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FISCHER TROPSCH UNIT
LEIPZIG GAS WORKS

Horne & Jones

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COMBINED INTELLIGENCE OBJECTIVES
SUB COMMITTEE

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FISCHER-TROPSCH UNIT
AT
LEIPZIG GAS WORKS.

Reported by

W.A.Horne, U.S.A.
J.P.Jones, U.S.A.

on behalf of

U.S.Technical Industrial Intelligence Committee.

CIOS Target No. 30/224
Fuels and Lubricants

22 July 1945.

COMBINED INTELLIGENCE OBJECTIVES SUB-COMMITTEE
G-2 Division SHAEF (Rear), APO 413

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Personnel of Team:

W.A.Horne) U.S. Petroleum Administration for War.
J.P.Jones)
L.L.Hirst) U.S. Department of the Interior, Bureau of Mines.
W.W.Odell)

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FISCHER TROPSCH UNIT AT THE LEIPZIG GAS WORKS.

Introduction.

The Fischer-Tropsch plant at the gas works of Leipzig, Germany, was being installed for the purpose of enriching the town gas for the city of Leipzig and at the same time to yield much needed recoverable liquid and solid hydrocarbon products. It was the smallest unit that was considered economically operable for this purpose and was 75% complete at the time the area was occupied, the last of April 1945. The plant was of usual design for operation at low pressure on cobalt catalyst; in fact, the reactors had been removed from the Lutzkendorf plant (30/5.08).

Description of Plant.

A simplified flow diagram is attached as Figure 1, and photographs of the plant are presented on Figures 2,3 and 4. The feed gas, a mixture of water gas and coke oven gas, was supplied by the gas works and the residual gas from the plant was to be returned to the gas works for admixture with water and coke oven gas and used in the Leipzig gas supply. The gas quantities and compositions were intended to be as shown in Table I. Although an activated carbon plant was being installed for the recovery of propane and butane, it was stated that it was only for possible future use. Hence, the propane and butane would be present in the residual gas, and the town gas would therefore be somewhat richer in C_nH_m and have a higher BTU content.

The mixed feed gas, supplied at 2300 mm. H_g by a blower at the gas plant, was to pass through an activated carbon coarse-purification unit containing a total of five tons (350-380 kg/cu.m.) of activated carbon prepared and supplied by I.G.Farbenindustrie. The unit consisted of three vessels (approx. 7 ft.diameter x 10 ft. high, back center Figure 4), each vessel alternately on 40-minute periods of adsorption-purification, steaming, and cooling. During the adsorption-purification period, the vessel on stream was to operate at atmospheric temperature and have a normal pressure drop of 400 mm. of Hg. The activated carbon was to be reactivated by steaming at 150-160°C. (maximum temperature of 170-180°C, or permanent damage to the carbon results). The cycle was to be completed by drying and cooling which was to be accomplished by recycling water-cooled residual gas over the activated carbon bed.

The gas then was to pass in parallel flow through a fine purification plant consisting of two units of three vessels each (approximately 8 ft. diameter x 8 ft. high, right, Figure 4), each vessel to contain 10 cu.m. of the usual iron oxide catalyst (total of 60 cu.m.). The gas was to be preheated sufficiently to maintain the temperature of this iron oxide catalyst at 250-300°C. This purification plant was expected to have a normal pressure drop of 500 mm. Hg.

The coarse and fine purification systems were stated to be oversize because it was anticipated that it might be necessary to use gas from the A.G.S.Werke, Böhlen (30/9.08) which was less pure than that from the Leipzig gas works.

The purified gas at 1200 mm. Hg. was then to pass in parallel flow into 4 units of 3 reactors per unit (each reactor approximately 16 ft. long, 6 ft. wide, 9 ft. high; see Figures 2 and 3). These were standard plate reactors (8 mm. spacing between 2 mm. fins) and were to operate at 185 to 200°C. and atmospheric pressure. Each reactor was to contain approximately 10 cu.m. of cobalt catalyst of 350 kg/cu.m. density which was to be supplied from the Lutzkendorf plant (30/5.08). Pressure drop through the catalyst bed was expected to be 500 mm. Hg. Boiler condensate from the gas works was to be used as the heat exchange medium for the ovens. It was to enter the lowest tubes and pass, by convection, upwardly through the remaining tube bundle. One steam accumulator was installed for each unit of 3 reactors (see Figure 3) for the recovery of the approximately 15-atmosphere steam, which was to be used either for the activated carbon regeneration or returned to the gas works.

The hot effluent from the reactors was then to pass into the bottom of a Raschig ring-packed water wash tower, (50 mm. pressure drop) the water and condensate to flow by gravity to separators and the wet gas was to be, either directly or through an activated carbon plant for recovery of propane and butane, returned to the gas plant. The two water-wash towers were approximately 50 ft. high and 4 ft. diameter, containing 6-2½ ft. beds of Raschig rings spaced at 1½-2 ft. intervals with intermediate distributors. The wash water (estimated 0.5% maximum acetic acid) with caustic, cooled in a spraytower and recycled.

The expected yield of liquid product was approximately 100 gms. per cu.m. consisting of 1/3 benzene, 1/3 medium oil and 1/3 wax. The liquid product (estimated at 500 T/Mo) was to be sent to Leuna or Lützkendorf for refining or further processing.

Personnel.

Ing. Bonnes, who was in charge of the installation of the plant for Lurgi, was interrogated on May 10, 1945, and served as a guide through the plant. The inspection and interrogation was by W.W. Odell, L.L. Hirst and W.A. Horne, and the photographs were taken by J.P. Jones.

W. A. Horne.
J. P. Jones.

TABLE I.

	Coke Oven Gas.	Water Gas.	Synthesis Gas.	Residual Gas.	City Gas.
Oven Gas	-	-	74,000	-	91,000
Water Gas	-	-	146,000	-	84,000
Residual Gas*	-	-	-	-	110,000
Normal cu.m./day	165,000	230,000	220,000	110,000	285,000
CO_2	2.4	5.0	4.1	8.1	5.4
C_nH_m	1.2	-	0.4	1.0	0.8
O_2	0.4	-	0.1	-	0.1
CO	5.7	38.0	27.2	21.3	21.2
H_2	59.0	52.0	54.3	37.5	48.6
CH_4	27.8	0.3	9.6	23.6	18.1
N_2	3.5	4.7	4.3	8.5	5.8
Kcals/Nm^3	-	-	-	-	4000
Density, Kg/Nm^3	-	-	-	-	0.632

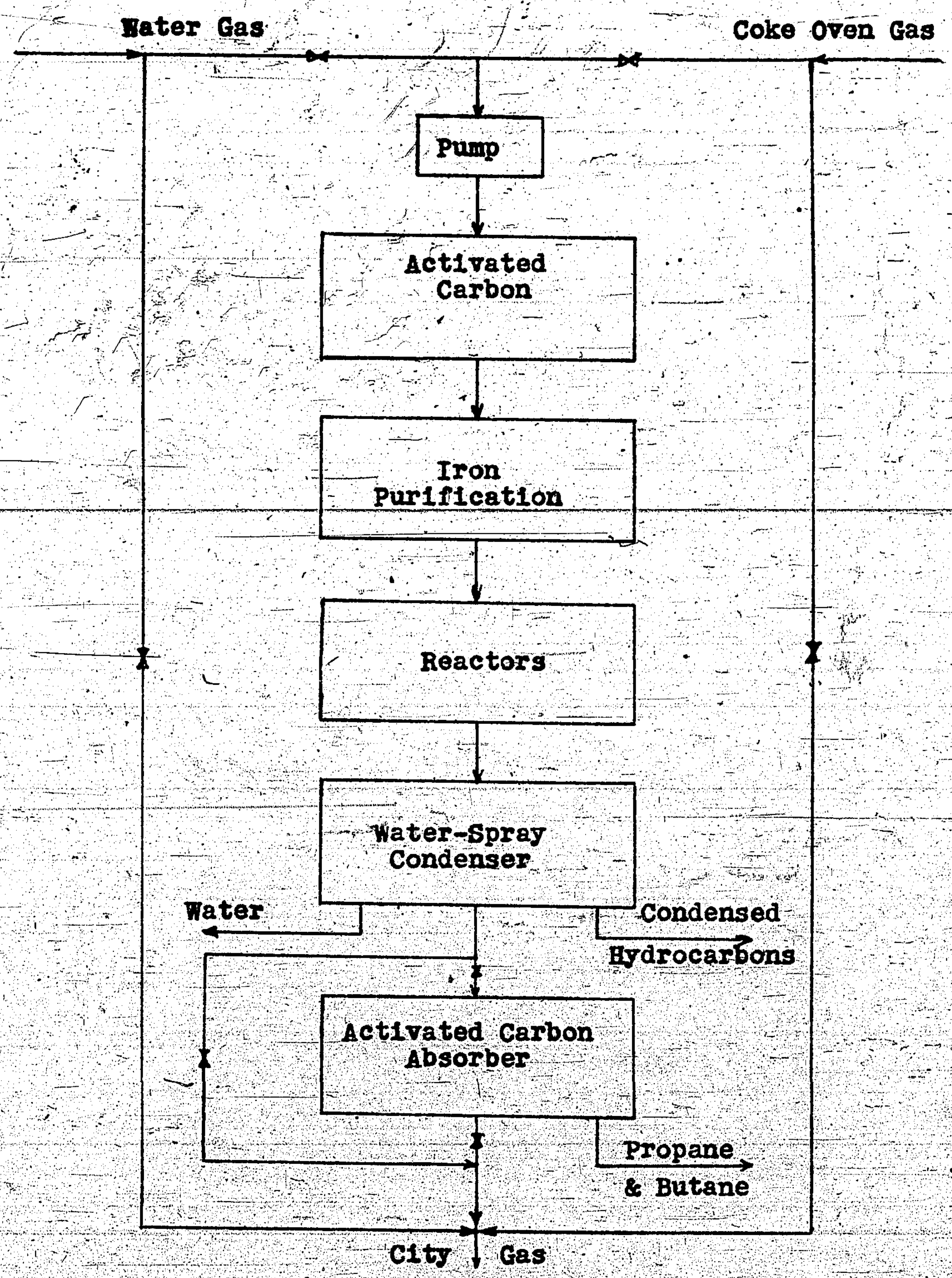

Figure I

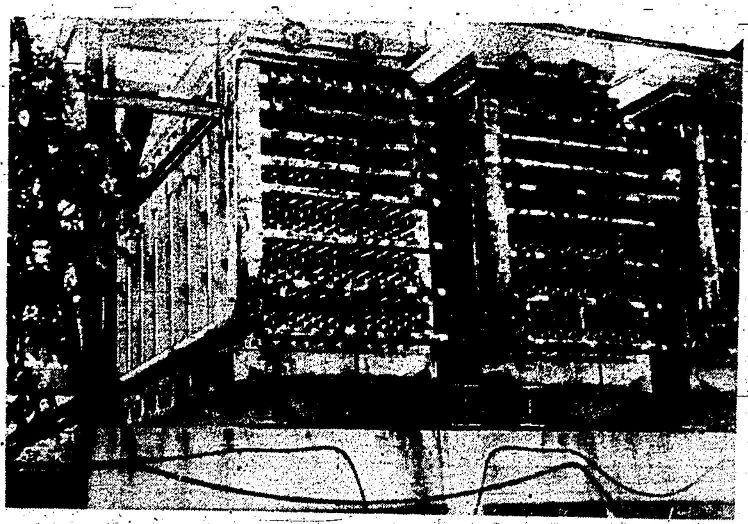

Figure 2.

End of Fischer-Tropsch Reactors, showing Coils and Piping for cooling Water.

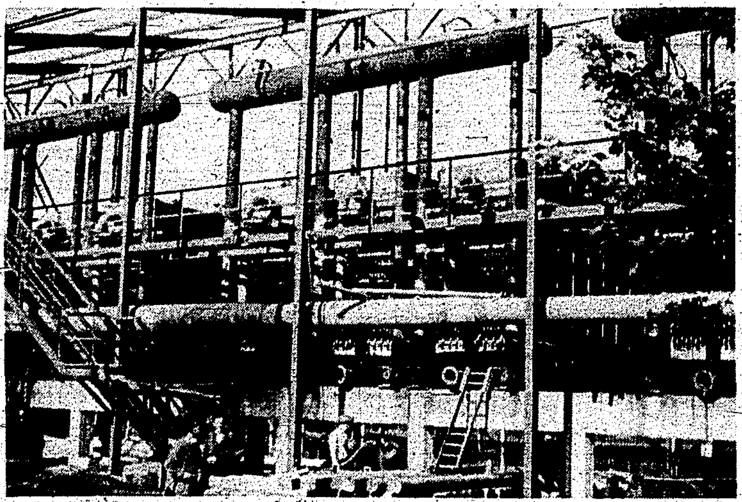

Figure 3.

Fischer-Tropsch Reactors showing Elevated Steam-Water Separators for Cooling System.

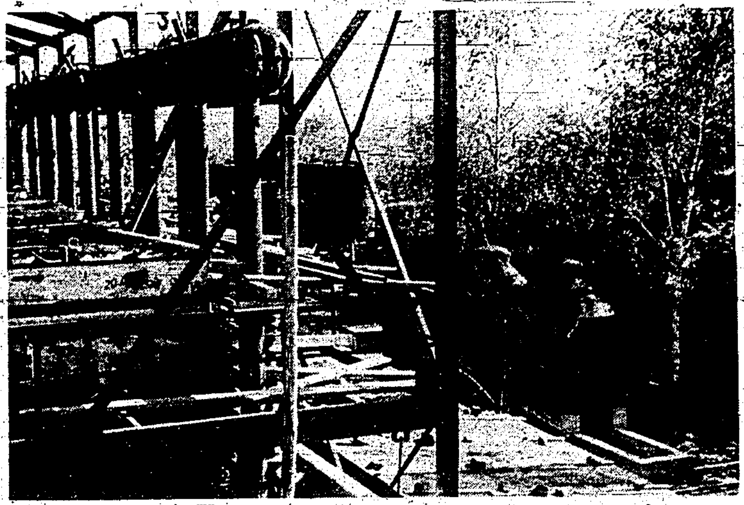

Figure 4.

Fischer-Tropsch Plant
Back Center - Charcoal Absorbers
Right - Organic S-Removal Reactors
Left - F.T. Reactors and Cooling
System.

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Report No. 290

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WIRTSCHAFTLICHE FORSCHUNGS G.M.B.H.
STASSFURT AND BAD BERKA

Reported By:

D. A. Howes Brit.
J. G. Allen U.S.
Hans Schindler U.S.

[1945]

This report has been declassified and released to the Office of the Publication Board by the War and Navy Departments.

NOTE: The Publication Board, in approving and disseminating this report, hopes that it will be of direct benefit to U. S. science and industry. Interested parties should realize that some products and processes described may also be the subject of U. S. patents. Accordingly, it is recommended that the usual patent study be made before pursuing practical applications.

7 p.

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Personnel of Team

D. A. Howes, British Ministry of Fuel and Power
J. G. Allen, U.S. Petroleum Administration for War
Hans Schindler, U.S. Petroleum Administration for War

INTRODUCTION

Several "WIFO" Underground Blending Stations have been located in Germany and inspected by different groups of investigators. This report, one of the series on this type of blending installation, covers the "WIFO" stations at Leopoldshall-Stassfurt and at Bad Berka near Weimar.

LEOPOLDSHALL-STASSFURT STATION

General Description

This WIFO Blending Station, having telephone connection Stassfurt 915 or 916, was visited on May 14, 1945, and the following information was obtained by interrogation of:

Engineer Lehmann, in charge of blending
Engineer Peters
Mr. Schnellenbach, Chief Chemist

Blending of motor gasoline and Diesel oils only is carried out at this location, the whole installation, with the exception of the laboratory and the general office, being underground in a salt mine. Construction started in 1935, the station was first used in 1938 and it operated continuously until April 10, 1945. The maximum output of blended fuels was stated to be 12,570 barrels per day. There are 110 tanks below ground with a total capacity of 1,390,000 barrels, the smallest tank is of 2,170 barrels capacity and the largest of 31,700 barrels capacity.

