas overhead from the methane column passes through the exchangers previously mentioned and is combined with the ethane gas stream and goes to the arc. Bottoms from this column are passed to the center section of the ethylene column.

(d) The ethylene column takes ethylene overhead as product, and after suitable heat exchange this material is sent to the styrene plant as purified ethylene. A 6 atmosphere ethylene refrigeration cycle, with 0.7 atmospheres suction, is used for reflux and cooling for the column as shown in the flow-sheet. Column bottoms, consisting primarily of C_2H_6, are flashed and after suitable heat exchange combined with the CH_4 cut and sent to the arc.

Prepared by:

G.M. MORROW,
Ensign, USNR.

120

[redacted]

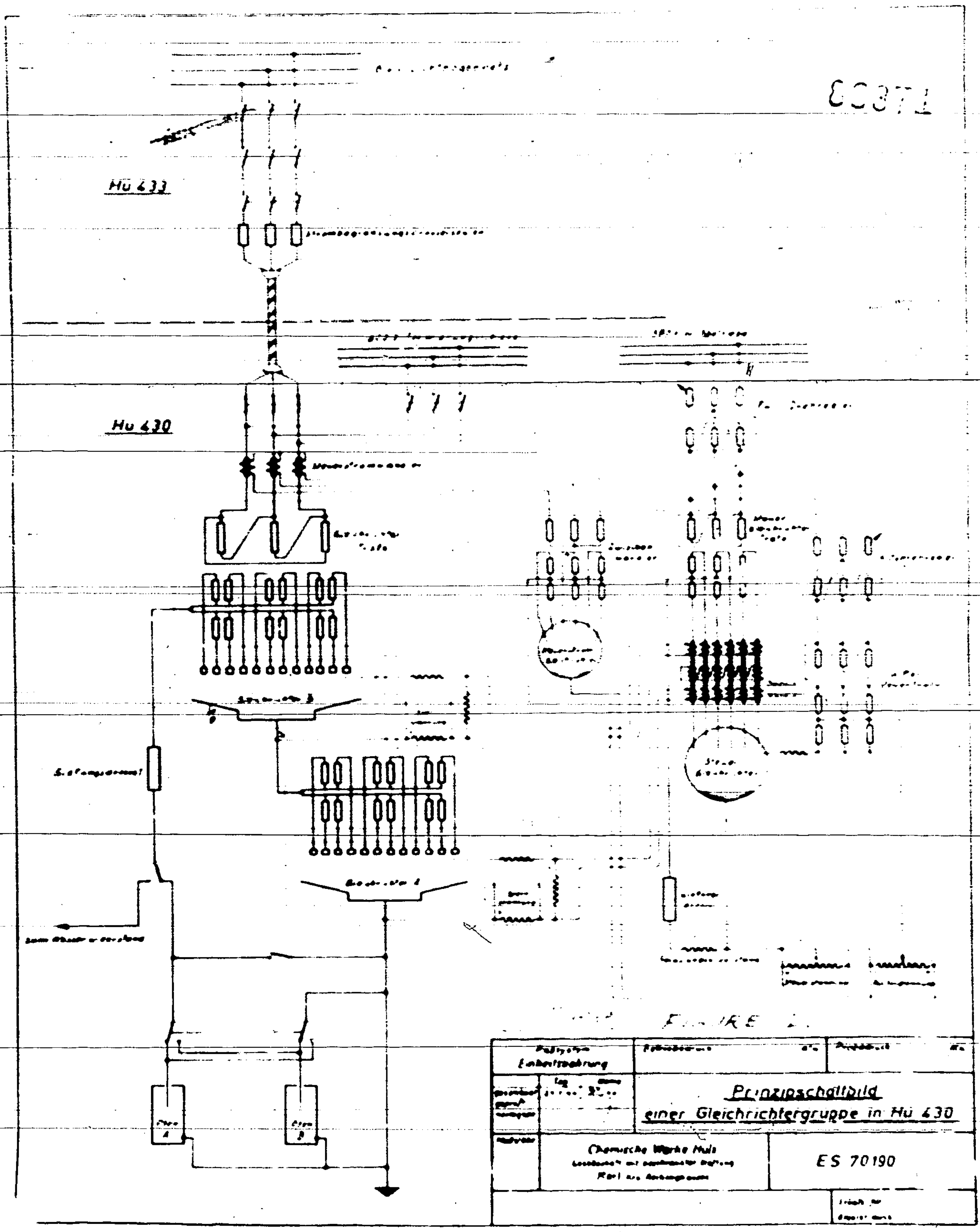
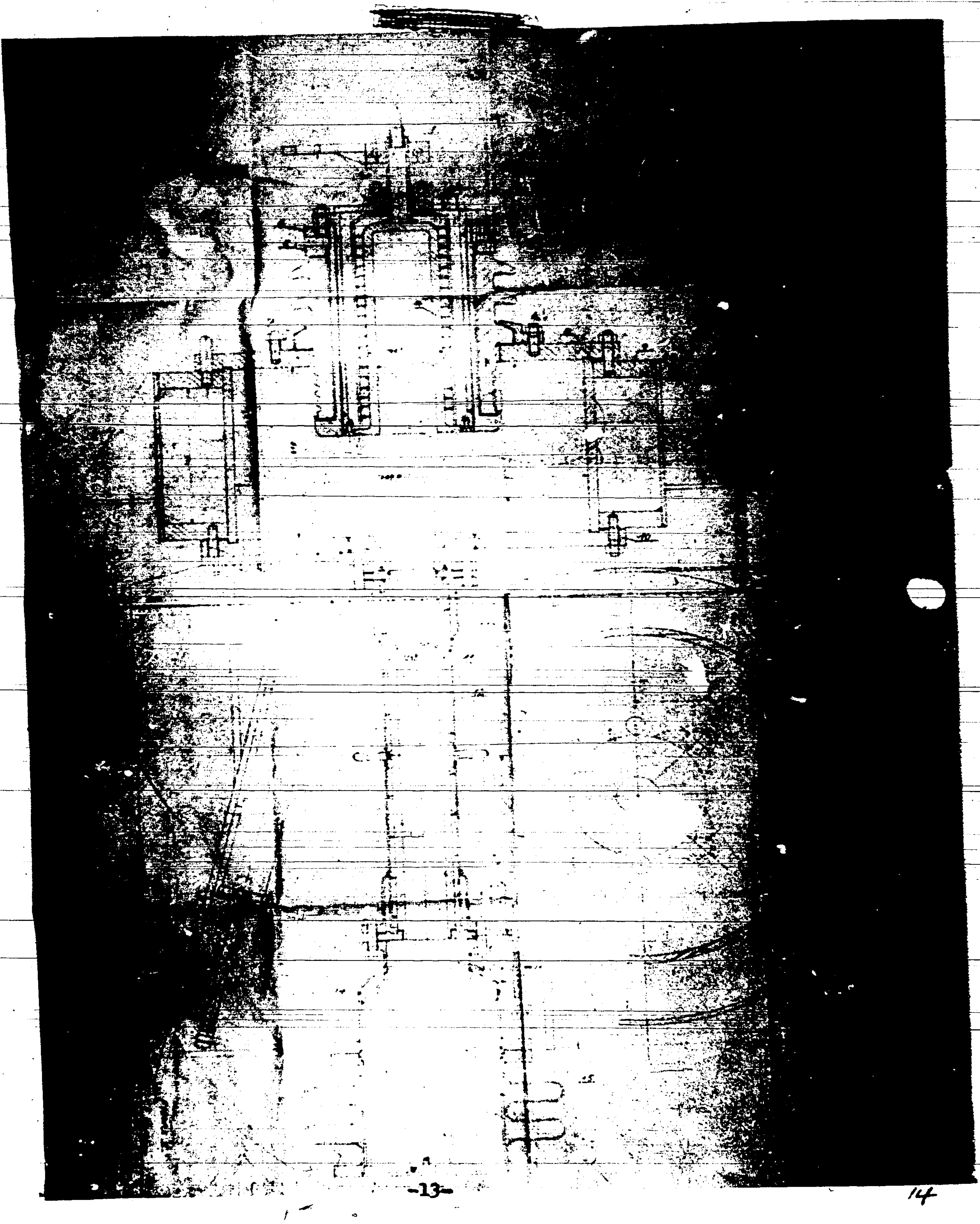


FIGURE 2.