These tanks are 918 feet below ground level and three pipe lines run up one of the shafts to receive and discharge oils from and to rail and road tank cars. These lines are about 8" ID. Gasoline or Diesel oil components or blends could be received or shipped out at the maximum rate of 12,570 B/D, except when two of the lines were used for circulation in adding tetra ethyl lead to a blend, the TEL addition being made on ground level. The reason for this was stated to be poor ventilation in the mine and the resulting health hazard. Carbon dioxide is used for fire fighting.

Motor Gasoline is blended from Hydro gasoline with or without benzol, plus TEL. Gasoline was received (by rail) mainly from Magdeburg (Brabag), Böhlen, Schwarzheide, and Leuna, the latter not recently.

Aviation Diesel Oil for the Luftwaffe comprises:

50% Fischer Tropsch Gas Oil. (DT.901)
45% Petroleum Gas Oil, 31° API (DT.150)
5% Spindle Oil

The minimum Cetane Number is 50, and the maximum API Gravity 43°.

Jet Propulsion Fuel Specifications

The latest specifications are given in a letter dated 14.11.44 from Zentralbüro für Mineralöl G.m.b.H., Dresden, to Mr. Schnellenbach at Stassfurt, which is translated below:

"Following our 'phone conversation this morning, we give below the analytical requirements for aviation fuels of the J- and JT series. All previous data are hereby superseded. The data now communicated are intended for your personal information only and may not be duplicated by you, or communicated to a third party.

Description Inspection	J.2	JT.401b	JT.402
Sp. Gr. at 15°C. Min.	0.800	0.780	0.800
(API at 60° F., Max.)	45.5	50.0	45.5
Vapor pressure, 100° F, psia, Max.	2.9	4.4	4.0
Viscosity at 68° F, °Engler, Min.	1.0	1.0	1.0
(SSU max.)	30	30	30
Viscosity at -4° F, °Engler, max.	3.0	8.0	-
(SSU max.)	105	280	-
Viscosity at 32° F, °Engler	-	-	3.0
(SSU)	-	-	105
Filtration Time, Sec., max.			
at -13° F	120	-	-
" -4° F	-	120	-
" 32° F	-	-	120
Pour Point, °F, min.	-13.0	-	About ≠ 14
Sulfur, %, max.	1.5	1.5	1.5
Phenol, Vol. %, max.	1.0	1.0	1.0
Aromatic Content, %, max.	45	-	-
Conradson Carbon Res., %, max.	1.5	1.5	1.5
Ash, %, max.	0.5	0.5	0.5
Lower Caloritic Value, Btu/lbs., min.	16,200	16,200	16,200
Corrosion, Zinc, mg., max.	4	4	4
Corrosion, copper	Neg.	Neg.	Neg.

"As you see from the above table, the phenol content is expressed in vol. %. Will you please bear this in mind in your future investigations. Kindly determine the values given above for all blends to be prepared in the blending programme of the J- and JT series and telegraph us the results. Power to release the blends is retained expressly by us."

Lubricating Oil Specifications

Although no lubricating oil blending was carried out at this WIFO Station, stocks of lubricating oil were received for storage and were also submitted to routine inspection in the Laboratory. Current specifications were as follow:

Description Inspection	SS 906	SS 903	Rotring
Sp. gr. at 20° C.	0.850-0.860	).850-0.860	0.885 Max.
(API Gravity at 60° F)	32.3-34.2	32.3-34.2	27.7 Min.
Viscosity, °Engler			
20° C	330-360	112	126 Max.
50° C	43-46	19-20	17.95Max.
100° C	5.8-6.0	3.3-4.0	2.61 Min.
(Viscosity, SSU)			
100° F	3300-3500	1300-1350	1270 Max.
130° F	1250-1300	550-630	500 Max.
210° F	205-220	120-140	90 Min.
Pole height, maximum	1.7	1.7	2.1
Slope constant, m	2.95-3.05	2.95-3.05	3.4 Max.
Viscosity Index, min.	108	108	98
Flash Point (open cup) °F.	437	437	509 Min.
Pour Point, F.	-13	-22	-0.4 Max.
Neutralization No., (mg KOH/g), Max.	0	0.1-0.2	0.06 Max.
Saponification No., (mg KOH/g), Max.	0.3	0.5	0.12
Conradson % Carbon Residue, Max.	0.2	0.2	0.25
Ash, %, Max.	0	0.01	0
Hard Asphalt %	0	0.03	0

Existing Stocks

These at the time of the visit were stated to be as follows:

Motor Gasoline	950 Barrels

Diesel Fuel of which	63,000	Barrels
	31,500	Barrels is Fischer Tropsch Gas Oil
	13,000	to 19,000 Barrels is finished blended fuel
T.E.L.	5,000	drums each of 200 litres capacity (Approx. 264,000 U. S. gallons.)
Ethylene Dibromide	3,000	drums each of 200 litres capacity (Approx. 159,000 U. S. gallons.)

Stocks of gold, platinum and cobalt were also in the mine. Details were given to the local Military Government. These stocks were under guard and were being examined by the U. S. Ordnance Department.

Laboratory

The laboratory is well equipped to carry out oil testing and the following engines are installed:

1 I.G. Prüfmotor
1 Deutz Diesel - single-cylinder
1 4-cylinder automotive engine coupled to a water brake.

Condition of Equipment

The storage facilities underground were stated to be intact, but were not inspected. The superstructure, containing the office and the hoisting equipment, were wrecked by the bombing of April 10, 1945, which shut down operations. Records were destroyed by displaced personnel in the vicinity after the bombing. The laboratory, located about 1/2 mile from the mine, suffered very little bomb damage.

BAD BERKA STATION

This target was visited on May 16, 1945. It is located in a woods about 5 miles east of Bad Berka.

No local operating personnel could be located, and no records other than shipping forms identifying it as an aviation fuel blending station were found. The place was under military guard.

The installation had several cone-roofed tanks camouflaged in the woods, but the main blending tanks, lines, etc., were located underground. No attempt was made to estimate the entire storage capacity or stocks on hand. A supply dump of aviation lube oil (S-3) in barrels was evidently maintained at this location also.

Blending components appeared to have been received by rail and shipped by rail or truck.

The entire installation had suffered considerable damage by bombing and did not appear to have been repaired since the attack.

OTHER WIFO STATIONS

Information was received that other Blending Stations are located at:

VORDEHEIDE	Near Lignitz
DERBEN (on the Elbe)	Aviation Fuel
HEILIGENSTADT	Near Kassel on the Kassel Nordhausen Road.

Maj. D. A. Howes
J. G. Allen
H. Schindler

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I. G. FARBENINDUSTRIE A. G., LEUNA
NITROGEN FIXATION PLANT

Hunter, R. M.

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COMBINED INTELLIGENCE OBJECTIVES
SUB-COMMITTEE

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I.G. FARBENINDUSTRIE AG
NITROGEN FIXATION PLANT
LEUNA, GERMANY.
10 May, 1945.

Reported By

R. M. HUNTER
TIIC Chemicals Representative
CWS HQ ETOUSA

2 June, 1945

CIOS Target Number 22/1(i)
Miscellaneous Chemicals

COMBINED INTELLIGENCE OBJECTIVES SUB-COMMITTEE
G-2 Division, SHAEF (Rear), APO 413

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PERSONNEL OF INSPECTION TEAM

R. M. HUNTER
TIIC Chemicals Representative
CWS, HQ ETOUSA

I.G. FARBENINDUSTRIE AG

NITROGEN FIXATION PLANT

LEUNA, GERMANY

1. INTRODUCTION

a. The Leuna Works of I.G. produces a number of products from the gases resulting from brown coal processing. Among the important products is synthetic ammonia. This operation is intimately dovetailed into the plant operations, and, as a result, was not assembled as a complete unit. The capacity of Leuna is given in "Economic Survey of Germany," Section I, page 48, as 2000 metric tons NH_3 per day. The persons interviewed insisted that the production was 1000 tons per day. However, since many other materials, as for example urea and nitrogenous fertilizers, are produced, the necessary raw materials and equipment for fixing 2000 metric tons may be present though not used specifically for the production of liquid NH_3.

b. Coal analyzing 53% H_2O, 6% ash is mined by open pit operations 5 miles from the plant. The 50 ft. seams are covered by a 100 ft. of overburden. The mining operation brings coal to the plant at a very low cost (estimated to be about 80-90 pfennig per ton delivered at plant).

c. The writer interrogated Dr. Kading of the Engineering Dept., and Mr. Braunsdorf, ammonia department superintendent. Time and wreckage of equipment did not indicate the necessity of a plant inspection.

2. PROCESS

a. A number of gases are used, but, in the main, the process resembles the usual producer gas and water gas operation, the CO being converted to CO_2 by iron oxide catalyst. CO_2 is removed by water at 25-30 atmospheres and a gas results which is composed of 1 volume N_2 and 3 volumes of H_2. About 3% CO remains which is treated with cuprous ammonia solution at 240 atmospheres. If the mixture is incorrect, it is adjusted by addition of N_2 from a Linde liquid oxygen plant. Such additions are made before the cuprous scrubbing. It was stated that no oxygen remains.

b. The new gas goes into the circulation system between the catalyst converter and the water cooler. At this point the gas is 150°C and 10-14% NH_3. Introduction at this point enables the removal of impurities in condensation of the ammonia. The quality of product is lowered by water and other impurities. The gas is cooled by water in concentric pipe coolers, the water being outside and arranged for counter flow. The river water varies from 1°C to 22°C. Cooling is to about 15°C above water temperature, largely due to dirty water fouling the surface. Such tubes are cleaned with difficulty. The gas leaves the water cooler, then passing to a cold exchanger, which cools to 0°C, then to a refrigerator cooled by boiling NH_3 at 0.4 atmosphere which is in a separate refrigeration system. This cools to -20°C, and strips the 10-14% gas to 3% NH_3; the condensate falling to a flask for withdrawal. The remaining gases go to the above cold exchanger and are reheated to +10°C, thence to the circulating pump, which discharges to the catalyst converter bomb. The above is the standard Haber flow. Warmer water would either require more refrigeration or would lower the converting efficiency.

3. NH_3 CONVERTER (See Appendix 1)

a. The catalyst converting bomb is 800 mm inside diameter and 12 meters long and has capacity of 30 tons NH_3/day. It contains 6 tons of catalyst (440 lbs. catalyst per ton NH_3/day). The catalyst occupies 9 of the 12 cubic meters and the interchanger of the catalyst 2½ meters. All internal parts of the bomb are made of S-2 steel containing 0.2% carbon, 0.4% Mn 0.2% Si; 5% P+S and zero % Cr, V and Ni. The pressure bomb vessels are also of S-2 steel since they never get above 100°C. Some vessels of newer construction were made of 1% Cr steel, allowing thinner walls. Apparently no great difficulties result from use of the above ordinary steel for catalyst vessels. If steel of 0.4% carbon is used for catalyst interior parts (subjected to H_2 and N_2 at 500°C and 240 atmospheres) brittleness and growth results. Some equipment of 0.2% carbon steel has suffered from embrittlement.

b. In the catalyst the gases from the circulating pump (10°C) go in the top, pass down the inner wall (keeping it cool), up around the tubes of the exchanger where it is heated to 400°C, then going up around the tubes in the catalyst body for further preheat and down the central well containing an electric heater, which is used if necessary to maintain 500°C, thence up around the central tube, and then down thru the tubes containing catalyst (temperature slightly above 500°C). The gas now containing 10-14% NH_3 passes down thru the preheater tubes and out at 150°C.

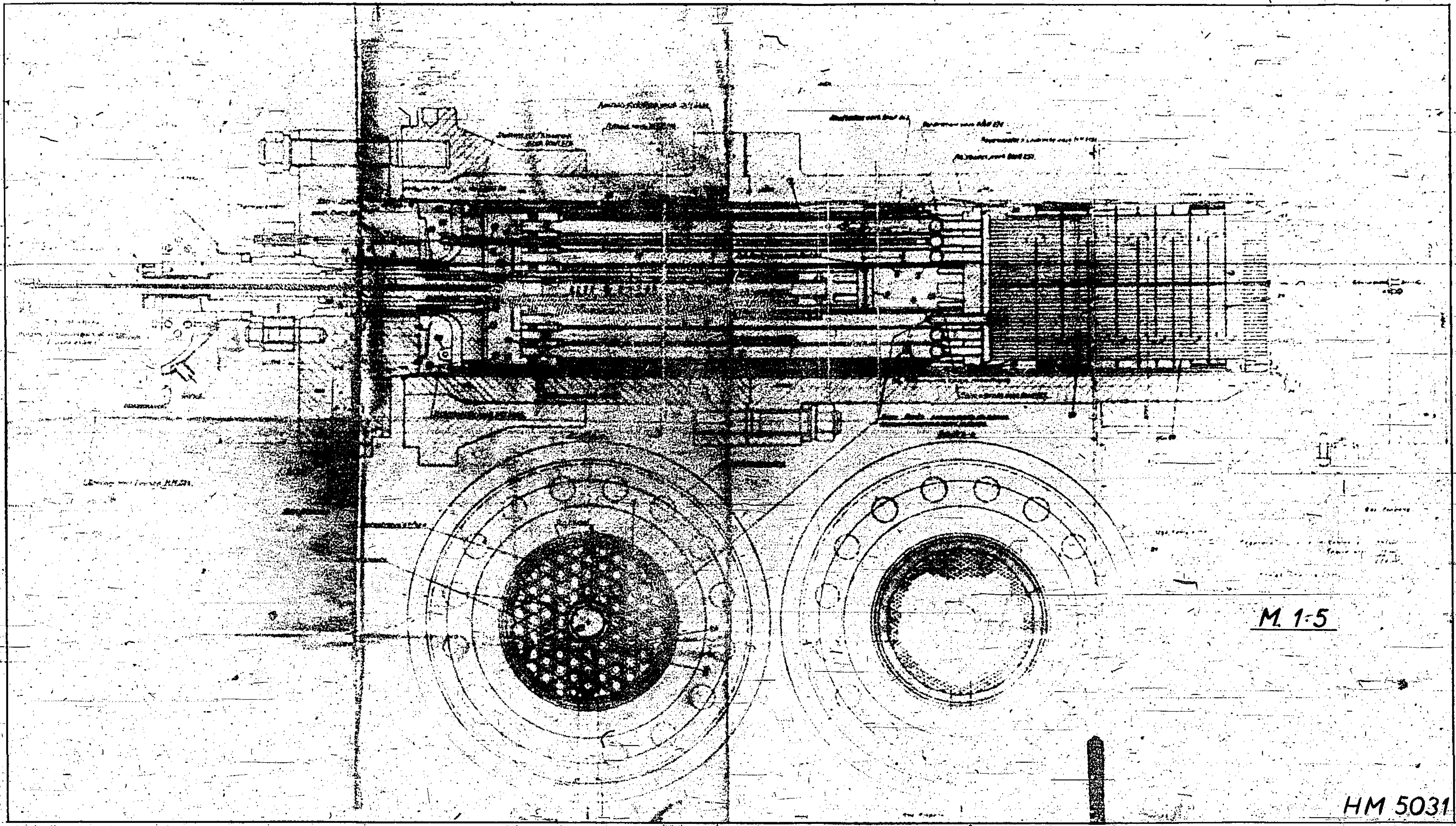
c. Failures are due to poisoning, but also due to failure of the interior S-2 apparatus. The tubes containing catalyst are the chief source of failure. They are rolled into the lower tube sheet, but float thru packing (to allow for thermal expansion) at the top; maintenance of this asbestos packing is difficult and construction uncertain. A failure here permits bypassing of the catalyst and the electric heater tube. The brittleness previously mentioned also causes breakage and failure.