13

380



15

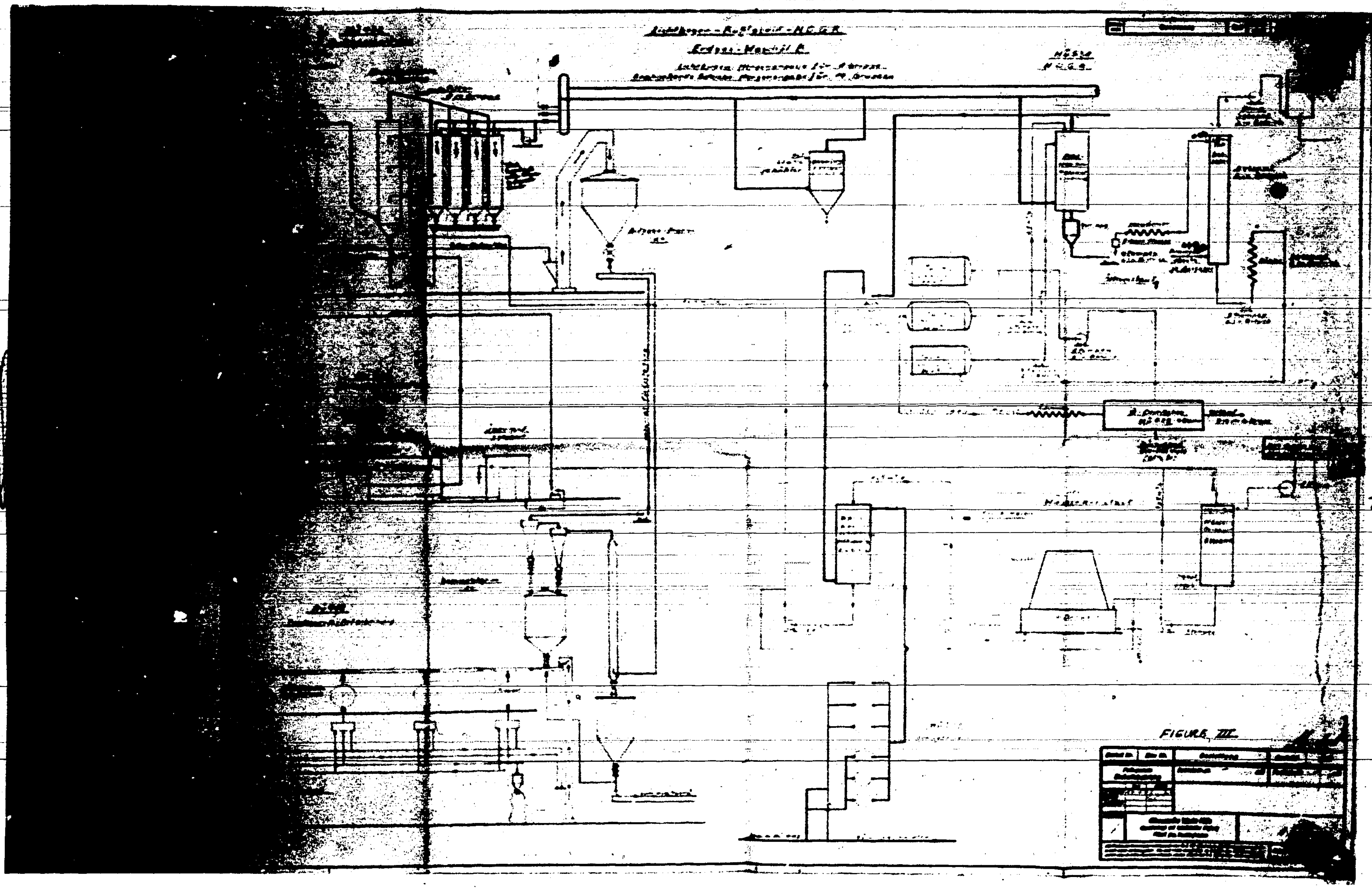


FIGURE III

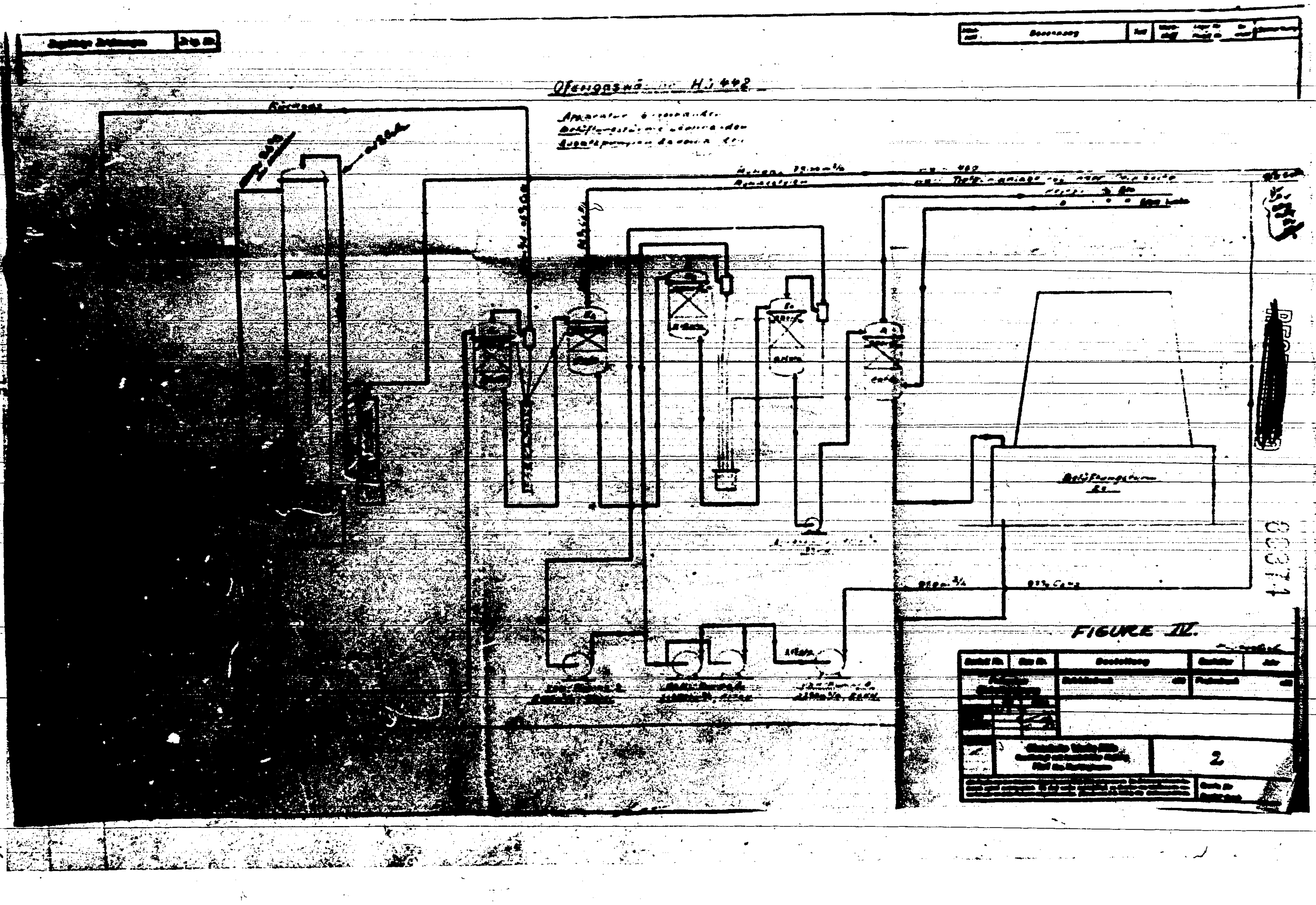


FIGURE IV.

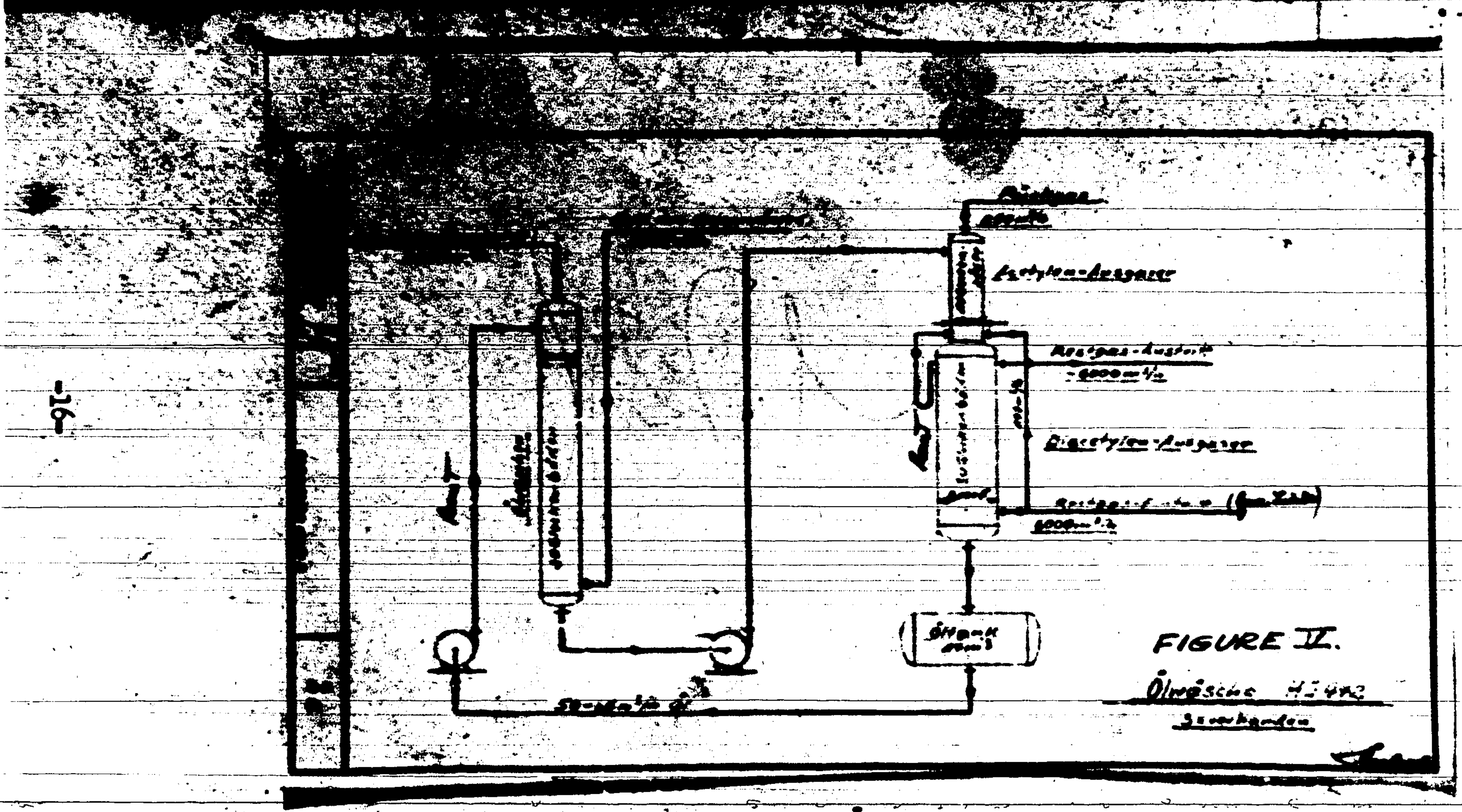

Acetylen-Ausgaser
Restgas-Austritt
~6000 m³/h
Diacetylen-Ausgaser
Restgas-Eintritt
6000 m³/h
Öltank

FIGURE II.

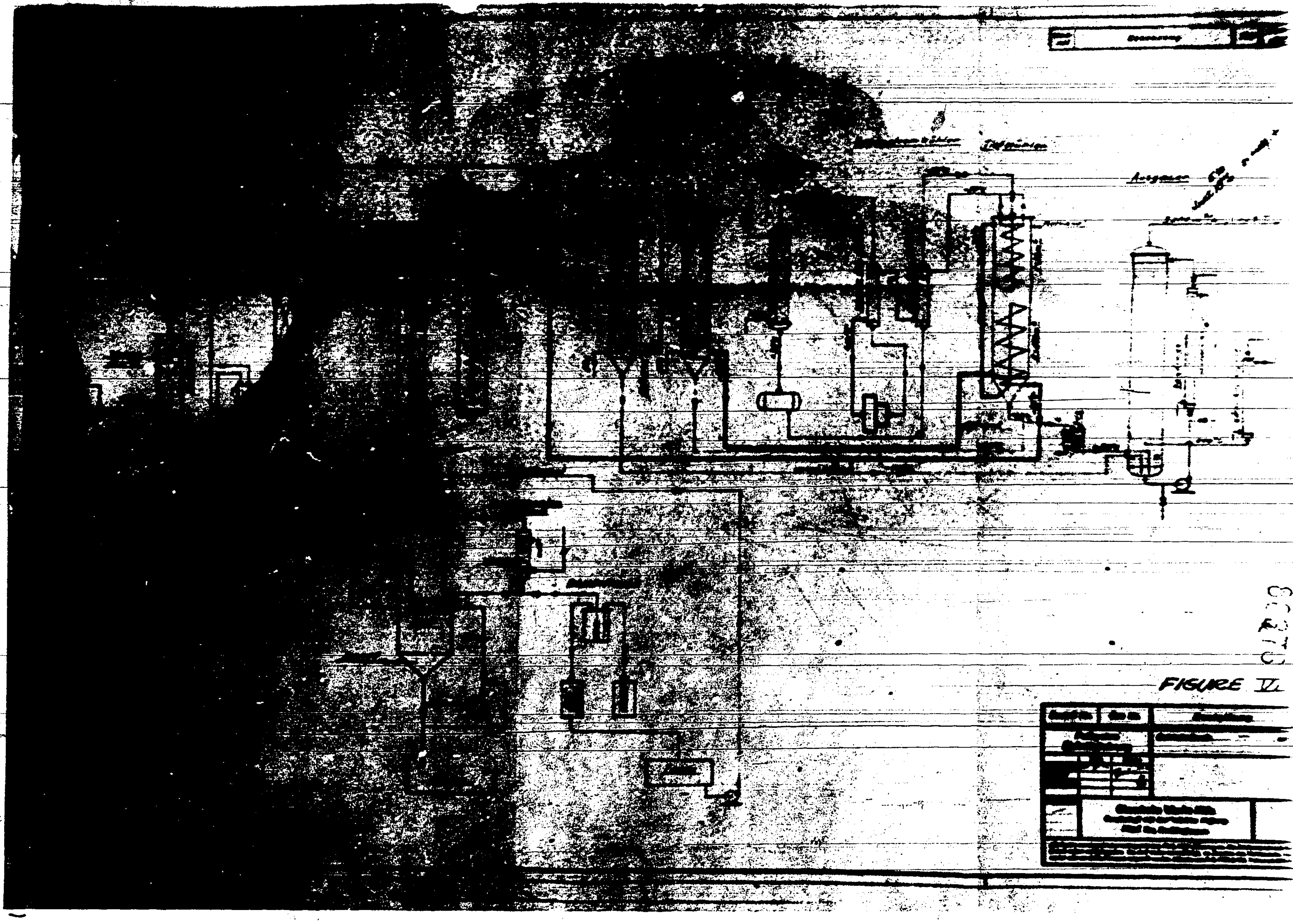
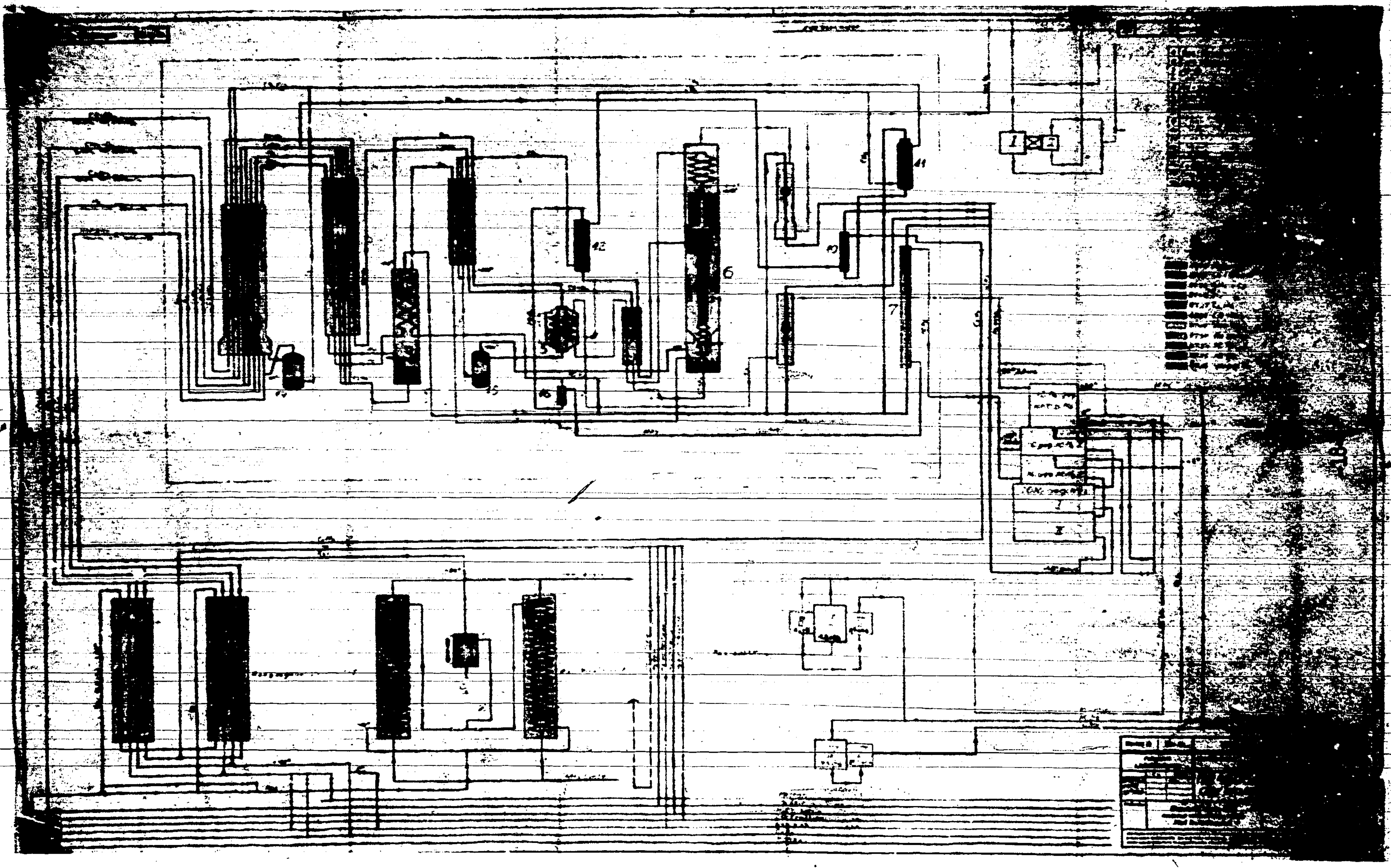