4. CATALYST COMPOSITION

a. Information on catalyst was specifically requested. This research is done at Oppau, where many tests have been made. Very few tests were made at Leuna and the catalyst analyses (stated) 0.5% K; 2.5% Ca, balance iron. Pure iron (preferably charcoal) is used in fine state, the K is added as the nitrate, and the Ca as lightly burned lime. The iron is melted by burning with O_2 till melted, the accelerators are mixed, cooled, crushed, and sized. They were unwilling to place a life on it for the above reasons, but stated it varied from 100 days to three years.

5. PRESENT CONDITION

a. The plant was built in 1916, and enlarged in the early twenties. The apparatus is bunched by units, pipes between units being long, particularly those to and from the circulators. Pressure drops are therefore large, and the circulators have heavy loads. High production aggravates all these difficulties. The Leuna plant is badly bombed, the pressure vessels being undamaged. It was stated that most damage was to piping and that they could start 100-150 tons almost at once, but that it would take a long while to get to 1000 tons per day. However, other parties working in this area have found that such statements are made for the purpose of "getting anything started." In this way, other facilities are always needed. Such statements should be discounted.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EDELEANU G.M.B.H., ALTENBURG

Jones, J. P

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COMBINED INTELLIGENCE OBJECTIVES
SUB-COMMITTEE

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EDELEANU G.m.b.H., ALTENBURG, GERMANY

Reported by:

J.P. JONES, U.S.A...

on behalf of

U.S. Technical Industrial Intelligence Committee

May, 1945

CIOS Target Number 30/89

Fuels and Lubricants

COMBINED INTELLIGENCE OBJECTIVES SUB-COMMITTEE
G-2 Division, SHAEF (Rear) APO 413

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H.M. Weir	
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PERSONNEL OF INVESTIGATING TEAM

G.S. Bays, Jr. W.A. Horne J.P. Jones B.L. MacKurick H.M. Weir	U.S.Petroleum Administration for War.
L. King.	British Ministry of Fuel and Power.

EDELEANU G.m.b.H.

Altenburg, Germany.

INTRODUCTION

The main offices of Edeleanu GmbH., together with the key officials, were evacuated to Altenburg Castle, Altenburg, Germany, in February 1945 from their permanent offices at Martin Luther Strasse 61-66, Berlin-Schöneberg. The following were interrogated in a conference room in their offices on 10 and 12 May, 1945.

Prof. Ernst Terres.	Manager
Dr. Karl Fischer.	Chemical Research
Alfred Hoppke.	Technical Chief
Henry Manns.	Chief Draftsman
Kurt Engfer.	Chief of Commercial Office.

In addition, the following technical men had been briefly interrogated, on 9 May, 1945, at the plant of A.G.S. Werke Espenhain, located north of Borna on the road between Leipzig and Altenburg.

Dr. Karl Mueller.
Dr. Widdecke.

It was subsequently learned that the offices and personnel of the company moved to Frankfurt A/M and they were briefly visited at Bleichstrasse 64 on 27 August and 3 September 1945 to obtain duplicates of documents lost in CIOS channels (See page 18).

SOLVENT EXTRACTION OF OILS

Hunter and Nash have previously shown how to record and evaluate data from the solvent extraction of mineral oils in isotherms on triangular coordinates. This method of presenation gives the following information for a given extraction temperature.

(a) Composition of particular extract and raffinate solution (as to solvent content) for a given charge stock.
(b) Densities of the resulting raffinates and extracts.

(c) The amounts of raffinate and extract solutions, and the yields of each.
(d) The best raffinate (with lowest density) and the best extract (with highest density) and the corresponding yields, obtainable in a multistage extraction.
(e) The amount of solvent required for such a multistage extraction.
(f) The number of stages which must be used for the extraction either at a constant temperature or at several temperature levels.

Such a representation on triangular coordinates gives no information as to the composition of an oil with reference to its refinability and also does not give any means of directly comparing different charge stocks on the basis of their paraffinicity, nor does it give a direct method of comparing the possibilities of various solvents, nor any information pertaining to the possible uses of temperature gradients.

A valuable supplement was found to the triangular coordinate system of presenting data, which answered all the above questions, but which did not give an indication of the amounts of solvent used nor of the solvent contents of the raffinate and extract solutions.

The information obtainable can be briefly summarized as follows.

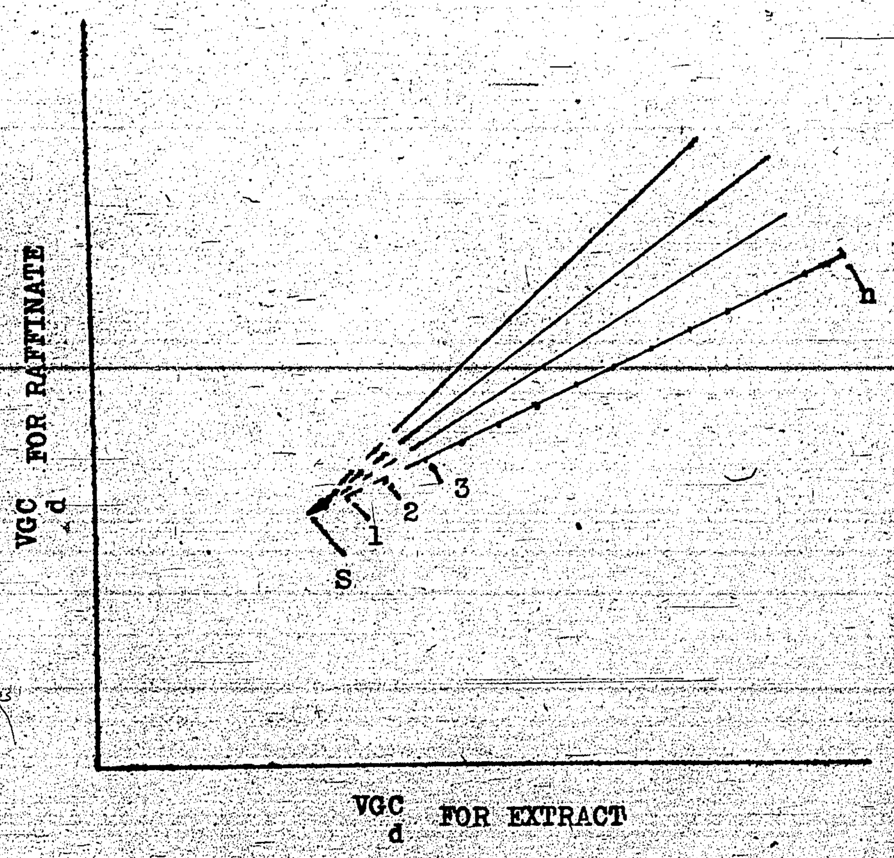
1) If the respective densities, or the viscosity - gravity constants, of the raffinate and extract for each stage are plotted as ordinates and abscissae, or vice versa, on a rectangular coordinate system, a straight line will result (i.e. such as any one of the lines in Fig. I).
2) Such a line will have a different slope for every charge stock, depending upon its content of paraffin, naphthene, aromatic, and olefin hydrocarbons, and an indication of the paraffinicity of the charge stocks is given by this slope, when using the same extraction conditions with different oils.
3) The lines resulting from plotting data obtained from the use of the same solvent with a given oil, at different temperatures, all intersect in a common point (See Fig. I).

4) The lines resulting from plotting data obtained from the use of different solvents with the same oil intersect in that same point.
5) As a result of this clear and simple method of representation the various solvents can be directly compared with each other.
6) The effect of the use of a temperature gradient can be readily recognized and evaluated.
7) This common point of intersection, through which all their extraction lines pass, makes it possible to establish which is the best raffinate (i.e. with the best possible index value) that it is possible to obtain from a given oil.
8) These straight lines give an insight into the composition of a given oil which can not be obtained by fractional distillation, nor fractional extraction, nor by other analytical data.

This knowledge, that such straight lines on a graph could be so obtained, induced the Edeleanu organization to evaluate in the same way data which had previously been obtained for other purposes and to verify and amplify the conclusions with systematic new research. This occupied the entire time of the organization after 1939. The benzine - SO_2 extraction apparatus at Courchelettes, France, with a capacity of about 65 metric tons a day and used since 1936, was employed with a different arrangement to find the answers to various questions using an Iraq oil. In addition experiments have been carried out with a lubricating oil distillate from Zistersdorf, Austria, and a paraffin cut from a Persion oil.

When experiments are carried out using the same solvent and extraction conditions, but with different charge stocks and the results are plotted as herein before described, the slope of the lines will be an indication of the paraffinicity of the charge stock. The steeper the line the more paraffinic is the oil.

Figure I shows diagramatically the lines which are obtained when working with one distillate as an extraction charge stock. If this charge is extracted at the same temperature with varying amounts of each of several solvents the results for each solvent will fall along one of such a group of lines. The fact that all of these lines cross at a common point of intersection shows that this point represents the best possible raffinate obtainable from this charge stock. The point can never be actually obtained experimentally but it can be more closely



RESULTS OF SOLVENT EXTRACTION OF AN OIL DISTILLATE

FIGURE I

approached with a charge stock having a low content of paraffin hydrocarbons than with a charge stock having a high content of paraffins.

The solid lines are in a range which it is possible to cover experimentally and the broken lines are extrapolations. A similar group of lines is obtained by extracting a charge with the same volume of each of several solvents at varying temperatures. The common point of intersection will be the same as obtained with the first group.

The big advantage of this system is that the common point of intersection (which represents the best possible raffinate) can be determined from four experimental runs to obtain two experimental points for each of two lines. Thus, the use of two different volumes of solvent for extraction at the same temperature will establish one line and similar use of another solvent will establish a second line, or use of the same volume of a solvent at two different temperatures will also establish one of the lines.

Straight lines, such as just discussed, are obtained only from extractions of a distillate. If the material being extracted is a residual fraction the lines will be straight for only a part of the distance from the common point of intersection, after which they will curve upwardly. The intersection point for such materials can be determined only by making a sufficient number of experiments to ensure that the data are in that part of the line which is straight.

It was further stated by the Edeleanu representatives that it is possible to determine the composition of an oil from any extraction line which passes through the common point of intersection, S. Such a line is divided into equal divisions, beginning with point 1. For each of these points the relative amounts, in per cent, of raffinate and extract can be determined. As the basis for this study is the assumption that the raffinate and extract for point 1, for example, have been produced by a separation of the raffinate from point 2, and likewise the raffinate and extract for point 2 have been produced from the raffinate of point 3, etc. Since the entire series starts with point "N" (highest density for an extract) and has developed from this first point to this latter extract and associated raffinate, it is possible to calculate for each point the amount of extract and raffinate as per cent of the charge stock, and since all raffinates (up to the point, S) are subjected to still further separations the composition of the charge stock can be obtained by adding to this raffinate, in proportional parts, the extracts corresponding to each differential of the line. If, on the basis of other data, the relationship of density to viscosity index is known for the same oil, it is possible to determine what relative amount of material of each viscosity index can be determined for each given amount of raffinate.

In Figure II, is shown such an analysis of an oil as a zig-zag line; the smooth curve represents the relationship of viscosity index to yield which has been determined from the relationships of density to yield. Such an analysis of an oil can be made when the initial lines (Fig. I) are drawn with either density or viscosity gravity constant as the basis for the coordinates.

AN OPTICAL METHOD FOR DETERMINING THE WAX CONTENT OF A WAX OIL MIXTURE.

A method was developed for determining the wax content of a wax-oil mixture containing about 20 to 60% of wax. This is done by measuring the amount of polarized light which will pass through a thin layer of the mixture

The analytical method is based on the fact that wax crystalls are doubly refractive while, on the contrary, oil is not. The determinations are made by using a small electric light (e.g. 6 volts, 5 amperes) as a source of light, passing the light through a collimating lens to make the rays parallel, through a red filter (because light of long wave length gives the best results), through a water filter (to absorb heat rays), through a Nicol prism (or other means of polarizing light), and through an iris adjusted to give a spot of light about 4mm. in diameter. The light is then passed through a thin layer of the wax - oil sample, through a second Nicol prism (or other means of neutralizing polarized light) and then is measured by a photoelectric element, preferably one which is arranged to give readings on a scale having 100 divisions.

The wax-oil sample can be conveniently measured on a microscope slide such as is used for making a blood count, preferably one with a chamber 0.100 mm. thick. This slide is warmed, a drop of the liquified wax-oil mixture is placed in it, the chamber is covered with a cover-glass which is securely clamped, and the wax is allowed to cryztallize. It is then brought to a standard temperature,

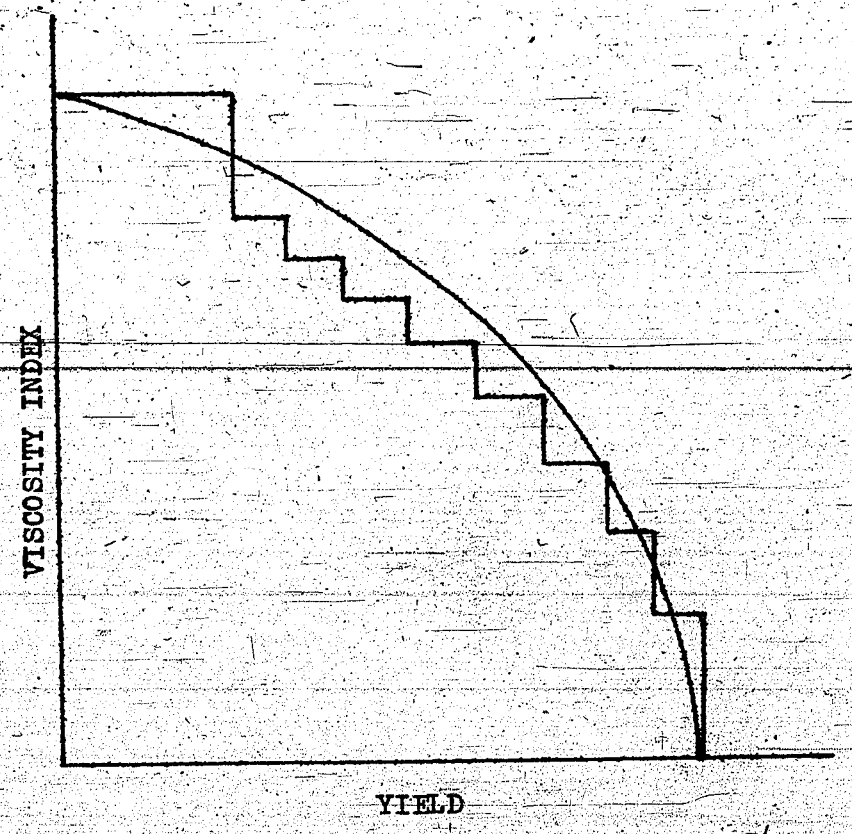


FIGURE II

as by being placed in a water bath at 20° C for about 5 minutes. It is then placed in the apparatus and two measurements are made; (1) with the Nicol prisms crossed to establish the amount of double refraction due to the wax-sample, and (2) with the Nicol prisms parallel to establish the turbidity of the sample. The source of light should be so adjusted that the photoelectric element registers between 70 and 90 on the scale when the Nicol prisms are parallel. In the range of 20 to 60% wax content the ratio of the scale reading for crossed prisms to the scale reading for parallel prisms is proportional to the wax content.

With a mixture having a higher content of wax, the mixture can be diluted with oil or a chamber is used with a thickness of 0.050 mm. If the mixture has a lower content of wax a chamber should be used with a thickness of 0.200 or 0.500 mm and a lower standard temperature, such as 0°C., should be chosen. It is recommended that calibration curves be drawn for each type of wax, by making measurements of mixtures made by adding known amounts of wax to an oil of low pour point.

SEPARATION OF TAR PRODUCED BY LOW-TEMPERATURE CARBONIZATION OF BROWN COAL.

A considerable amount of work was carried out just prior to, and during the first part of, the war on the use of selective solvents to effect a fractional separation of tar produced from the low-temperature carbonization of brown coal. The research work was carried out at the Rositz plant of the Deutsche Erdoel-A.G. (Mineraloelwerke Rositz)*, and a commerical plan was built at Espenhain (A.G. Sächsiche Werke - Espenhain)* based upon the process so developed. The raw tar is first subjected to fractional distillation, the wax-containing distillate fraction is first extracted with liquid sulfur dioxide, to the extract the wax-free distillate fraction is added and the mixture is extracted with naphtha to form a diesel oil and a heating oil, and the raffinate is subjected to a solvent dewaxing using dichloroethane, first at about 5°C. to form a hard wax and subsequently at -20°C. to form a soft wax and a second diesel oil. This work is more fully described in a paper presented by Prof. Ernst Terres at a metting at Halle, Germany, on 26 June, 1942, a translation of which is Appendix A of the present report.

*See the CIOS report on this target.

The production of a hard wax substantially free from oil, and used as a raw material for the production of fatty acids by oxidation, was aided by a special continuous band filter, briefly described on pages 11 to 14.

In order to obtain suitable results when attempting similar treatment of petroleum waxes, it was stated to be necessary to pay attention to the differences between these materials. As discussed in Appendix A, it was found that hard wax from brown coal is composed almost exclusively of straight-chain paraffin hydrocarbons and the corresponding soft wax is composed of isoparaffin hydrocarbons, and moreover it consists of a single homologous series. Wax in mineral oil consists throughout of straight chain paraffin hydrocarbons and about a dozen different isoparaffins of any given molecular weight.

A cracking distillation of tar from brown coal results in a conversion of isoparaffin hydrocarbons into normal paraffin hydrocarbons (by removal of the side chain). In actual practice a two-stage distillation was necessary (with some cracking in the second stage) to produce a white hard wax.

A CONTINUOUS BAND FILTER FOR WAX.

In order to produce a hard wax with a low-oil content it was found desirable to design a new type continuous filter. This was developed in cooperation with Maschinenfabrik Buckau R. Wolf A.G., Magdeburg, 82/84 Schönebecker Strasse.

The filter consisted of a series of individual filter pans, attached to an endless chain travelling along a horizontal path, as shown in Fig. III. This was called a continuous band filter (Bandzellenfilter). Each filter pan had a horizontal filter surface, and the space underneath the filter surface was connected to a source of suction through a hollow shoe sliding along a hollow rail (See Fig. IV) and pressed down against the rail by a spring. As any single pan travelled horizontally from one end of the filter to the other it received a charge of wax-oil solvent slurry, the liquid was removed by suction, and one or more portions of solvent was introduced, with the resulting liquid being drawn off. By the time the pan reached the end of the horizontal path the wax had been washed substantially free from oil. The pan then passed around the end sprocket wheel and the wax cake was blown out by blowing air (or an inert gas) through a short hollow rail and the same hollow shoe. The wax was removed through a screw conveyor

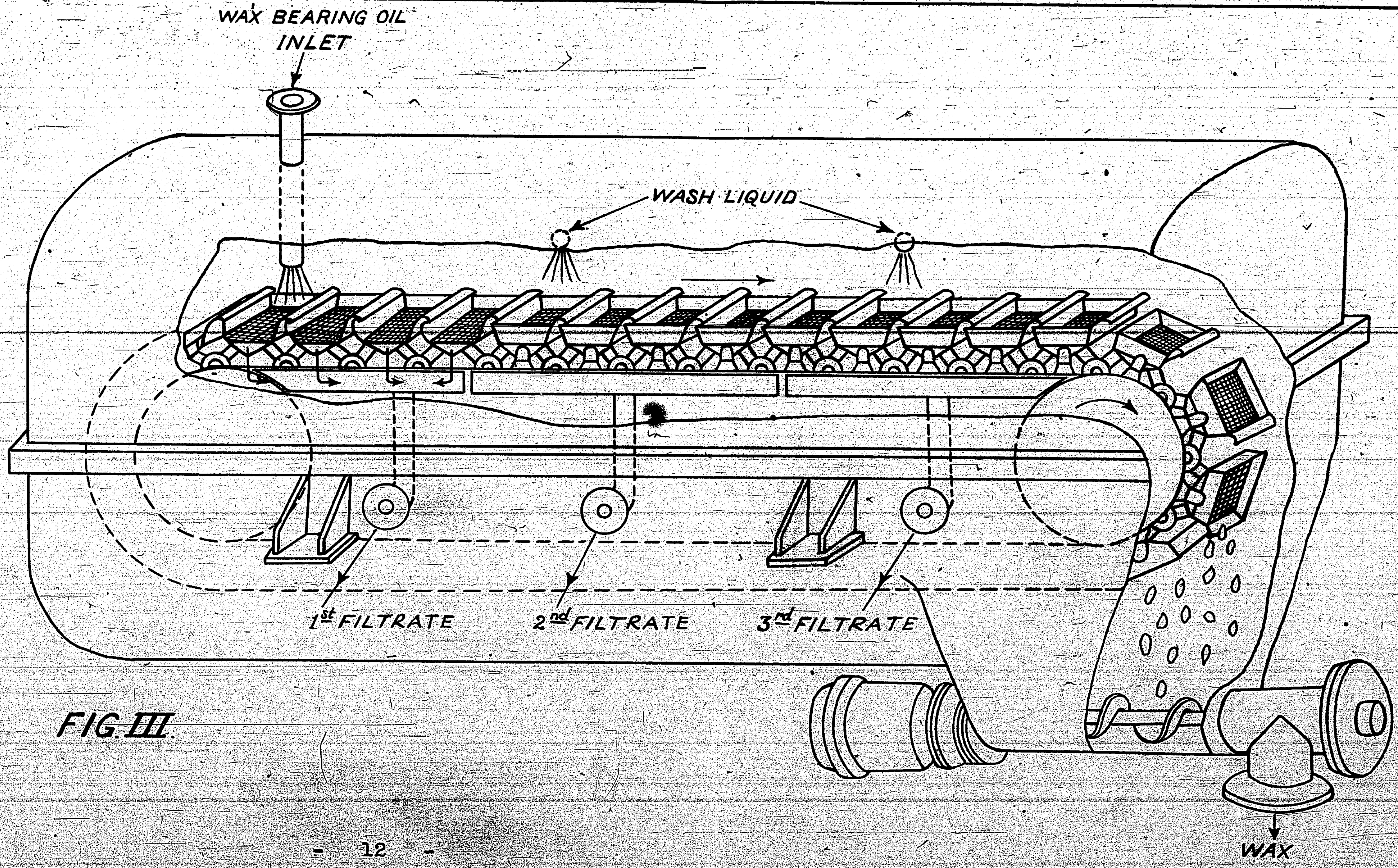

WAX BEARING OIL
INLET
WASH LIQUID
1st FILTRATE
2nd FILTRATE
3rd FILTRATE
WAX

FIG. III.

and the empty pan travelled back for further use. The entire filter was enclosed in a pressure-tight shell, with the interior maintained at about 1.1 atmospheres pressure, absolute. If air was used to blow the wax cake free from the filter pan it was recycled in a closed cycle. The last wash liquid was used as solvent for the initial wax-oil mixture.

The drawing of Fig. III is an illustrative sketch of the filter used at Espenhain, where six separate units were in service. The cross sectional sketch of Fig IV. A is that of the type used at this same plant. There were 40 individual pans per filter unit each about 0.43 meters wide and about 1.84 meters long. As a result there were 17 filter pans in use at any time, and the linear speed was about 1.5 meters per minute.

Four units of an improved version of this filter were installed at an underground lubricating oil plant at Porta, near Minden, known as Dachs I. This plant never operated and was designed for use with natural petroleum. The individual filter pans were 3.6 meters by 0.5 meters. The filtrate was drawn off through two conduits, as illustrated in Fig. IV B. In this model the weight of each filter pan was supported by two sliding shoes. There were 40 pans in each filter, with 16 to be in use at any one time. The linear speed was to be 0.0073 to 0.0442 meters per second, or 0.442 to 2.652 units per minute, with the end sprocket wheels turning at 0.117 to 0.702 RPM. A diagramatic sketch is shown as Fig. V.

The surfaces of the hollow rails and of the shoes which slide over them are sufficiently well machined so that, when lubricating with a suitably heavy oil, an effective seal is formed. The blanks between sections of the hollow rails are longer than the effective length of a shoe, and the space between two adjacent shoes is covered by a leather section which effectively seals the intervening space.

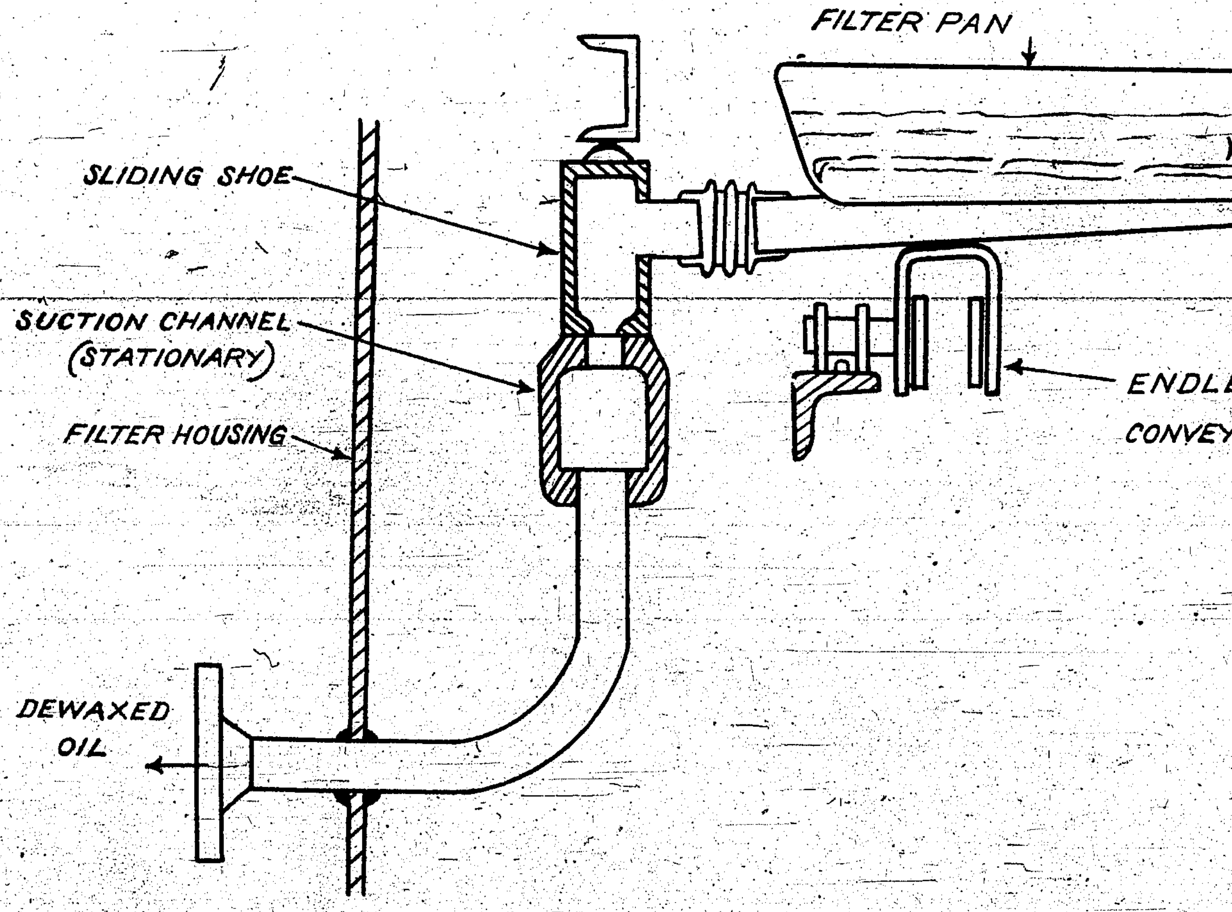


FIG. IV. A.

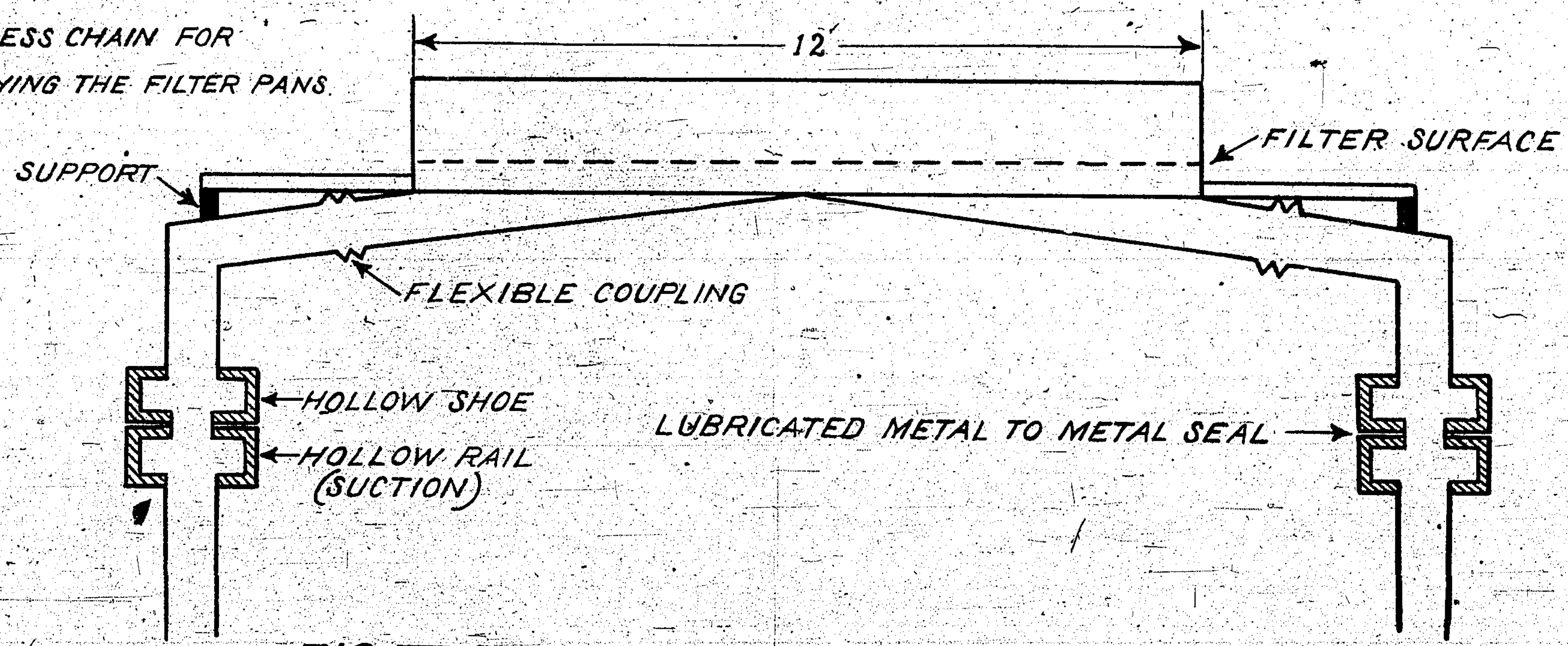


FIG. IV. B.