FIGURE V

19

65377

[redacted]



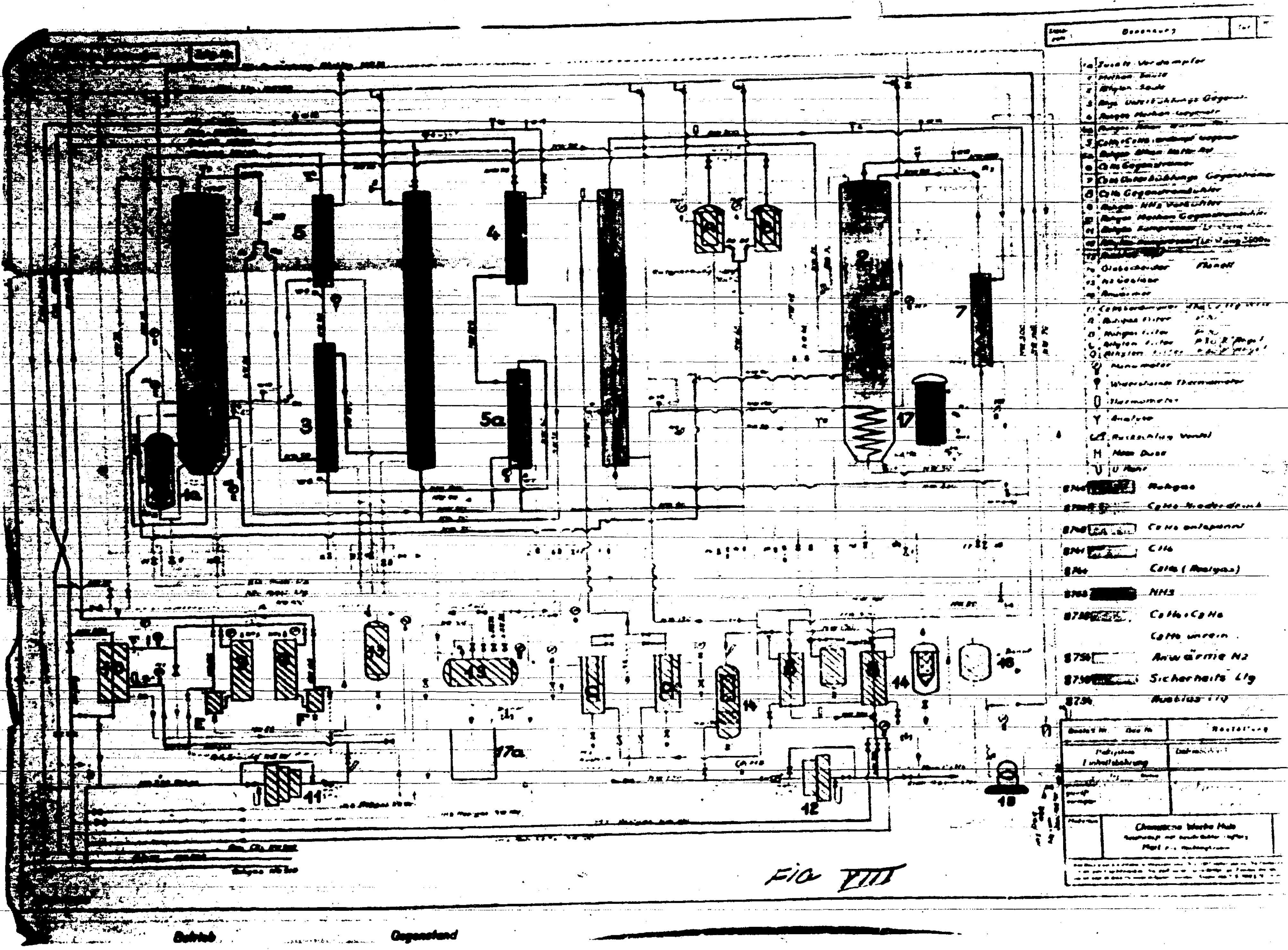
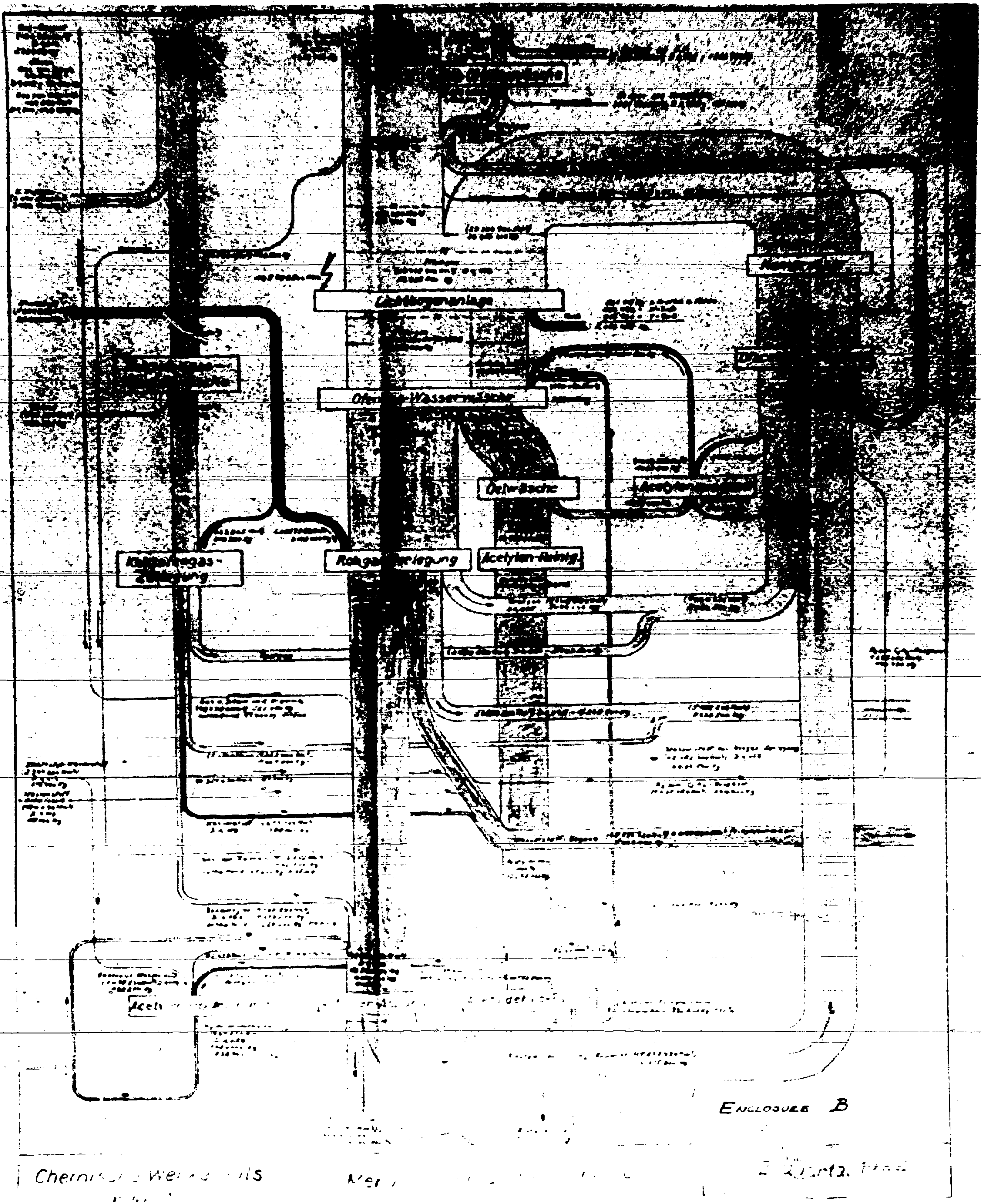
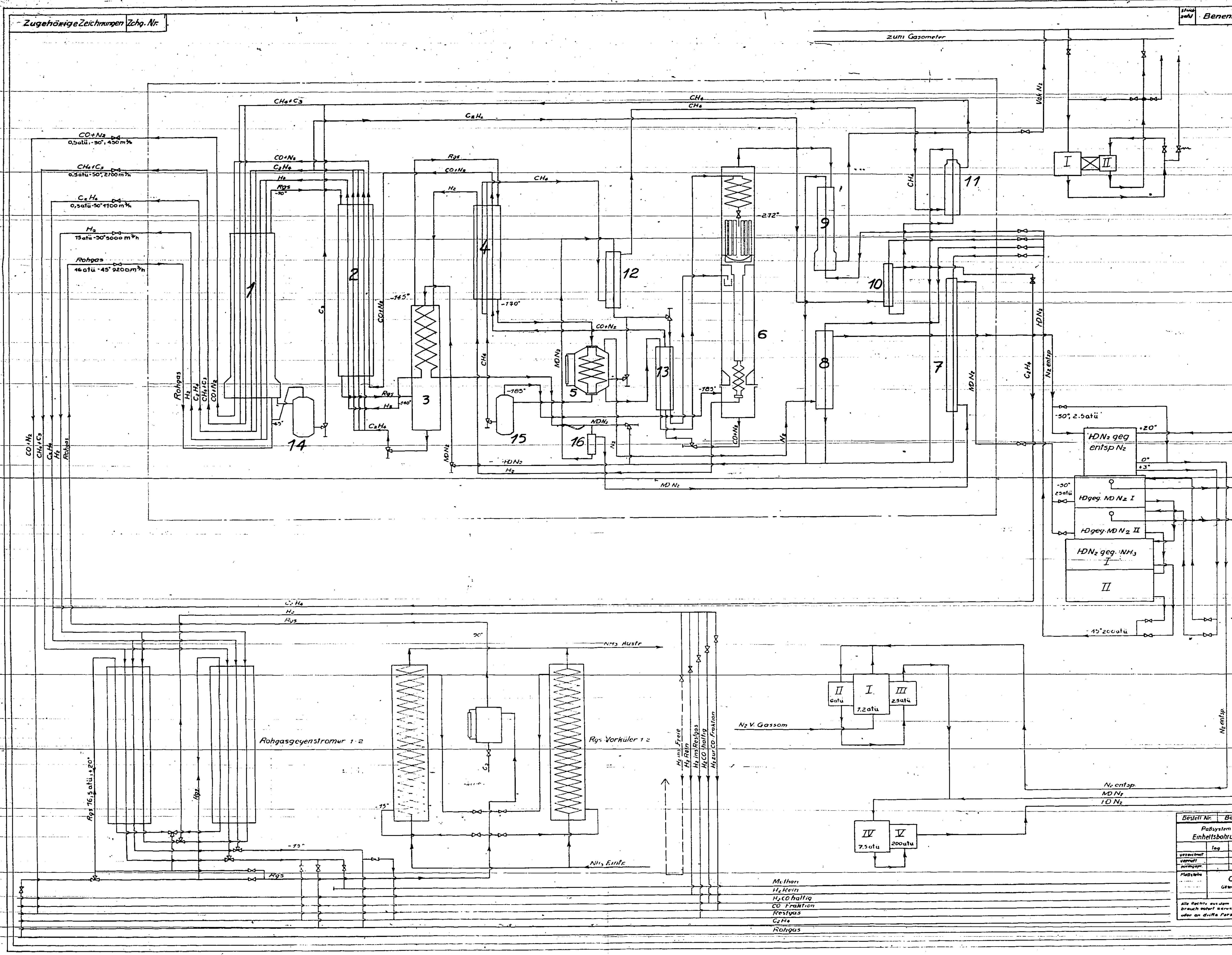

Benennung
Zusatz Verdampfer
Methan Säule
Äthylen Säule
Gegenstromer
Gegenstromkühler
Gegenstromkühler
Manometer
Thermometer
Analyse
Rückschlag Ventil
U Rohr
Rohgas
C_2H_4 entspannt
C_2H_4
C_2H_4 (Restgas)
NH_3
C_2H_4 unrein
Anwärme N_2
Sicherheits Ltg
Ausblas Ltg
Bestellung
Chemische Werke Hüls
Betrieb
Gegenstand
1a
2
3
4
5
5a
7
11
12
14
16
17
17a
18
E
F

Fig VIII


Lichtbogenanlage
Oelwäsche
Acetylen-Reinig.
Rohgaszerlegung
Chemische Werke Hüls

ENCLOSURE B

Zugehörige Zeichnungen Zchg. Nr.



Stückzahl	Benennung	Teil	Werkstoff	Lager Nr. / Modell Nr.	Gewicht	Bemerkung

1	Rgs.-Gegenströmer warmer Ast.
2	C_2H_4 Verdampfungsgegenströmer
3	MD N_2
4	CH_4
5	N_2-Verdampfer
6	Vakuum-Verdampfer mit Waschsaüle
7	Kreuzgegenströmer HD N_2 - MD N_2
8	-"- -"- HD N_2 - entsp N_2
9	-"- -"- HD N_2 - Vak N_2
10	-"- -"- HD N_2 - C_2H_4
11	-"- -"- HD N_2 - CH_4
12	-"- -"- MD N_2 - CH_4
13	Unterkühlgegenströmer für Vak N_2 u. Wasch N_2
14	C_3 Abscheider
15	CH_4 Abscheider
16	MD N_2 Abscheider

☐ 8746 Rohgas
☐ 8355 C_3 (Gasol)
☐ 8737 CH_4+C_3
☐ 8748 H_2
☐ 8737 C_2H_4
☐ 8736 CO+N_2
☐ 8744 Vak. N_2
☐ 8734 N_2 entsp.
☐ 8754 MD N_2
☐ 8735 HD N_2
☐ 8738 Wasch N_2

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FIGURE VII

Bestell Nr.	Bau Nr.	Bestellung		Besteller	Jahr
Paßsystem Einheitsbohrung		Betriebsdruck atü		Probedruck atü	
	Tag / Name	Hü 460 Gesamtschema der Wasserstoffboxen 1-5			
verzeichnet / verprüft / normgepr.					
Maßstabe	Chemische Werke Hüls Gesellschaft mit beschränkter Haftung Marl Krs Recklinghausen		4a		

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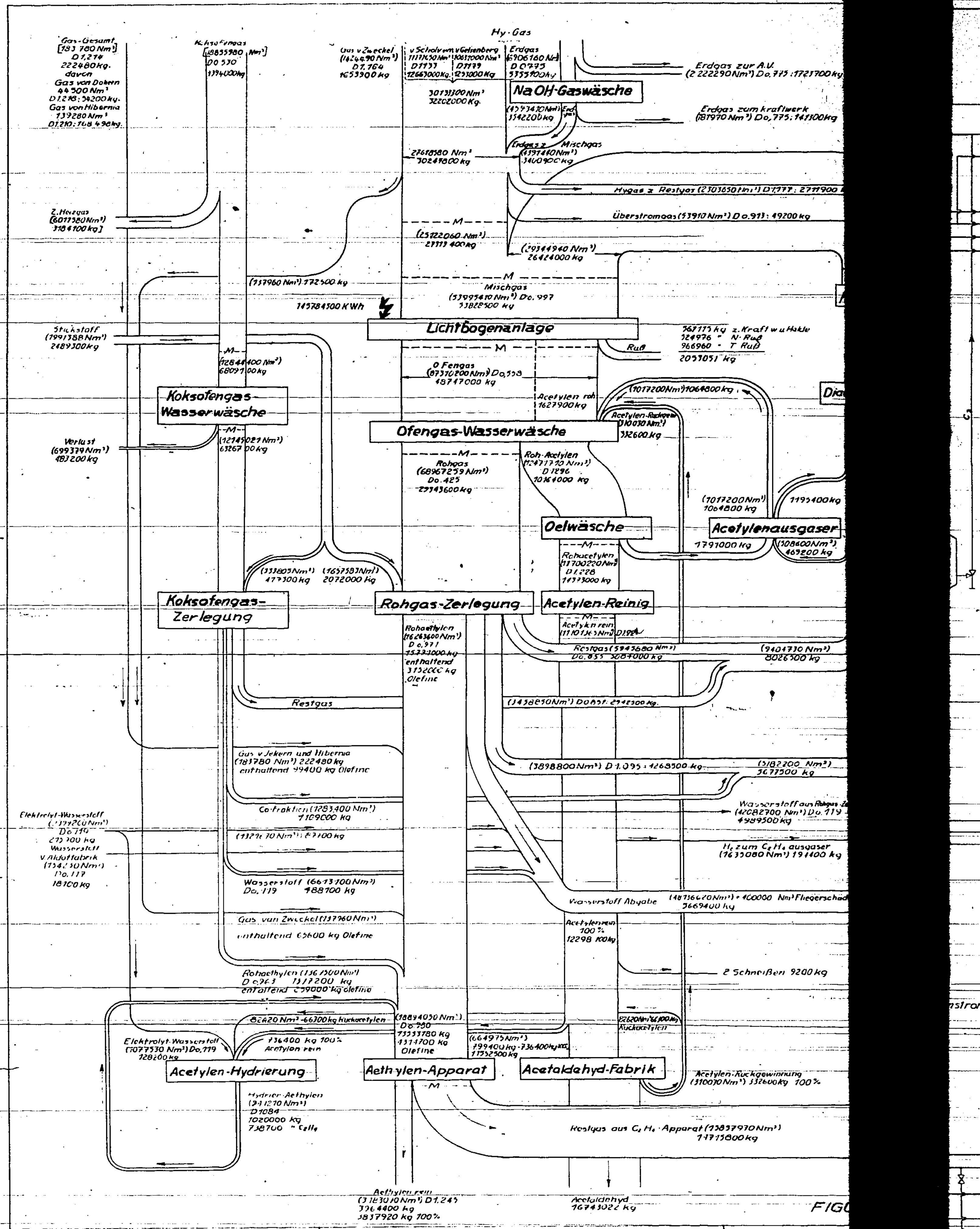

Chemische Werke Hüls
Gruppe 1

Mengenschema-Gasbetriebe

2.Qua

NAVAL TECHNICAL MISSIO
TECHNICAL REPORT
FIGURES VII & I
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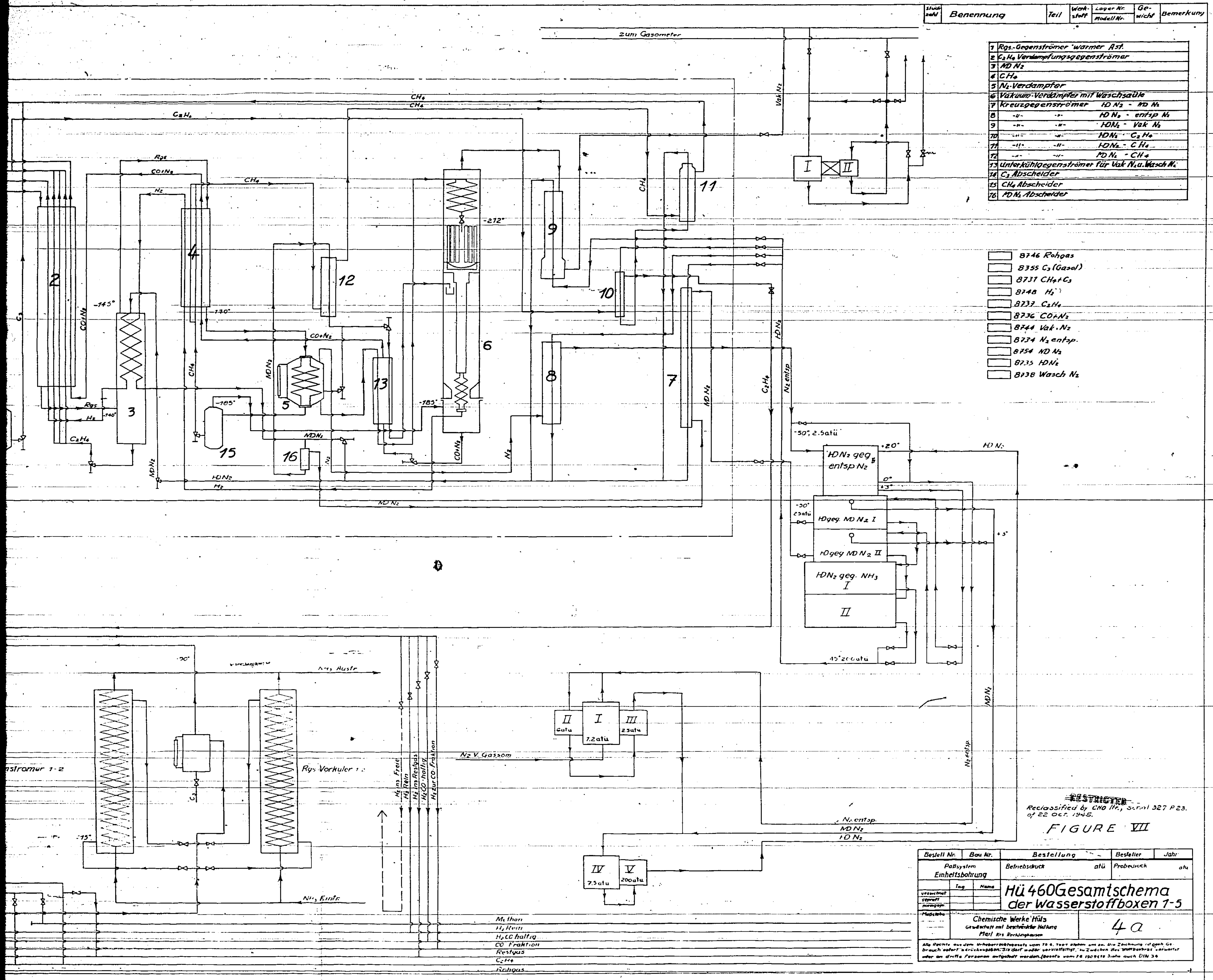