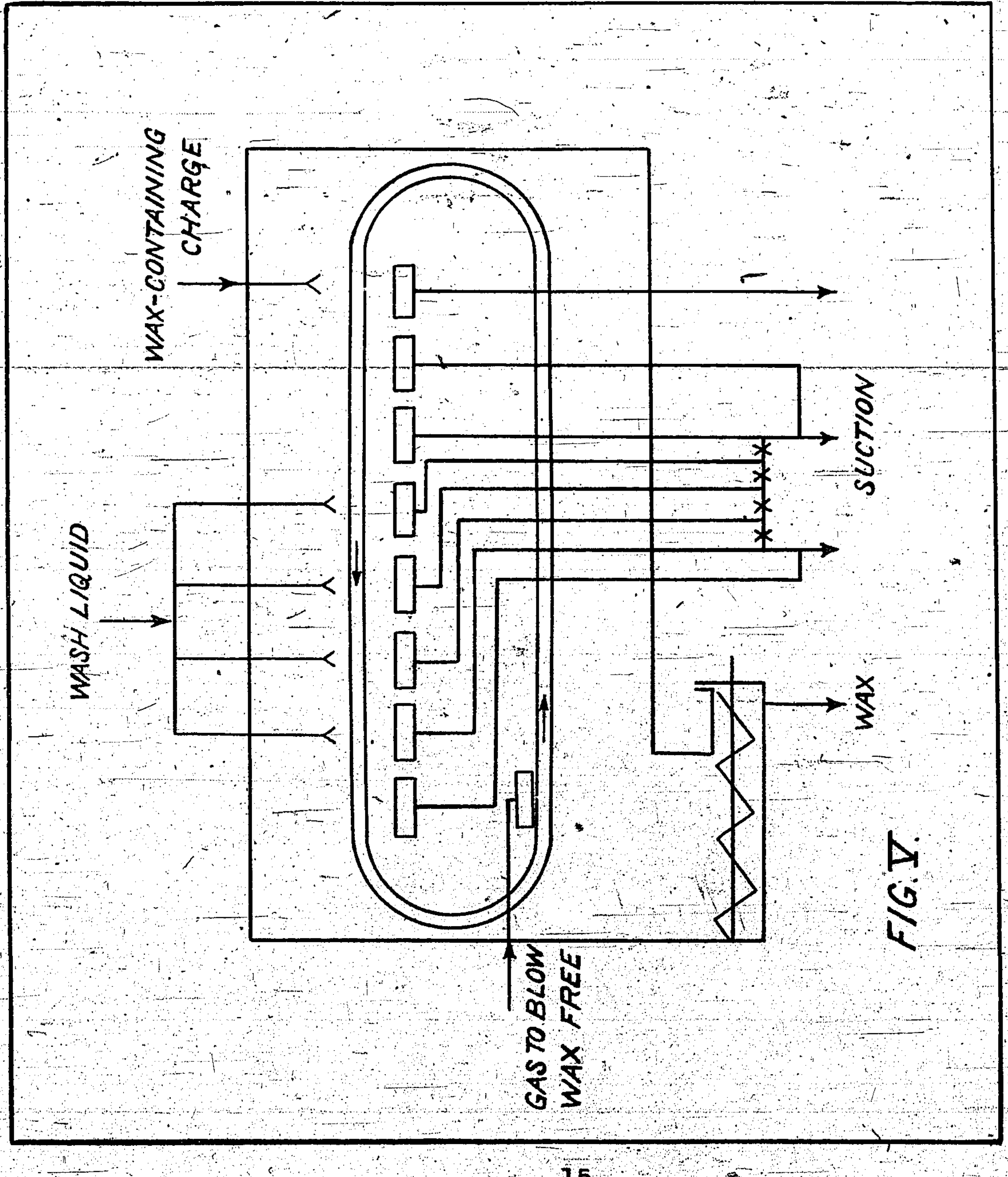

WAX-CONTAINING CHARGE
WASH LIQUID
SUCTION
WAX
GAS TO BLOW WAX FREE

FIG. V.

CATALYTIC CRACKING OF DIESEL OIL.

Shortly before the war some laboratory scale experimental work had been carried out on lowering the pour point of diesel oil by a mild catalytic cracking. The charge stock contained 5 to 8 per cent wax and had a pour point of 5 to 7° C. This was passed at about 30 to 50 atmospheres pressure and 400 to 410° C (not higher than 420° C) over a solid catalyst with a contact time of about 30 minutes to one hour. The product had the following approximate composition.

Gasoline	10%
Diesel Oil	85%
Residue	5%
	100%

No normally gaseous products were produced. The gasoline had an octane number of about 40 to 45. The diesel oil had a cetane number of about 60 to 65 and a pour point of about -10° to -20° C. The residue was a very good pour point depressant.

Two catalysts were used. The first was granular bauxite, impregnated with 5 to 10 per cent of potassium hydroxide, prepared by soaking the bauxite in a 20% aqueous solution of the hydroxide. The other consisted of equimolar proportions of solid sodium and calcium hydroxides, without any carrier. It was stated that a good catalyst life was realized. At the start of a run the activity of the catalyst decreased a little, and then remained constant for quite a while.

This information was given from memory and with considerable reluctance. It was stated that the experimental data had been left in the Berlin laboratory, and that the work had been started on the basis of prewar discussions with Anglo-Iranian Oil Co.

GERMAN OIL SUPPLIES

Speaking from memory and without preparation, Prof. Terres gave the following estimates of German oil supplies during the war.

Source	Metric Tons per Year.
Hydrogenation	2,000,000
Rumania	5,000,000
Austria	1,500,000
Poland	1,500,000
Dorabitsch	500,000
Hanover Area	250,000
Heide	120,000
Pechelbrun	75,000
	10,945,000

Hydrocarbon material obtained from brown-coal tar, most of which was used as charge to hydrogenation, was estimated as follows.

Place	Metric Tons per Year.
Espenhain	350,000 (1)
Böhlen	300,000
Regis (Rositz)	200,000 (2)
Deutzen	100,000
Grube Leopold	100,000
Magdeburg	300,000
Brüx	400,000
Zeitz	350,000
Ruhland (near Dresden)	400,000
	2,500,000

(1) Of this Prof. Terres estimated that 180,000 tons were treated in Espenhain (not hydrogenation) and 170,000 tons were sent to Böhlen for treatment by hydrogenation. See also CIOS report A.G. Säshsische Werke - Espenhain.

(2) This was not charged to hydrogenation.

Other plants for treating brown coal tar were listed as follows, but no estimates could be made of their capacities.

Lätzkendorf
Heydebreck
Hube - Fahrenholz
Schwartzheide

DOCUMENTS

The documents in the following list were obtained at the end of the interrogation. These documents were turned into the G-2 Document Section of the 12th Army Group at Wiesbaden, Germany, on 19th May 1945, for forwarding to London through CIOS channels. The list is a copy of the inventory sheets, accompanying these documents, which were addressed to W.C. Schroeder. Although a copy of the inventory was promptly received by CIOS in London (on 23 May, 1945) the documents themselves had not been received by the middle of September 1945 and CIOS has been unable to locate any trace of them. On 3 September, 1945 duplicates of items 16 (without accompanying drawings) and 11 were obtained (see page 3) and Appendix A is a translation of item 11. Figure IV.B. was copied from item 9 before the documents were turned in, and Fig. V was copied from item 10 at the same time: Fig. III and IV.A were obtained on 3 September, 1945 in Frankfurt a/M.

1. Schema der Paraffin-Gewinnung 20-10417 (for Espenhain)

2. Schema einer Entparraffinierungs-anlage 10-10595
   (for Espenhain)
3. Lageplan der Teerzerlegung Espenhain 10-10345

4. R. Wolf-Bandzellenfilter 3.6 m brt. AS 12565

5A, Schema der Teeröl-Extraction (Espenhain), 20-10406
5B. (2 copies)

6.A, Positionsliste der Apparate und Maschinen (2 copies)
B.

7.A, Schema einer Anlage 2. Entraffinierung usw. 393
B,C. Dachs I, 30-11825 (3 copies)

8. Lieferungsumfang (for 393 Dachs I)

9. Section thru "Bandfilter"

10. Schema eines Wolf Bandzellenfilters, 5 PF 107
   (2 copies)
11. Die Zerlegung von Schwelteeren usw. (Reprint)

12. Schema der Paraffin-Tarnierung 20-104171 (3 copies)

13. Positionsliste...zum Fliess-Schema 20-104171 (3
   copies)
14. Schema der Teeröl-Extraktion 20-104061

15. Positionsliste...zum Fliess-Schema 20-104061

16. Zusammenfassung Ausführungen, ZA. 455 33/F8.

APPENDIX A.

THE USE OF SELECTIVE SOLVENTS TO SEPARATE VARIOUS FRACTIONS FROM TAR PRODUCED BY LOW-TEMPERATURE CARBONIZATION OF BROWN COAL AND OIL SHALE (1)

By Prof. Ernst Terres, Edeleanu GmbH.
(Translated by J. Paul Jones, TIIC,
Fuels and Lubricants Team).

Short Review of the Development of Refinery Methods Using Selective Solvents*

About 40 years ago Edeleanu first tried to refine mineral oils with selective solvents. Sulfur dioxide was first used because it would remove tarry acids and could easily be separated from both the extract and raffinate. During the first twenty years (of above 40 years) it was applied to low-boiling fractions and lubricating oils successively. In 1929 Edeleanu and N.V. de Bataafsche Petroleum Maatschappij (Shell) jointly developed the use of a second solvent with sulfur dioxide, such as benzene, and the benzol-SO_2 process resulted.

A large number of other solvents were also found, in the course of the years (2). In 1921 F. Schick (Deutschen Erdoel - A.G.) found phenol and its homologes useful for refining lubricating oils, which Standard Oil Co. of New Jersey utilized about 1930 as a new development. The selectivity of this solvent was varied by adding small quantities of water. In 1923 Eichwald of Stern - Sonneborn A.G. (now Rhenania - Ossag) took out a patent covering the use of furfural, which was used on a commercial scale by the Texas Co. Standard Oil Co. of Indiana used Chlorex. ($\beta\beta'$ - Dichlordiethylether) about 1930 as a selective solvent for lubricating oil, and about 1932 Max B. Miller and

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1) A paper given June 26, 1942 at Halle (Saale) Germany, before a committee on carbonization and gasification of the Deutschen Braunkohlen - Industrie Vereins (German Brown Coal Industrial Organization).
* The sections so marked are presented only in abstract form while subsequent sections are translated in detail.
2) Terres gives notice here of Edeleanu patents.

Malcolm H. Tuttle, of New York, introduced the use of propane-cresol mixtures in their Duosol process, after Union Oil Co. of California had used propane as a deasphaltizing and dewaxing medium in 1929 and Prof. van Dijch of B.P.M. (Shell) had discovered the principle of the Duosol process.

About twenty years ago dewaxing with selective solvents was carried out. The first process, with the exception of the old procedure of using benzol as a solvent, was in 1928 with the benzol - acetone process of the Texas Co. Then in 1929 came the use of propane for dewaxing, by the Union Oil Co. About the same time Edeleanu Co. developed the benzol - SO_2 dewaxing which was combined with extraction using the same solvents in a different ratio. About 1926 Separator - Nobel developed centrifuge dewaxing with trichloroethlene (Barisol process), and in 1937-1938 the Deutsche Erdoel - A.G. built a dichloroethylene dewaxing plant at their Wilhelmsburg plant. In this dewaxing process the primary goal was the production of an oil with a low pour point from a wax - containing lubricating oil fraction, together with a wax residue containing more or less oil, up to about 60% or more, depending upon the charge stock and the viscosity of the fraction. By repulping, i.e. by mixing the wax-oil slurry (Gatsch) with pure solvent at a low temperature and by a second filtration a wax residue could be obtained containing 5-10% oil from many petroleums or oil fractions. A second method of removing oil from oil-wax slurries was recrystallization, i.e. a complete solution of the slurry in fresh solvent, cooling the solution to a dewaxing temperature, thereby crystallizing the wax, and subsequently filtering the mixture. Then first came the development, which will be described hereinafter, of a dewaxing process to separate directly an oil-free wax, or an oil-free hard wax and an oil-poor soft wax, to replace the sweating process used up to that time.

The development of apparatus kept abreast with this physical-chemical development.

In the treatment of tar from low-temperature carbonization the use of selective solvents was introduced at an early date, but remained as simple isolated process steps. Thus, mention should be made of the use by E. Graefe, in 1911 at the Riebeck Montanwerke, of an alcohol washing treatment for the removal of creosotes and resinous and asphaltic materials from such raw tars and tar distillates. During World War I (1916) the Deutsche Erdoel - A.G. had a plant at Rositz for the extraction of a distillate from brown coal tar and its separation into a wax raffinate and a wax-free extract by means of liquid sulfur dioxide, built by Edeleanu Co; the raffinate was further treated to recover wax while the extract was used as an axle lubricant. About six years ago (1936) at this same Rositz plant, a large experimental unit was built for the extraction of such distillates with phenol.

All these procedures dealt only with a partial treatment of the tar from low-temperature carbonization. Six years ago (1936) we undertook a complete separation of such a tar into diesel oil, heating oil, hard wax and soft wax in a continuous process. The following discussion deals with this work.

EXTRACTION WITH SELECTIVE SOLVENTS AND ITS REPRESENTATION ON A TRIANGULAR GRAPH*

Briefly, selective solvents have the property of being completely miscible with those constituents of an oil having a certain chemical structure, while other chemical types are insoluble or only slightly soluble in a given temperature range; as a result with an oil in this temperature range two separate liquid layers are formed. Thus, liquid sulfur dioxide, phenol, furfural and Chlorex are completely miscible with aromatic and olefinic substances up to a certain molecular weight while, in a given temperature range, they dissolve napthenic hydrocarbons only slightly and paraffinic hydrocarbons still less; the latter layer is the raffinate while the first, and heavier layer is the extract. Liquid propane has exactly the opposite properties, and in the presence of one of the selective solvents just mentioned goes into the raffinate.

Solubility and selectivity change with temperature, the first increasing and the second decreasing with increase in temperature, and for every solvent-hydrocarbon mixture there is a critical temperature above which there is complete miscibility and no separation of phases.

At a constant temperature there is a similar change in solubility and selectivity, as the solvent becomes richer in the dissolved material. A multistage, counter-

current extraction is therefore necessary. The goal of an extraction is to obtain a hydrocarbon raffinate as free as possible from extract components and an extract similarly free from raffinate components. This is generally obtained not with multistage isothermal operation but with a temperature gradient as well, with as high a temperature as possible on the raffinate side, and as low a temperature as possible on the extract side, and with countercurrent operation so that only an almost purified raffinate comes into contact with a clear solvent.

The relationships can be seen on a triangular graph, first used by Hunter and Nash. The solutions consist of solvent, raffinate and extract. Since the last two are quite similar an additive property is generally chosen, such as the specific gravity or, for lubricating oil, the viscosity-gravity constant. Thus, artificially, the three phases can be illustrated quite simply and one need only to determine the solvent content of the solution and the density of the solvent-free oil.

As illustrated with reference to Fig. 1, the top of the triangle represents the solvent (100%) while the divisions of the base of the triangle represents the gravity range (e.g. D_{70}) under consideration. Along every straight line drawn from the apex of the triangle to the base, the ratio of raffinate to extract is constant. Each such straight line, therefore, represents all solutions having the same ratio of extract to raffinate, i.e. solutions of oil components with solvent having constant specific gravities in the region of 0 to 100% solvent. In order to define a solution of an oil, it is necessary to stipulate the amount (in per cent) of solvent on the particular straight line which corresponds to the specific gravity of the oil.

For every formation of separate phases there are obtained two numerical values, one for the raffinate solution and the other for the corresponding extract solution. A curve is obtained by plotting the values of corresponding raffinate and extract solutions, when various amounts of solvent are employed and when the density of the oil component of the solutions is changed by admixing raffinate or extract to the original charge stock.