Stückzahl	Benennung	Teil	Werkstoff	Lager Nr. / Modell Nr.	Gewicht	Bemerkung
1	Rgs.-Gegenströmer warmer Ast.					
2	C_2H_4 Verdampfungsgegenströmer					
3	MD N_2					
4	CH_4					
5	N_2-Verdampfer					
6	Vakuum-Verdampfer mit Waschsäule					
7	Kreuzgegenströmer HD N_2 - MD N_2					
8	-"- -"- HD N_2 - entsp N_2					
9	-"- -"- HD N_2 - Vak N_2					
10	-"- -"- HD N_2 - C_2H_4					
11	-"- -"- HD N_2 - CH_4					
12	-"- -"- MD N_2 - CH_4					
13	Unterkühlgegenströmer für Vak N_2 u. Wasch N_2					
14	C_3 Abscheider					
15	CH_4 Abscheider					
16	MD N_2 Abscheider					

☐	8746 Rohgas
☐	8355 C_3 (Gasol)
☐	8731 CH_4+C_3
☐	8748 H_2
☐	8737 C_2H_4
☐	8736 CO+N_2
☐	8744 Vak. N_2
☐	8734 N_2 entsp.
☐	8754 MD N_2
☐	8735 HD N_2
☐	8738 Wasch N_2

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FIGURE VII

Bestell Nr.	Bau Nr.	Bestellung	Besteller	Jahr
Paßsystem Einheitsbohrung		Betriebsdruck atü	Probedruck atü	

	Tag	Name
verzeichnet		
geprüft		
normgepr.		

Hü 460 Gesamtschema der Wasserstoffboxen 1-5

Maßstabe

Chemische Werke Hüls
Gesellschaft mit beschränkter Haftung
Marl Krs Recklinghausen

4a

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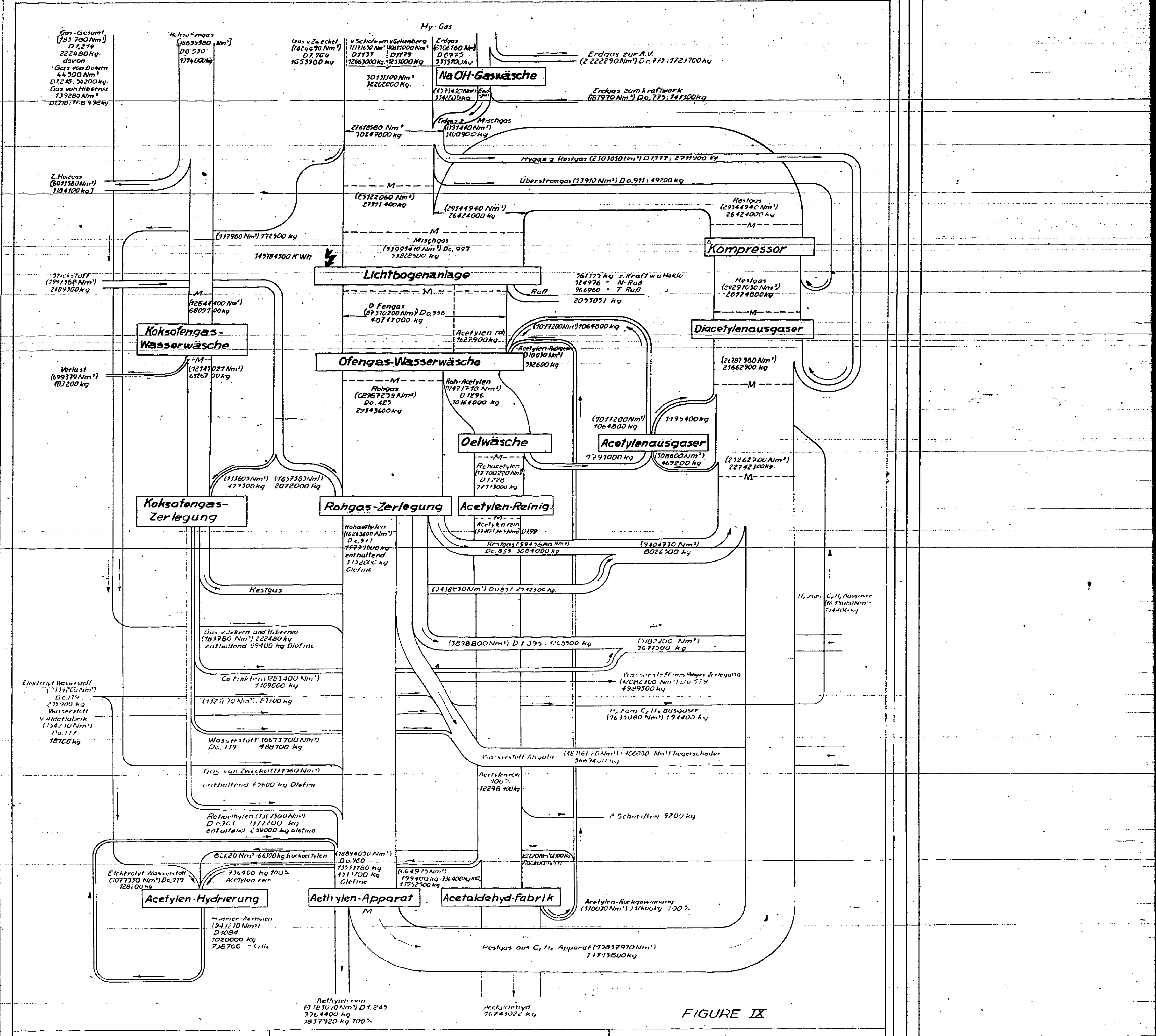

FIGURE IX

Chemische Werke Hüls Gruppe 1	Mengenschema-Gasbetriebe	2. Quartal 1944

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NAVAL TECHNICAL MISSION IN EUROPE
TECHNICAL REPORT Nº 115-45
FIGURES VII & IX
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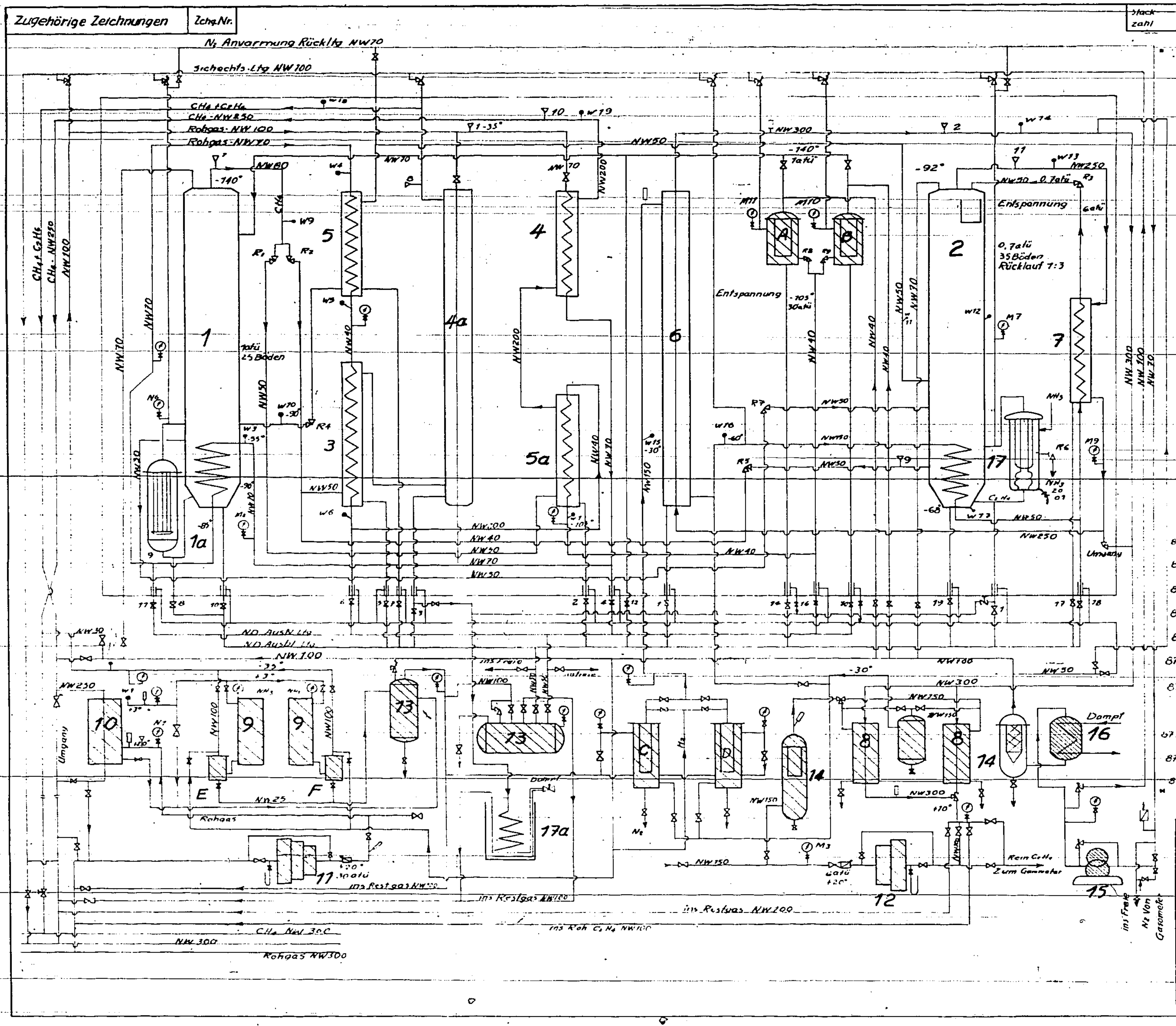

Betrieb Gegenstand

Stück zahl	Benennung	Teil	Werkstoff	Lager Nr. Modell Nr.	Gewicht	Bemerkung

1a	Zusatz-Verdampfer		
~~1~~	~~Methan-Säule~~		
2	Athylen-Säule		
3	Rhgs. Unterkuhlungs Gegenstr.		
4	Rohgas Methan Gegenstr.		
4a	Rohgas Athan Warmer Ast		
5	$C_2H_4+C_2H_6$ Verdampf Gegenstr.		
5a	Rohgas Athan Kalter Ast.		
6	C_2H_4 Gegenströmer		
7	C_2H_4 Unterkühlungs Gegenstromer		
~~8~~	~~C_2H_4-Gegenstromkühler~~		
9	Rohgas NH_3 Vorkühler		
10	Rohgas Methan Gegenstromkühler		
11	Rohgas Kompressor (Leistung 4000 m³/h Roh-C_2H_4)		
12	Athylen Kompressor (Leistung 3800 m³/h C_2H_4)		
13	Ausblas Topf		
14	Ölabscheider Flanell		
15	N_2 Gebläse		
16	Anwärmer		
17	C_2H_6 Verdampfer	17a	C_2H_6 Verdampfer
~~A~~	~~Rohgas-Filter P70~~		
B	Rohgas Filter P70		
C	Athylen Filter P80	E	Rhgs Filter P80
D	Athylen Filter P80	F	Rhgs Filter P80
⍉	Manometer		
●	Widerstands-Thermometer		
▯	Thermometer		
Y	Analyse		
⊠	Ruckschlag-Venil		
‖	Mess-Düse		
∪	U-Rohr		

8745	▭	Rohgas
8750	▭	C_2H_4 Niederdruck
8748	▭	C_2H_4 entspannt
8741	▭	CH_4
8714	▭	C_2H_6 (Restgas)
8753	▭	NH_3
8735	▭	$C_2H_4+C_2H_6$
	▭	C_2H_4 unrein
8734	▭	Anwärme N_2
8739	▭	Sicherheits-Ltg
8734	▭	Ausblas Ltg