The resulting curve is an isotherm. Inside the curve is the region of separate phases and outside is the region of homogeneous solutions.

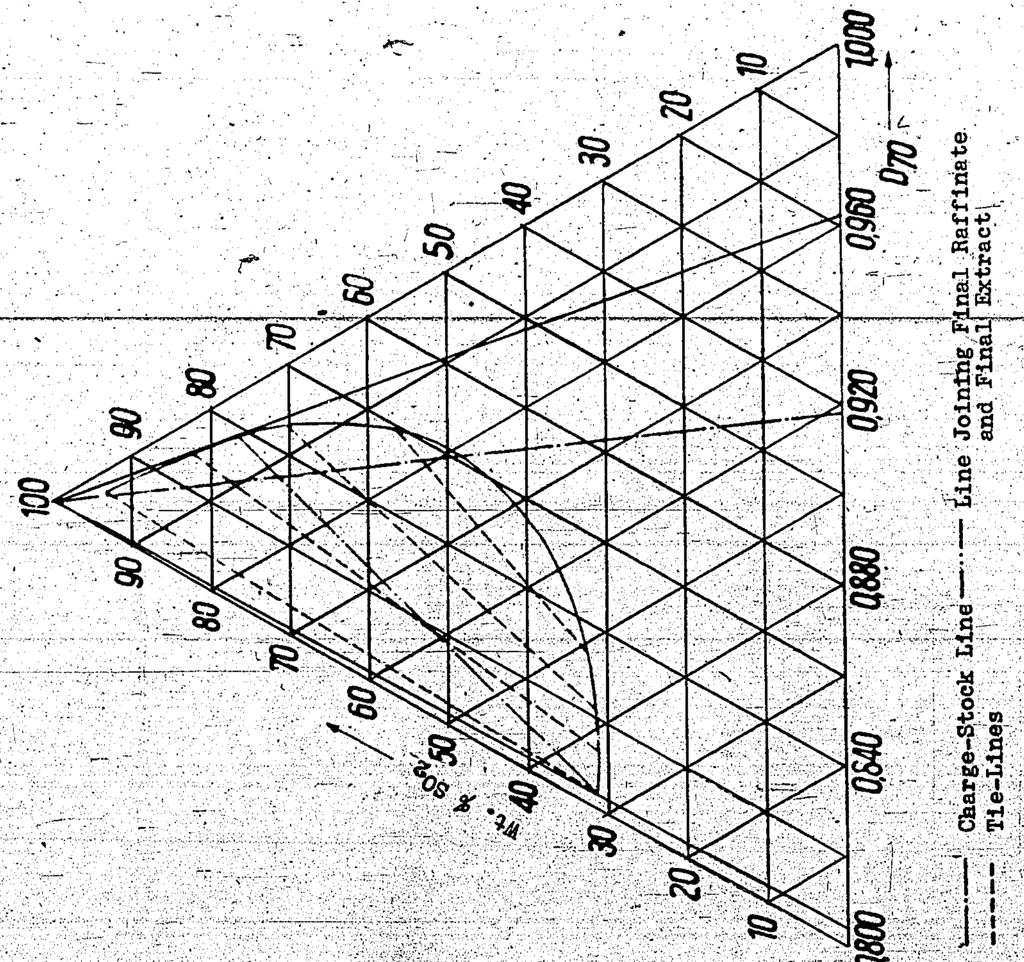


Fig. 1 TAR DISTILLATE FROM LOW-TEMPERATURE CARBONIZATION OF BROWN COAL, SO_2-EXTRACTION AT 40°C.

From such an isotherm it is possible to obtain any desired knowledge concerning the relationships of the solvent and charge stock, the characteristics of the raffinate and extract, the amounts of raffinate and extract, the raffinate which is theoretically the best that can be obtained, and the extract with the highest possible specific gravity when working at the given extraction temperature with the given solvent, and also the theoretical yield of these latter two materials. For such a determination it is of course, necessary to have the raffinate and extract solutions truly in equilibrium at the specified extraction temperature. But the data also lie on the curve when the raffinate and extract are not in equilibrium since the curve represents all possible heterogeneous solutions of the same charge stock and solvent irrespective of whether or not there is an equilibrium; but it must be remembered that the lines joining corresponding raffinate and extract points have different slopes when the solutions are in equilibrium than when they are not.

Such a curve is called a boundary-curve and the lines joining corresponding extract and raffinate points are called tie-lines.

Fig. 1. shows such a boundary curve for a tar from low-temperature carbonization of a brown coal with liquid sulfur dioxide as the selective solvent. The tie-lines are shown for the experimentally determined equilibrium values for the raffinate and extract solutions. Also shown is the straight line representing the specific gravity of the charge stock (D_{70}=0.918). It can be seen that all of the tie-lines obtained from this charge stock with various amounts of solvent intersect this straight line, i.e. the charge-stock line. These points of intersection represent the composition of the solution (oil and solvent) before it separates into extract and raffinate phases; as a result these points represent the initial mixture and show how much solvent and oil have been added.

The raffinate solutions lie along the lower branch of the curve, and the best possible raffinate is the point at the end of this branch of the curve; the extract solutions lie along the upper part of the curve and the extract with the highest possible specific gravity lies at the point where a line from the apex of the triangle is tangent to the curve. From the diagram it can be seen that a good raffinate is always obtained in the initial mixture with a large amount of solvent and likewise that the density of the raffinate is lower with larger amounts of solvent; but the corresponding extract is not sufficiently freed from raffinate.

The line joining the raffinate having the lowest density and the extract having the highest density intersects the charge-stock line, and this point of intersection represents the composition of the hypothetical initial mixture of oil and solvent from which can be determined the amount of solvent necessary to effect the separation into the desired final raffinate and extract. Since the desired raffinate and extract are not corresponding points on the boundary curve, this separation can only be obtained in a plurality of isothermal stages.

However, every tie-line is cut into two parts by the charge stock line. The two resulting parts of the lines are proportional to the amounts of extract and raffinate solutions which correspond to this tie-line, and the part from the raffinate point to the charge-stock line corresponds to the amount of extract solution and the other part of the line corresponds to the amount of raffinate solution. Likewise the relative amounts of final raffinate and extract solutions represented by those parts of the line which join the raffinate of lowest density and the extract of highest density and resulting from a cutting of it by the charge-stock line into two parts, are obtained as the final result of a multistage extraction of the charge stock using the relative amounts of solvent and charge stock corresponding to the point of intersection of this line with the charge-stock line.

In Fig. 2 there is shown schematically how a concentration of the extract can be obtained. The raffinate and extract solutions R_1 and E_1, which define the upper tie-line, show that with a large amount of solvent a good raffinate can be obtained (with a low density) and that this raffinate can be still further improved by using more solvent under certain conditions, i.e. if the tie-line does not correspond to extract E_1, the density of which shows that it contains an appreciable amount of unremoved raffinate constituents; the use of more solvent will not further separate extract E_1, since an increase of solvent above the amount represented by E_1, will result only in a homogeneous solution. If the solution E_1 has

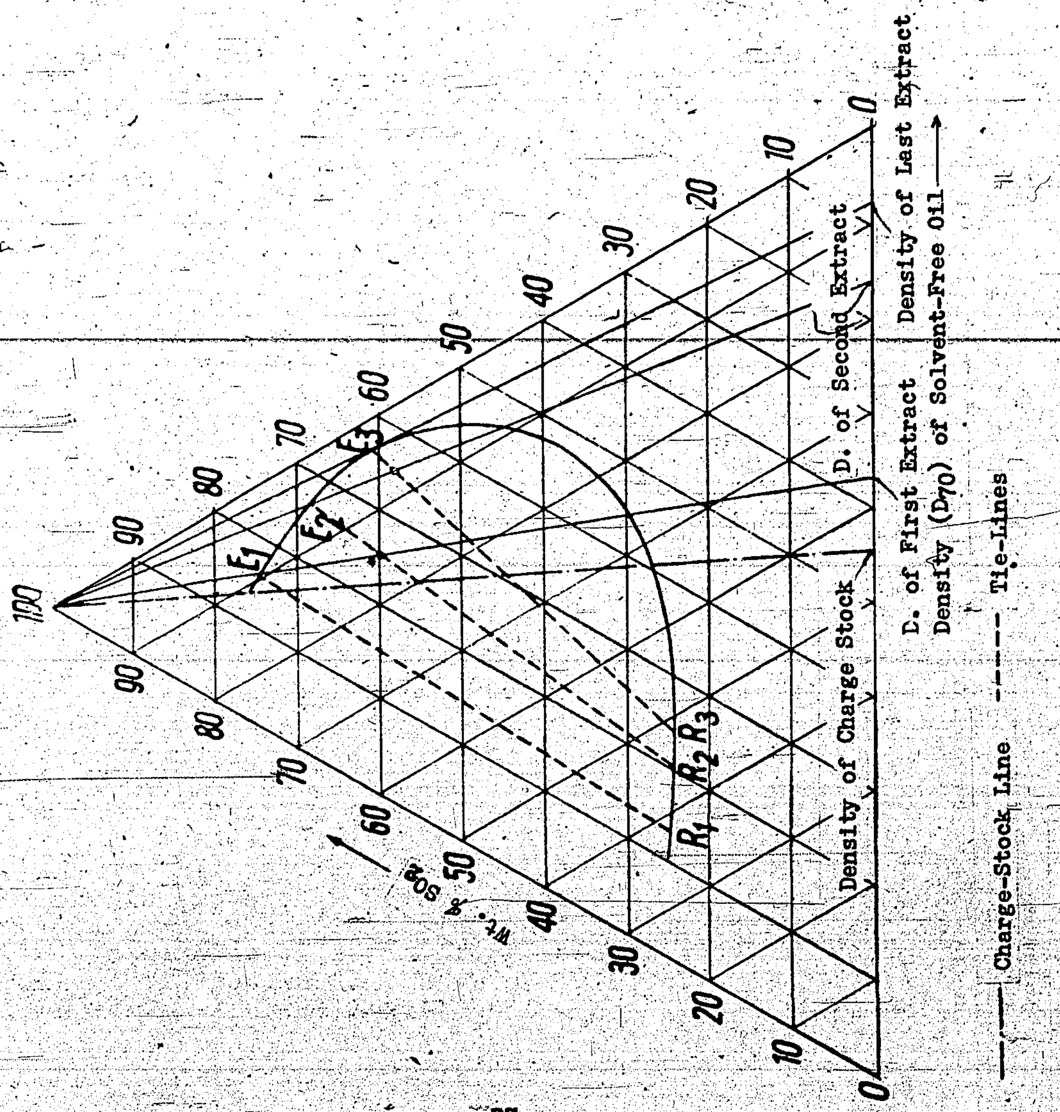
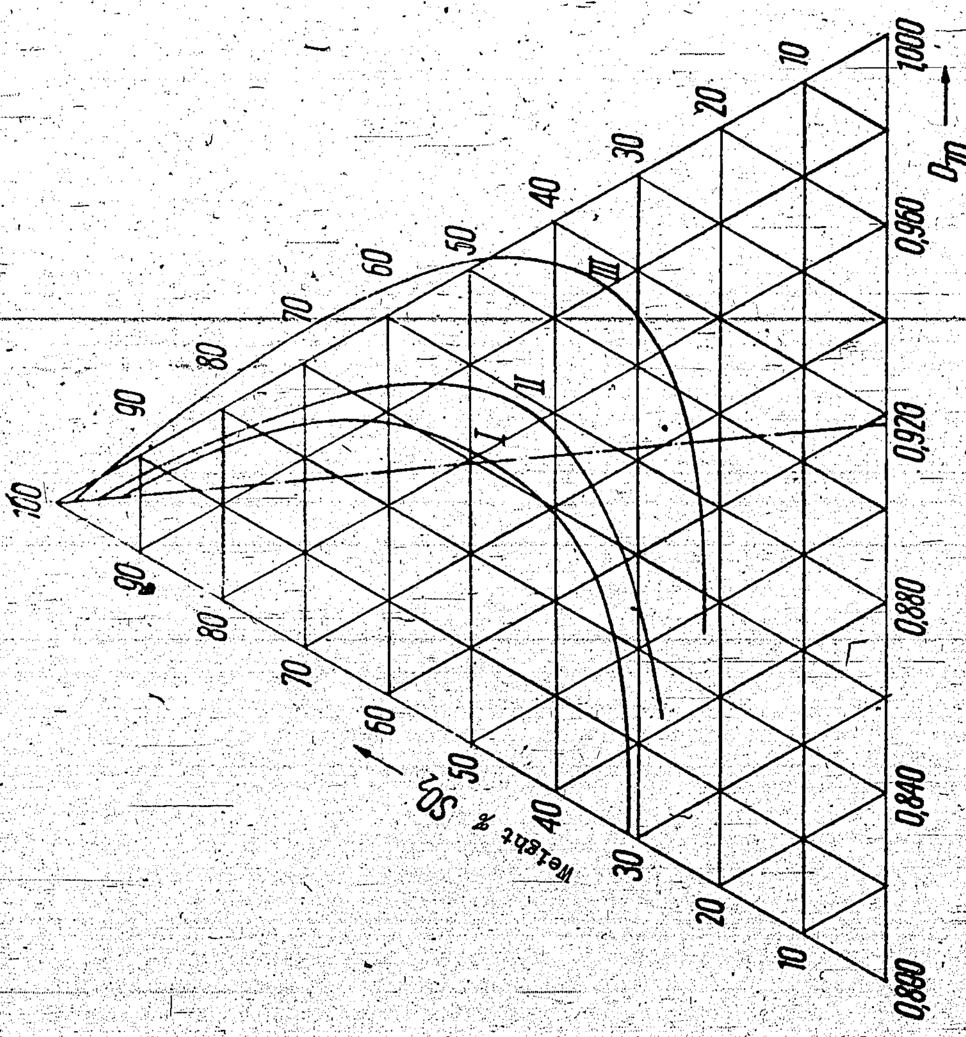


Fig. 2 ISOTHERMAL SEPARATION OF THE EXTRACT SOLUTION BY CHANGING THE CONCENTRATION OF SOLVENT

its solvent content decreased the point E_1 moves along a line extended through it from the apex into a region of two phases, and a new separation of the extract takes place, forming a new raffinate and a new - more concentrated - extract. Thus, if the SO_2 content of the extract solution E_1 is decreased from about 75% to 60%, either isothermally or by treatment at a higher temperature with subsequent cooling to the isotherm temperature, there is formed a new raffinate solution R_2 and a new extract solution E_2 which has a higher density, for the extract, than E_1. The extract solution E_2 can be further separated by a further removal of solvent; thus by decreasing the SO_2 content from about 67% down to about 57% (See Fig.2) the extract solution E_2 separates into a new raffinate solution R_3 and a new extract solution E_3. When solution E_3 is obtained there can be no further separation of the extract solution by decreasing the solvent content, since E_3 is the point at which a line through the apex of the triangle is tangent to the curve and it represents the extract of greatest density obtainable from the charge stock at the extraction temperature. Raffinate solutions R_3 and R_2 can likewise be separated stepwise into new raffinate and extract solutions by addition of solvent, and the final raffinate solution may be R_1 or a solution with a still lower density. Accordingly, by stepwise decrease of the solvent contents of the extract solutions and stepwise dilution with solvent of the raffinate solutions it is possible to separate the charge stock into the desired final raffinate and extract solutions. Such a separation of the extract solution by removal of the solvent is effected in practice by use of the back-wash procedure, for example, whereby in the region of a concentrated extract solution a further increase of the extract density and a new separation of a raffinate phase is obtained by removing a part of the extract solution from the extraction system, vaporizing a part of the solvent and cooling the residue to the extraction temperature and returning it to the system. However, other considerations prevent such a procedure from being actually used; in practice the solvent is not partially vaporized, as just discussed, but instead the amount of solvent is decreased by admixing with the solvent-rich extract solution a solvent-free charge stock or a solvent-poor raffinate solution. The following procedure is used in order to operate within the limits of Fig. 2; the charge stock is mixed with extract solution E_2, having about 67 weight per cent SO_2 whereby there results an isothermal separation into extraction solution E_3 (61 wt.% SO_2) and a raffinate solution R_3; the raffinate solution R_3 with about 25 weight per cent of SO_2, (See Fig. 2) is mixed with extract solution E_1



—·— Charge-Stock Line for the Various Charge Stocks

Fig. 3 SO_2-EXTRACTION, ISOTHERMALLY AT 40°C.
I Tar Distillate from L.-T.C. of Brown Coal; II Shale Oil Distillate;
III Heavy Petroleum Distillate (Persian Wax Cut).

having 75% SO_2 and thereby is formed raffinate solution R_2 and extract solution E_2; raffinate solution R_2 is then separated, by mixing with pure solvent, into raffinate solution R_1 and extract solution E_1 having about 75 weight per cent SO_2.

The boundary-curves just described for a specific charging stock are characteristic for the type of oil used and for the solvent discussed. Fig. 3 illustrates three separate boundary curves placed upon the same triangular coordinates. The left hand curve (I) represents a distillate from a tar from the low-temperature carbonization of brown coal (a), the middle curve (II) a shale oil distillate, and the right hand curve (III) a wide cut of a paraffinic lubricating oil. All three charge stocks have the same density of 0.918 and the curves are comparable. The three oils are distinguishable in that the two-phase area increases from the L-T-C. tar distillate to the mineral oil, that accordingly the paraffinic part increases in the same direction, and also that at the same time the densities of the extract hydrocarbons increase in the shale oil and in still greater degree in the mineral oil. In a corresponding manner, the treatment of these charge stocks and the resulting products are very different.

(a) Hereinafter referred to as "L-T.C. Tar". J.P.J.

TREATMENT PROCEDURES FOR MINERAL OIL, SHALE OIL AND TAR FROM THE LOW-TEMPERATURE CARBONIZATION OF BROWN COAL.

In Figures 4, 5 and 6 are shown in simplified form, a procedure for the treatment of each of the above raw materials.

First will be discussed the treatment for mineral oil, Fig. 4. Each oil is fractioned by distillation, first at atmospheric pressure and finally under vacuum. Each of these fractions may be solvent refined. For gasolines the extract is the valuable part; extracts containing about 95% aromatics have octane numbers of 92 to 95 and are used as components of aviation gasoline or as sources of benzene and its homologes. Such high concentrations for the extracts are obtained by low-temperature extraction of the gasoline fraction with SO_2, alone or together with a supplementary solvent (such as propane) at temperatures down to -60°C or by use of SO_2 extracts (from -10 to -20°C) of a gasoline fraction as extraction mediums for higher

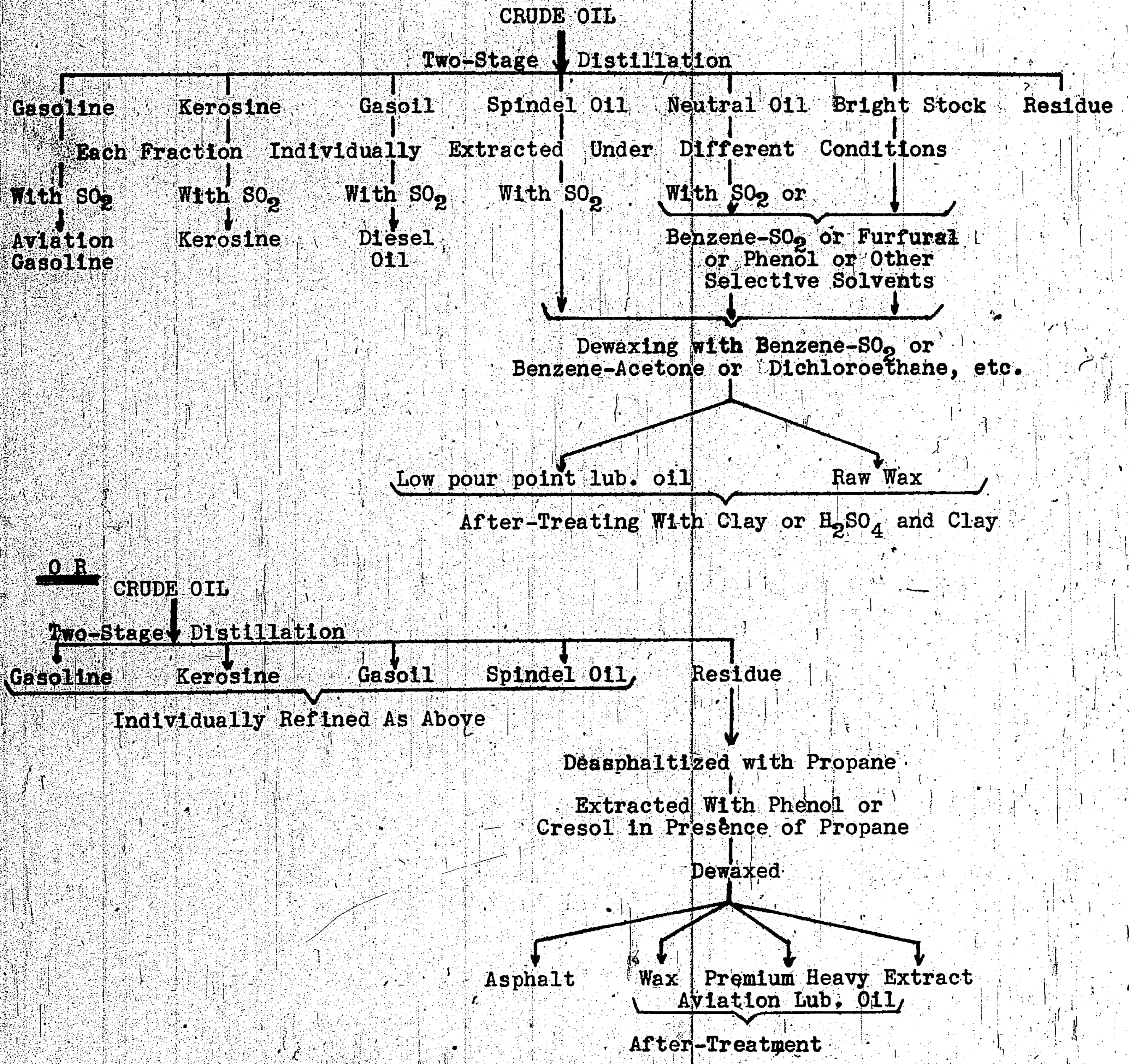


Fig. 4 SEPARATION OF PETROLEUM OIL

boiling fractions, such as lubricating oil, with distillation of the light gasoline extract from the heavier lubricating oil extract. In the next fraction the raffinate is the valuable product. Liquid SO_2 is satisfactory as extraction medium down to medium heavy machine oils, and does not have any economical substitute for extraction of kerosine and gas oil. With the more viscous fractions the solvent power of SO_2 is not strong enough and the extraction is carried out with benzol-SO_2, or furfural, or phenol, etc., i.e. with solvents of lower selectivity but greater solvent power for the material to be removed. In addition, all such higher fractions of paraffin-base or mixed-base oils must be dewaxed to obtain oils with low pour points as well as raw wax. All products require further more or less drastic refining with sulfuric acid and/or clay, depending upon the requirements as to color and stability.

If desired, the distillation of the crude petroleum can be carried to a long, or short, residuum which can then be deasphaltized, solvent extracted, dewaxed, and treated, in order to make a product such as aviation lubricating oil.

Figure 5 shows a treatment of shale oil, comprising fractional distillation of the raw oil in two steps into a gasoline, a wax-free fraction, a wax-containing fraction, and a residue. The wax-free fraction has a low pour point and is practically a finished diesel oil. The wax-containing fraction can be solvent extracted with SO_2 into a wax-containing SO_2 - raffinate and a wax-free SO_2 extract; the latter is a finished heating oil after separation of the solvent. The SO_2-raffinate is freed from SO_2, dissolved in dichloroethane, and from the solution hard wax is separated at +5° C. and from the resulting filtrate, after the addition of some SO_2, soft wax is separated at - 20°C. The wax-free filtrate is distilled under vacuum to form a diesel oil and, as desired, several heavy lubricating oil distillate fractions, with a heavy residuum. In such a case the various products named require drastic further refining.

The separation of tar from the low-temperature carbonization of brown coal is shown as Fig. 6. Up to the SO_2 extraction the treatment is about the same as that of the shale oil; also the dewaxing of the SO_2 raffinate is the same, except that the resulting wax-free filtrate yields a diesel oil fraction. A second diesel oil fraction is obtained from the SO_2 extract, without vaporization

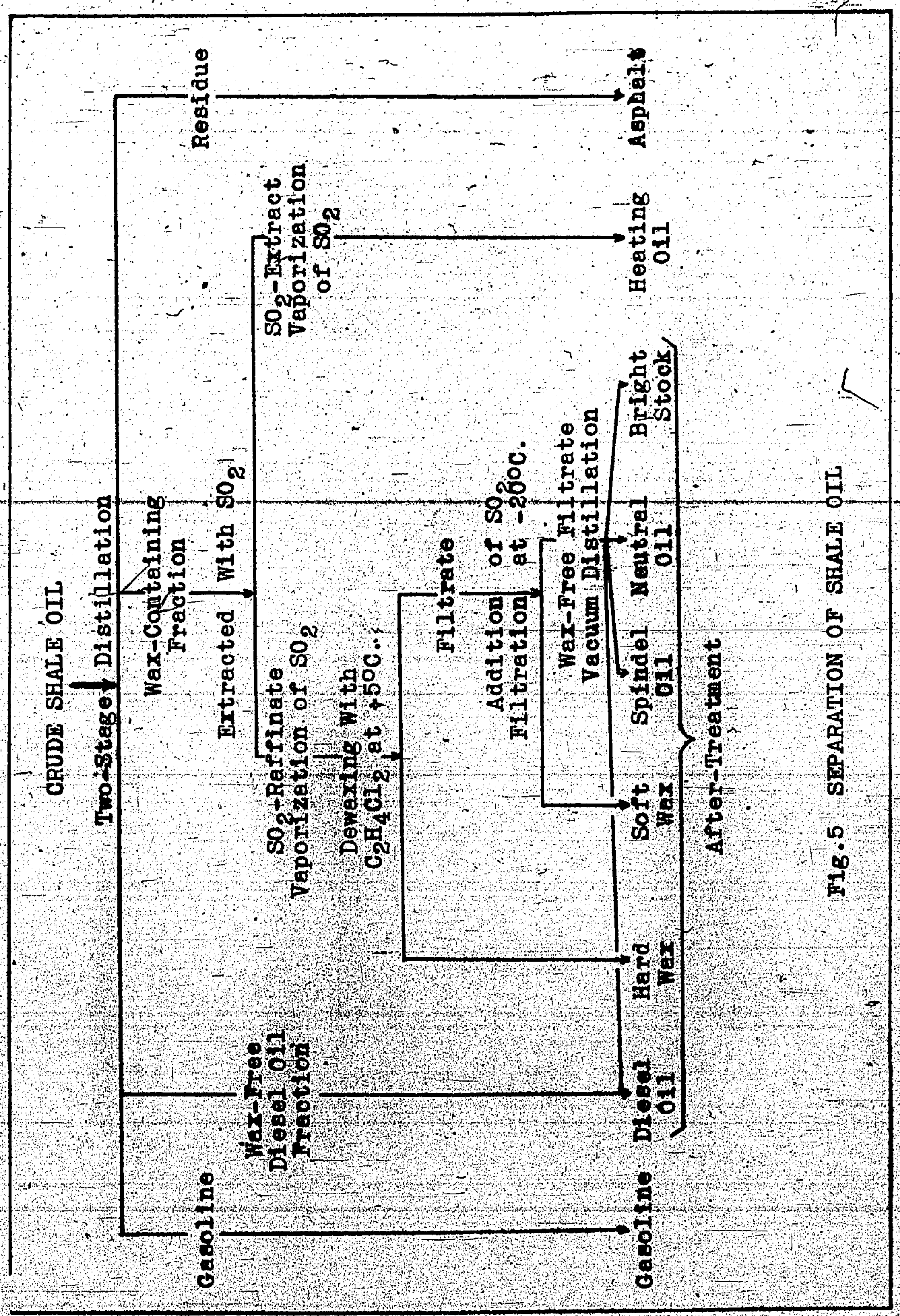


Fig.5 SEPARATION OF SHALE OIL

of the SO_2, by extraction with a light naphtha fraction after adding a wax-free middle oil fraction; the resulting extract is a finished heating oil after removal of the solvent. In this treating scheme it is possible to produce electrode coke by coking the distillation residue (b).

The selective treatment of this L-TC. tar includes three principal stages:

1. Extraction of the wax-continuing fraction with SO_2;
2. Extraction of the resulting SO_2 extract with naphtha after addition of the wax-free fraction; and
3. Fractional separation of hard and soft wax with dichloroethane from the SO_2 raffinate after removal of SO_2.

(b) This treatment was carried out, substantially as shown, at A.G. Säschsigeswerke - Espenhain. JPJ.

These three stages will now be considered separately.

THE SEPARATION OF TAR FROM LOW TEMPERATURE CARBONIZATION OF BROWN COAL INTO TAR SO_2 - RAFFINATE AND AN SO_2 EXTRACT.

Reference should be made back to the boundary curve for L-T.C tar distillate. The curve shown in Fig. 7 was obtained at 40°C. We have already learned to determine from it the initial mixture of oil and solvent, the amounts of the respective extract and raffinate solutions, and also the characteristics of the solvent-free raffinate and extract. Still more can be obtained, however.

The goal of the extraction is to obtain, from the charge stock under the stipulated conditions, the best raffinate (from the lower left hand part of the curve) and the extract with the highest specific gravity. If these two points are joined by a line the point where this line intersects the charge-stock line, as we have already seen, indicates the amount of charge stock and of solvent necessary for this separation; in this case about 100 parts by weight of oil and 250 parts of solvent. We already know that such a separation into this raffinate and an extract of maximum specific gravity can only result from a plurality of stages. Further, we can determine the theoretical number of stages for such a separation as the characteristics of extract and raffinate solutions in each stage. The basis for such a determination can be obtained by construction.