Bestell Nr.	Bau Nr.		Bestellung	Besteller	Jahr
Paßsystem Einheitsbohrung			Betriebsdruck atü	Probedruck atü	
	Tag	Name			
gezeichnet					
geprüft					
normgepr.					
Maßstab	Chemische Werke Hüls Gesellschaft mit beschränkter Haftung Marl Krs. Recklinghausen				
Alle Rechte aus dem Urheberrechtsgesetze vom 19.6.1901 stehen uns zu. Die Zeichnung ist nach Gebrauch sofort zurückzugeben. Sie darf weder vervielfältigt, zu(…) des Wettbewerbs verwertet oder an dritte Personen mitgeteilt werden. (Gesetz vom 7.6.1909) Siehe auch Din 34				Ersatz für Ersetzt durch	

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TECHNICAL REPORT NO. 115-45
FIGURE VIII

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80331

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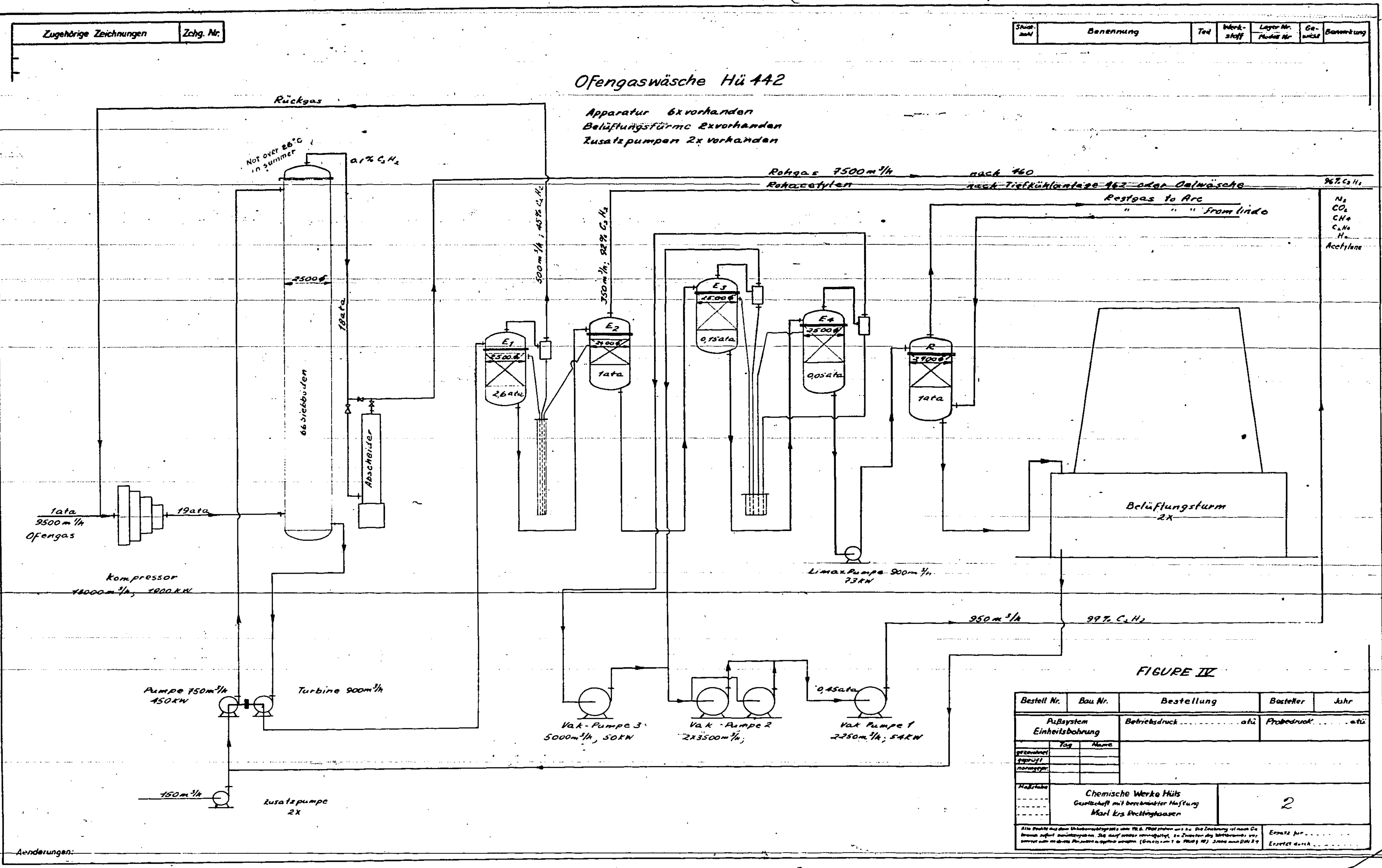
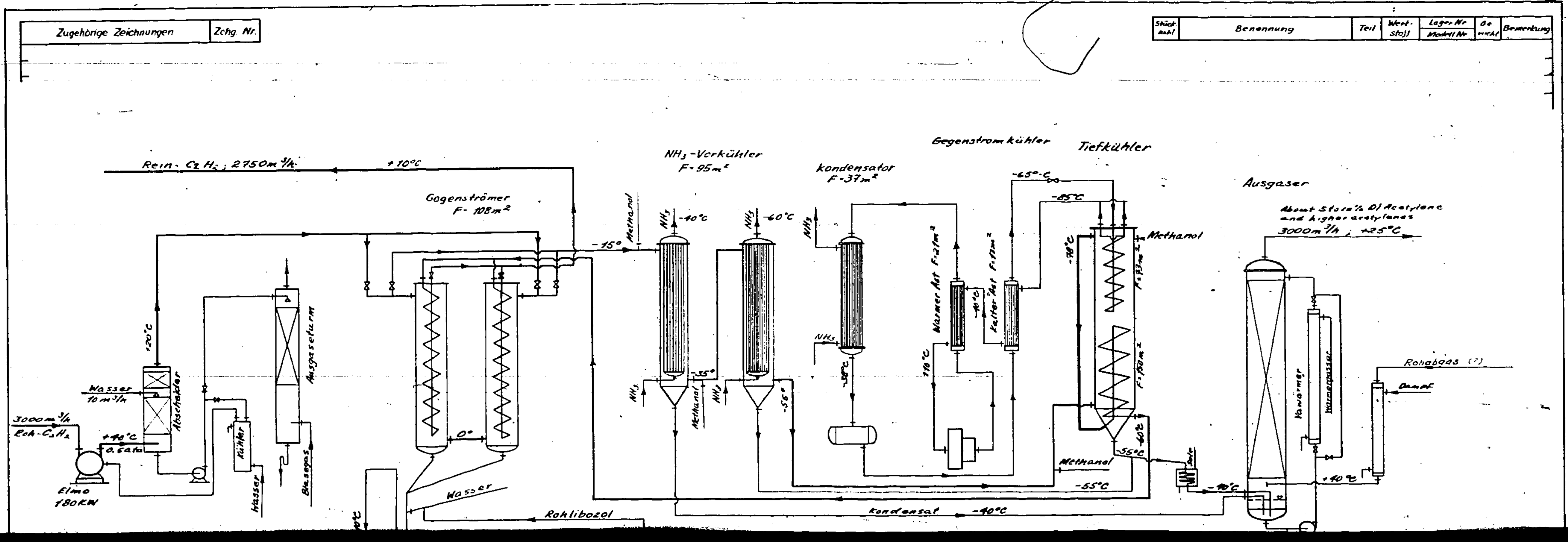

Zugehörige Zeichnungen
Zchg. Nr.
Stück-zahl
Benennung
Teil
Werk-stoff
Lager Nr.
Modell Nr.
Ge-wicht
Bemerkung
Ofengaswäsche Hü 442
Apparatur 6x vorhanden
Belüftungstürme 2x vorhanden
Zusatzpumpen 2x vorhanden
Rückgas
Not over 26°C in summer
0,1% C_2H_2
2500⌀
18ata
66 Siebböden
Abscheider
1ata
9500 m³/h
Ofengas
19ata
kompressor
18000 m³/h, 1800 KW
500 m³/h ; 45% C_2H_2
350 m³/h ; 92% C_2H_2
Rohgas 7500 m³/h
nach 460
Rohacetylen
nach Tiefkühlanlage 462 oder Oelwäsche
96% C_2H_2
Restgas to Arc
" " " from linde
N_2
CO_2
CH_4
C_2H_4
H_2
Acetylene
E1
2500⌀
2,6ata
E2
2400⌀
1ata
E3
2500⌀
0,15ata
E4
2500⌀
0,05ata
R
3900⌀
1ata
Belüftungsturm
2x
Limax Pumpe 900 m³/h
73KW
950 m³/h
99% C_2H_2
Pumpe 750 m³/h
450KW
Turbine 900 m³/h
Vak-Pumpe 3
5000 m³/h, 50KW
Vak-Pumpe 2
2x3500 m³/h;
0,45ata
Vak Pumpe 1
2250 m³/h; 54KW
150 m³/h
Zusatzpumpe
2x
Aenderungen:
Bestell Nr.
Bau Nr.
Bestellung
Besteller
Jahr
Paßsystem
Einheitsbohrung
Betriebsdruck .... atü
Probedruck ...... atü
Tag
Name
gezeichnet
geprüft
normgeprüft
Maßstab
Chemische Werke Hüls
Gesellschaft mit beschränkter Haftung
Marl Krs Recklinghausen
2
Ersatz für
Ersetzt durch

FIGURE IV


Zugehörige Zeichnungen
Zchg. Nr.
Stück-zahl
Benennung
Teil
Werk-stoff
Lager Nr.
Modell Nr.
Ge-wicht
Bemerkung
Rein-C_2H_2 ; 2750 m³/h
+10°C
Gegenströmer
F- 108 m²
NH₃-Vorkühler
F = 95 m²
kondensator
F = 37 m²
Gegenstromkühler
Tiefkühler
Ausgaser
About 5 to 10% Di Acetylene and higher acetylenes
3000 m³/h ; +25°C
-15°
Methanol
NH_3
-40°C
-60°C
-35°
-56°
-38°C
Wasser
10 m³/h
3000 m³/h
Roh-C_2H_2
+40°C
0.6ata
+20°C
Abscheider
Ausgaseturm
Kühler
Wasser
Blasegas
Elmo
180KW
0°
Wasser
Rohlibozol
Wärmer Ast F = 21 m²
Kalter Ast F = 12 m²
-40°C
+10°C
-65°C
-85°C
-78°C
F = 73 m²
F = 130 m²
-60°C
-55°C
Methanol
-55°C
Sole
-40°C
kondensat -40°C
Vorwärmer
Wärmeaustauscher
+40°C
Rohabgas (?)
Dampf

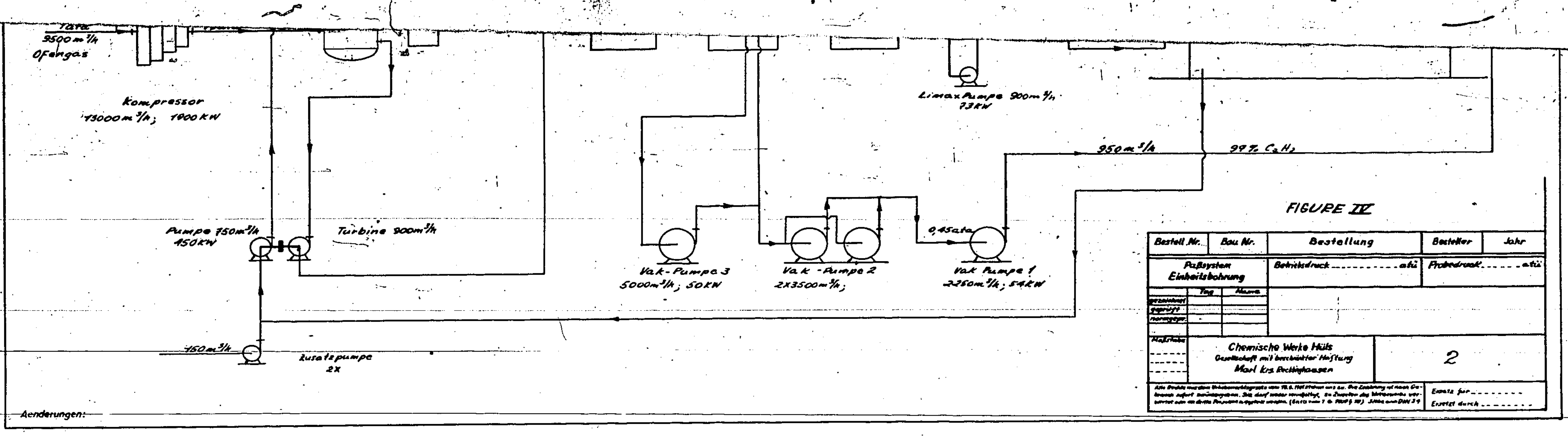


FIGURE IV

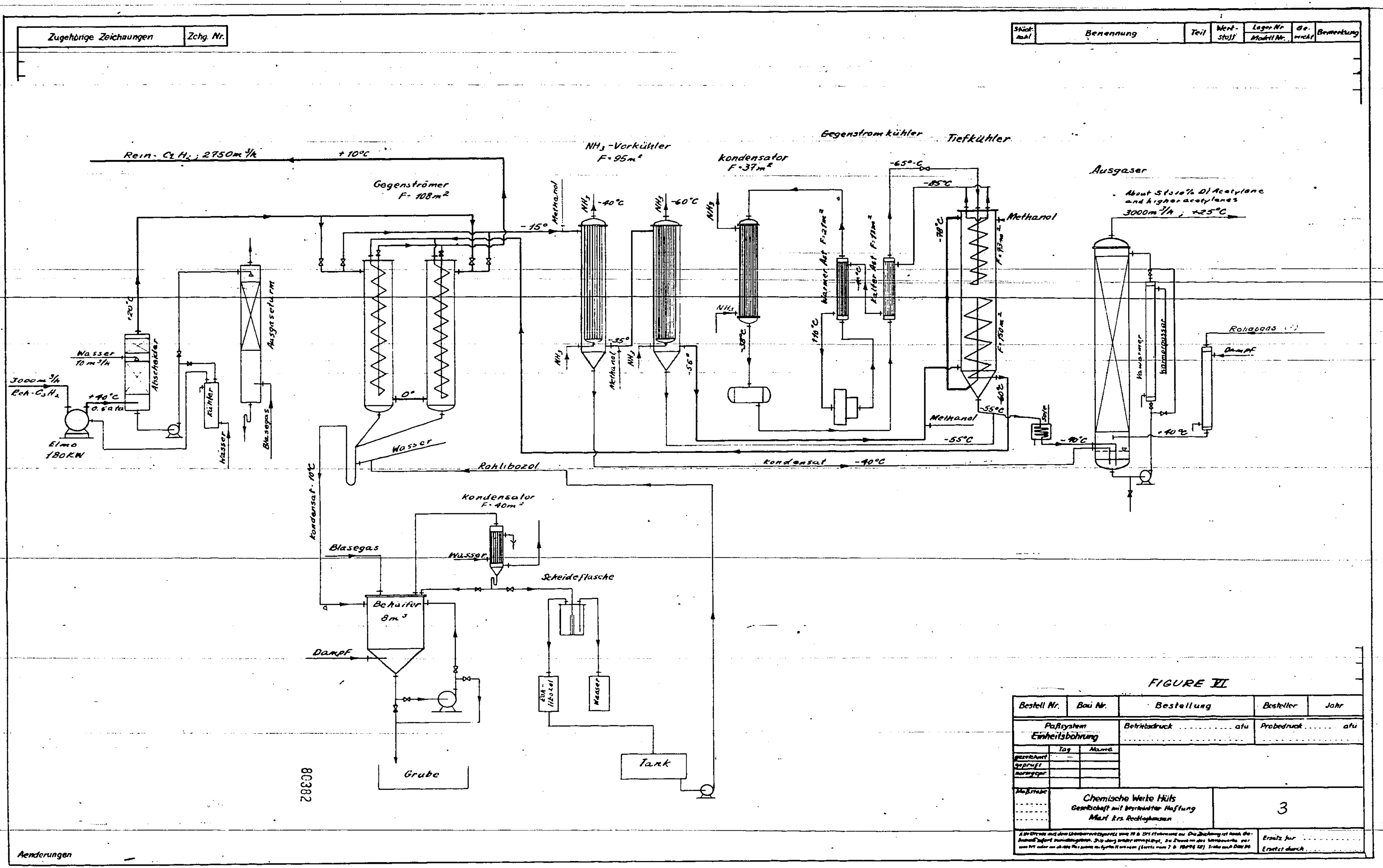


FIGURE VI

Bau Nr. .... Betrieb .... Gegenstand ....

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TECHNICAL REPORT NO. 155-45
FIGURES IV & VI

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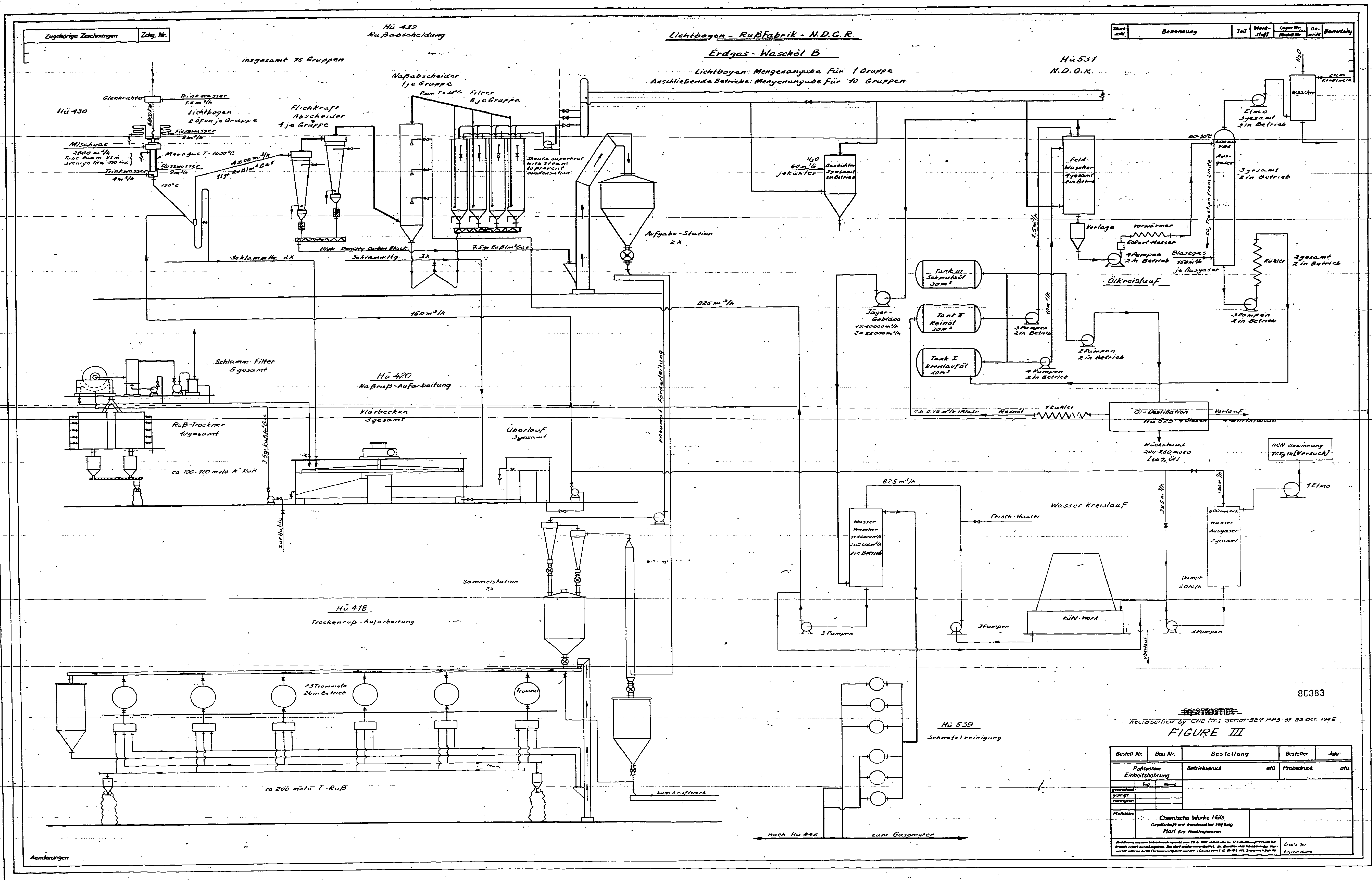

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FIGURE III

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FIGURE III
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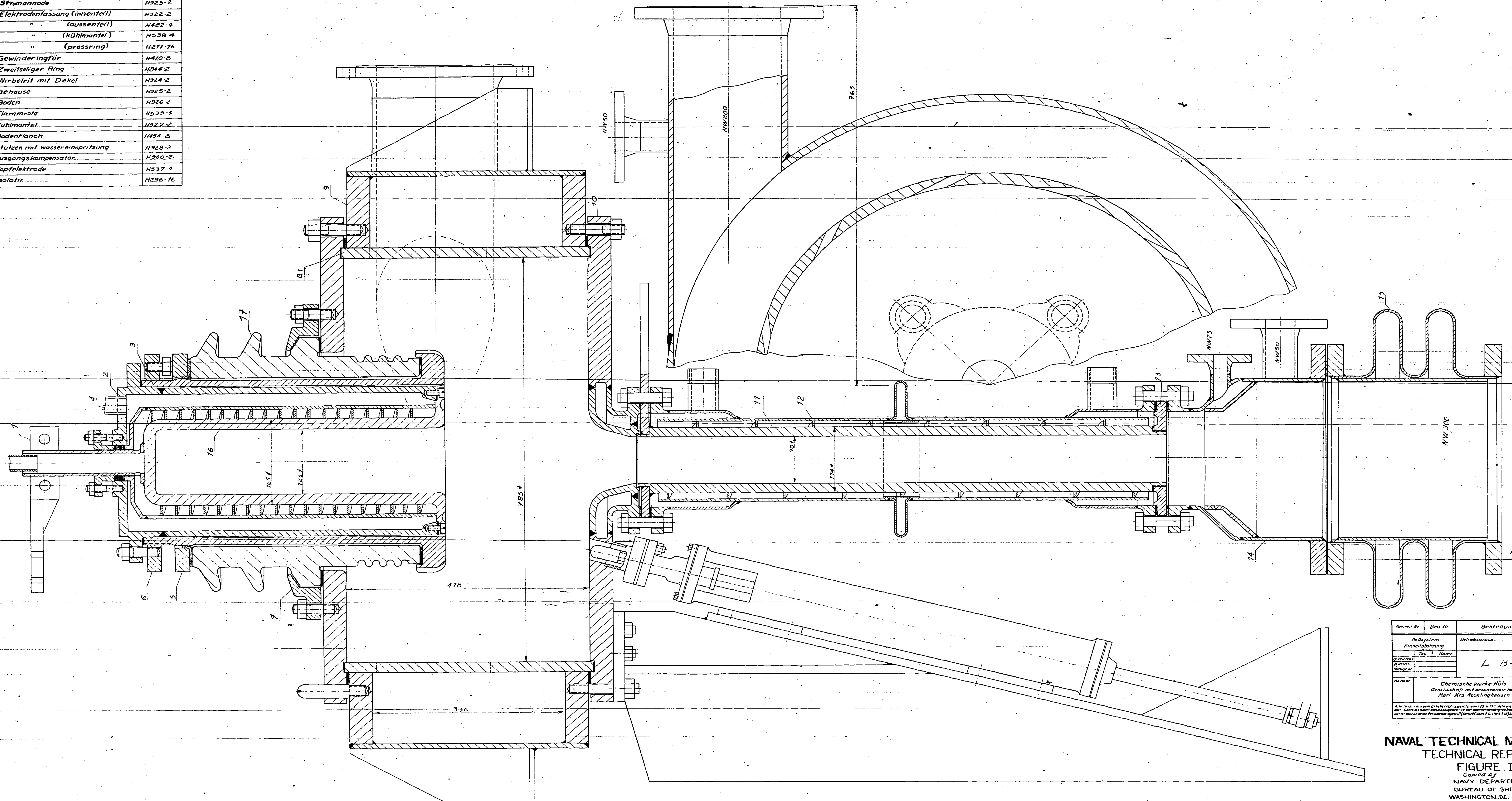
BUREAU OF SHIPS DR. NO. 841088

Teil	Zugehörige Zeichnungen	Zchg.-Nr.
1	Stromannode	H923-2
2	Elektrodenfassung (innenteil)	H922-2
3	" (aussenteil)	H482-4
4	" (kühlmantel)	H538-4
5	" (pressring)	H211-16
6	Gewinderingfür	H420-8
7	Zweitseliger Ring	H844-2
8	Wirbelrit mit Dekel	H924-2
9	Gehause	H925-2
10	Boden	H926-2
11	Flammrohr	H539-4
12	Kühlmantel	H927-2
13	Bodenflanch	H454-8
14	Stutzen mit wassereinspritzung	H928-2
15	Ausgangskompensator	H900-2
16	Topfelektrode	H537-4
17	Isolatir	H296-16



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Bestell Nr	Bau Nr	Bestellung	Besteller	Jahr
Pa Bsystem Einheitsbohrung		Betriebsdruck ... atü	Probedruck ... atü	
gezeichnet / geprüft / normgeprüft — Tag / Name		L-B-ofen		
Maßstab	Chemische Werke Hüls Gesellschaft mit beschränkter Haftung Marl Krs Recklinghausen	H696-1		
			Ersatz für Ersetzt durch	

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FIGURE II
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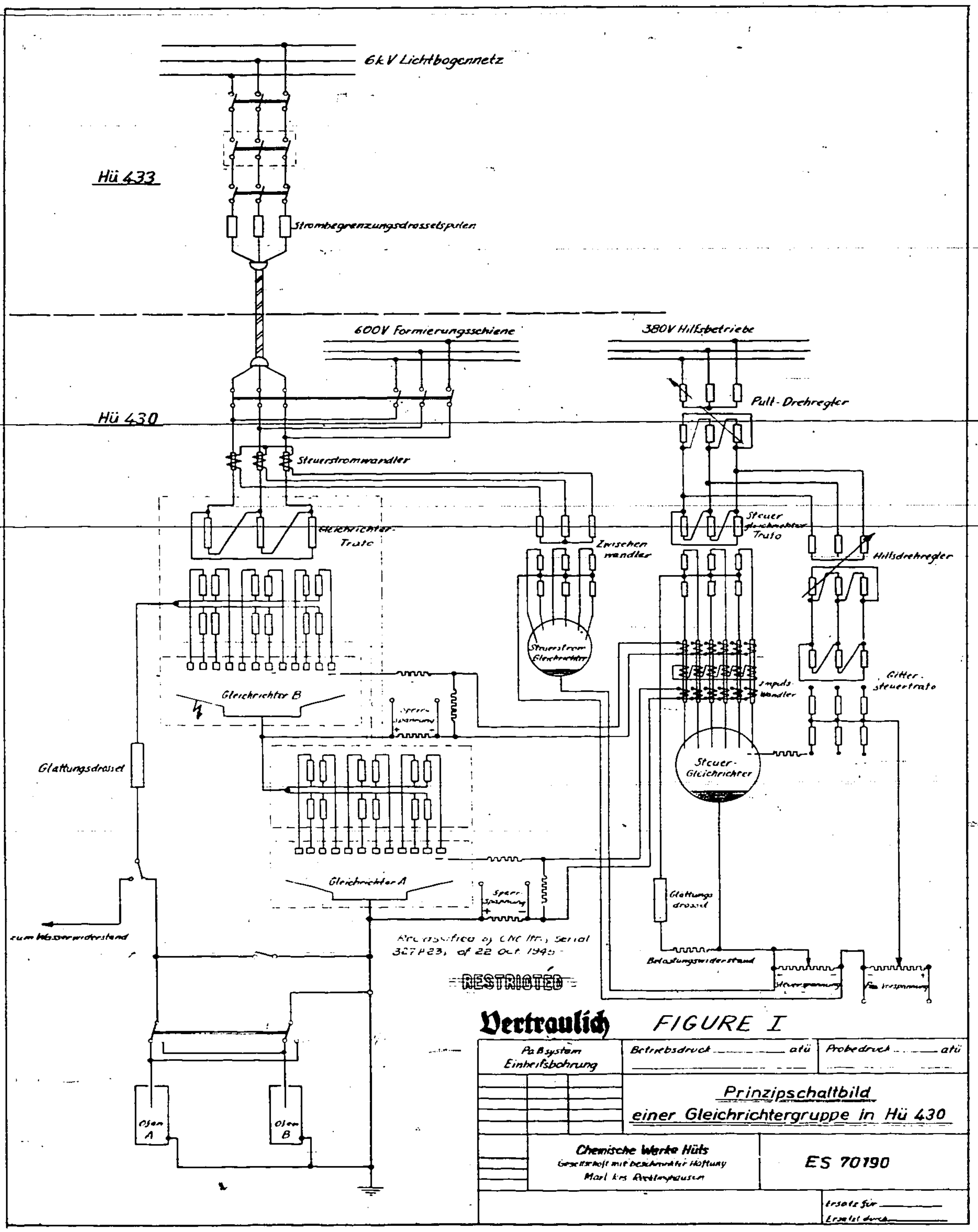

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Vertraulich FIGURE I

Paßsystem Einheitsbohrung	Betriebsdruck ______ atü	Probedruck ______ atü
	Prinzipschaltbild einer Gleichrichtergruppe in Hü 430	
Chemische Werke Hüls Gesellschaft mit beschränkter Haftung Marl Krs. Recklinghausen	ES 70190	
		Ersatz für ______ Ersetzt durch ______

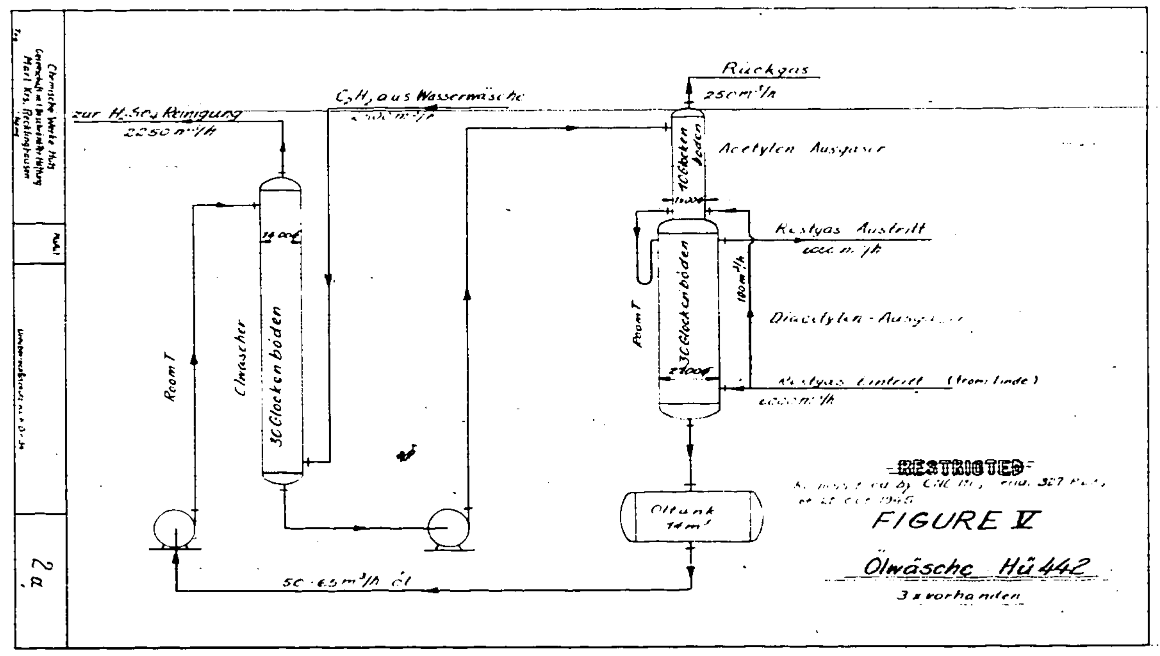

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FIGURE V

Ölwäsche Hü 442

3 x vorhanden

NAVAL TECHNICAL MISSION IN EUROPE
TECHNICAL REPORT NO. 115-45
FIGURES I AND V

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TECHNICAL REPORT No. 145-45

THE MANUFACTURE OF AVIATION GASOLINE IN GERMANY

July 1945

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To : Chief of Naval Operations (OP-16-PT).

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SUMMARY

This report records information obtained by technical investigators on the quantity, quality, composition, and manufacture of German aviation gasolines during the past war years.

Figures for the quantities of components and finished gasolines produced are presented and analyzed. The qualities and compositions of the different grades are shown and discussed.

The methods and plants used in Germany for synthesizing isoparaffins, for manufacturing base stocks, and for synthesizing aromatics are described. Process and operating data are given for these operations, particularly where the practice is new or different from that used in the United States.

The synthesis of nitration grade toluene is described in an appendix.

There are attached to the original copy of this report several German documents which will serve to elaborate some of the subjects covered herein.

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THE MANUFACTURE OF AVIATION GASOLINE IN GERMANY

1. Introduction.

It was well known that Germany had always depended largely on synthetic operations for her liquid fuel supply. As the air force of that nation grew and developed, and its fuel requirements increased both in quantity and quality, it was correctly concluded that synthetic oil plants had kept pace with the aircraft development and continued to be the main source of fuel supply.

The ever increasing quality of aviation gasoline used by the Allies was paralleled by that of the German supply. The many new processes applied in America for manufacturing high quality gasolines were well understood by the Germans. They obtained information through Allied technical publications, through analysis of gasoline from captured planes, and otherwise. At the same time, German research in great force was supplying new processes, many the same as those being developed by the Allies, to their own operations. Toward the end of the war the quality of fuel being used by the German fighter planes was quite similar to that being used by the Allies.

In entering Germany to study their manufacture of aviation gasoline, it was to be expected therefore that many processes and develoments would be found that were the same as those in use in America. Also, from examination of the gasoline in captured enemy planes, it was believed that no radically new compounds were being synthesized by the enemy. It could be anticipated, however, that new manufacturing techniques and technology might be found, that new designs in engineering might be seen, or that new or better catalysts might be in use in the various synthetic processes.

In the course of the technical survey being reported herein, most of the plants that manufactured aviation gasoline components were visited. Many industrial and government technical people were interrogated. A great variety and volume of technical and operating documents were obtained and studied.

In the following sections are discussed the overall German position on supply of aviation gasoline, and there are described the plants and processes producing the isoparaffin, base stock, and

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1. Introduction (Cont'd.)

aromatic components. Some of the newer research work is described. The manufacture of nitration grade toluene is also reported, because its production was rather closely related to the aviation gasoline systems.

2. Supply and Composition of Aviation Gasolines.

(a) Supply and Sources.

The German aviation gasoline volume came very largely from the synthetic oil plants that hydrogenated coals and coal tars. A very small volume only came from petroleum, while essentially none came from the Fischer-Tropsch plants. Some components in small volume came from various chemical plants.

Parallel to the situation in the United States, great efforts were put forth continually in Germany to increase the supply of aviation gasoline. Much of the new construction was never completed due firstly to Allied bombing and then to termination of the war.

In Table I is given a partial breakdown of the sources and volumes of supply of aviation gasolines and their components.

TABLE I.

Sources and Supply of German Aviation Gasoline.
(All figures are barrels per day)

Company and Location	Total Aviation Components	Base Stocks & Aromatics	Synthetic Isoparaffins
I.G. - Leuna	6,900	5,500	1,400
Brabag - Böhlen	4,100	4,100	-----
Brabag - Magdeburg	2,750	2,750	-----
Hibernia - Scholven	5,800	4,400	1,400
Gelsenberg - Gelsenkirchen	8,000	8,000	-----
Pölitz A.G. - Pölitz	13,900	12,400	1,500
Rheinbraun - Wesseling	2,750	2,750	-----
Ruhröl - Welheim	1,100	1,100	-----
Sudetendeutsche - Brüx	5,500	5,500	-----