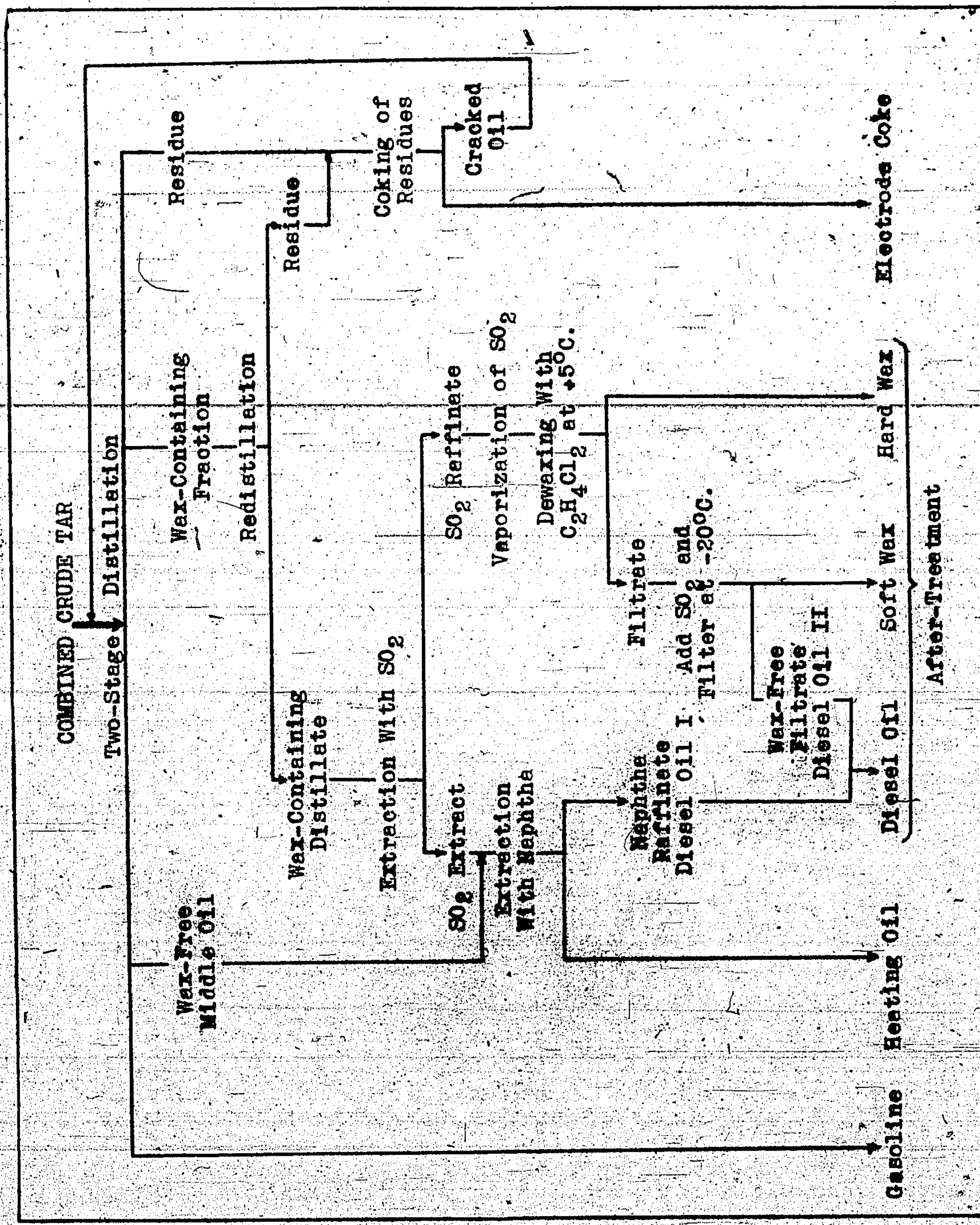


Fig. 6. SEPARATION OF TAR FROM LOW-TEMPERATURE CARBONIZATION OF BROWN COAL

It is clear, that the sum of the charge stock plus solvent is equal to the sum of the raffinate plus extract solutions, since the latter result from the first two or, expressed differently, in a given unit of time the amounts of raffinate and extract solutions removed from the extraction system are equal to the amounts of charge stock and solvent entering the system. Furthermore, the two amounts of liquid which flow countercurrently through a single cross section of the extraction system, in a given unit time, have a simple straight-line relationship. At the extract side the final extract solution flows out and the charge stock in; at the raffinate side the final raffinate solution flows out and the pure solvent in.

Accordingly, the final raffinate solution (at the left branch of the curve) and the pure solvent (top of the triangle) should be considered together, as should the solvent-free charge stock (intersection of the charge-stock line with the base of the triangle) and the final extract solution (point of tangency on the boundary curve). If these points are joined, two lines are obtained which intersect outside the triangle at the point S. This is the case not only for the end stage, but also for each intermediate stage of the extraction.

If, for each of the intermediate stages, the numerical value is experimentally determined for each intermediate raffinate solution which comes into each stage for separation in admixture with the extract solution from the preceding stage, and similarly the numerical value is determined for the resulting extract, and if these two points are joined by a straight line, an extension of this straight line also passes through the point S. This fact has a mathematical basis, and it can be demonstrated that it must be so. For the present it is enough to know that it is so. Accordingly the point S can always be determined from the points for the final raffinate solution and the apex of the triangle, the first extract solution and the point of intersection of the charge-stock line with the base of the triangle. Furthermore with the point S, it is theoretically necessary to obtain a desired final raffinate and extract from a given amount of charge stock and of solvent.

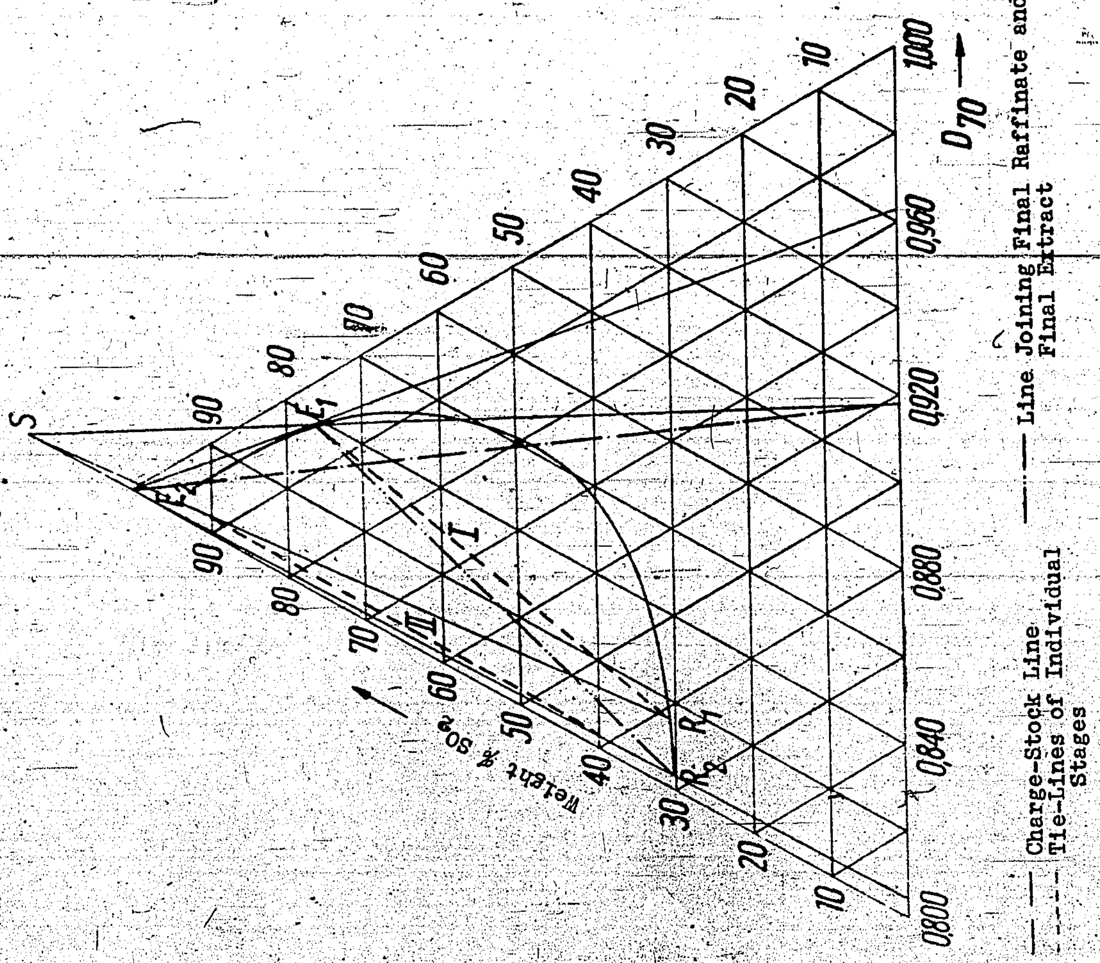


Fig. 7 TAR DISTILLATE FROM L.-T.C. OF BROWN COAL, SO$_2$ EXTRACTION IN TWO STAGES AT 40°C.

A counter current extraction takes place in the manner now to be described. The penultimate extract E_2 and the charge stock are mixed in the first stage, and there is then separated a final extract E_1 and an intermediate raffinate R_1. This intermediate raffinate is defined by the tie-line corresponding to the final extract. In the second stage this intermediate raffinate R_1 is mixed with the intermediate extract passing from the third stage (3) and similarily there is likewise separated a raffinate and an extract (i.e. the penultimate extract just mentioned). The location of the point representing this extract on the boundary curve is as yet unknown; however it is known that it must be the point of intersection of the boundary-curve and the line joining this intermediate raffinate with the point S. If this point is determined in this manner, the tie-line of this point again indicates the corresponding raffinate, and a determination of each succeeding point may be made in the same manner.

It can be seen that by an isothermal extraction of L-T.C. tar distillate at 40° C it is possible to separate it in two stages and, with a given ratio of charge stock and solvent, into the best possible raffinate and the extract with the greatest density. This is descernable from the divergence of the tie-lines. The more markedly the tie-lines diverge, the greater is the extraction effected in each stage and the fewer the stages necessary to obtain the best possible separation. However, for mineral oils at least three or four, or even more, stages are necessary to obtain a good final raffinate and extract.

In actual practice the extraction is carried out with a temperature gradient as well. Thus a final extract obtained at 40° C. can be further separated by cooling to a lower temperature. This is shown in Fig. 8. This distillate is separated at 40° C. and at -10° C. For this purpose a boundary curve for -10° C. is drawn. The extract with the highest density is determined from the point of tangency with the boundary curve of a line drawn through the apex of the triangle.

(3) As will be seen from the discussion presented hereinafter, there is no third stage with L-TC. tar, since the intermediate raffinate R_1 is separated by the pure solvent (SO$_2$) into E_2 and R_2.

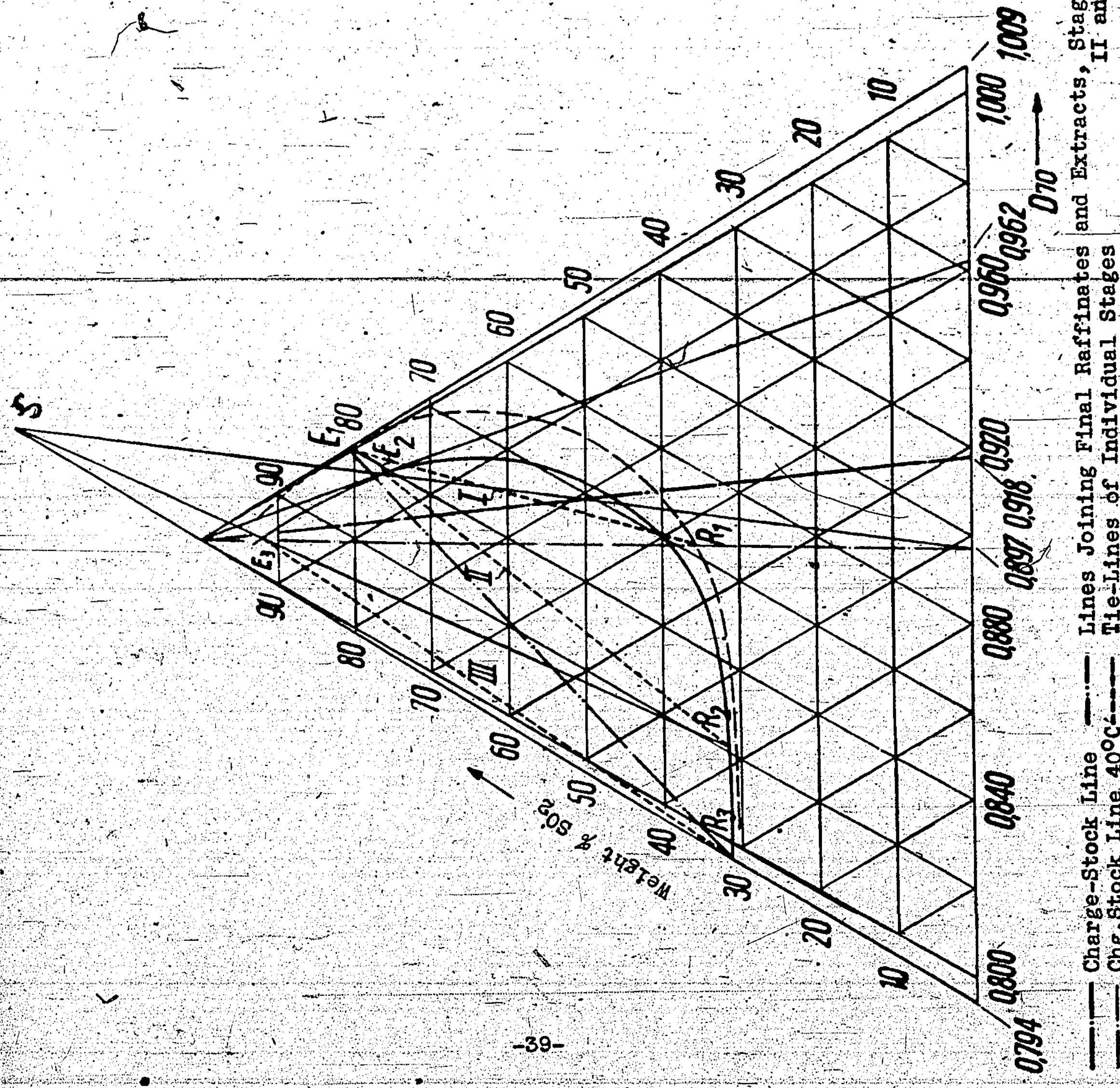


Fig.8 THREE-STAGE SO_2 EXTRACTION AT 40, 40, & -10°C., BROWN COAL TAR DISTILLATE

The separation of the L-TC tar is carried out in three stages: A first stage at -10°C, from which the final extract is obtained and to which the charge stock is added (4) and extracted by admixture with the final extract solution from the stages operated at 40°C., and two other stages operated at 40°C. The pure solvent is charged to the third stage, from which the final raffinate solution is obtained.

In the first stage the charge stock (D_{70}=0.918) is mixed with the final extract E_2 from the 40°C stage (extract density, D_{70}=0.962, SO_2 content of this extract solution about 77% by weight) and at -10°C is separated into the final extract solution E_1 (extract density, D_{70}= 1.009, SO_2 content of this solution about 89% by weight) and an intermediate raffinate solution R_1 (raffinate density D_{70} = 0.897, SO_2 content of this solution about 36% by weight). The latter raffinate solution R_1 is the charge stock for the 40° stage. In the second stage it is mixed with the extract solution E_3 of the third stage (extract density D_{70}=0.878, SO_2 content of this solution about 93% by weight) whereby it is separated into the extract solution E_2 (extract density D_{70}=0.962) and a second intermediate raffinate solution R_2 (raffinate density D_{70}=0.820, SO_2 content of this solution about 32% by weight). This intermediate raffinate solution R_2 is then mixed with pure solvent and separated into the extract solution E_3 (extract density D_{70}=0.878) and the final raffinate solution R_3 (raffinate density D_{70}= 0.794, SO_2 content of this solution about 32% by weight). These two 40° stages are operated in a single extraction tower, which is suitably designed without division into separate stages.

The densities of the raffinate and extract will now be examined to judge the extraction results obtained by this treatment.

(4) As is apparent, the results of the -10° stage can be obtained in two ways, either by cooling the final extract of the 40° stage or by simultaneous introduction of the charge stock into the -10° stage whereby the material in admixture with the extract from the 40° stage, is separated into a final extract (-10° C) and an intermediate raffinate.

With a completely isothermal extraction at 40°C there was obtained from a charge stock with D_{70}=0.918 a final raffinate with a density of 0.802 and a final extract with a density of 0.962. By operating a stage at -10°C the final raffinate is improved to a density of 0.794 because the soft wax, which is held in the final extract at 40°C., has gone into the raffinate, and as a result the density of the final extract obtained at -10° C has increased to D_{70}=1.009.

From these results can be calculated the increased yield of raffinate resulting from adding the stage operated at -10° C. With a straight treatment at 40°C in two stages, there is obtained 27.5% by volume of raffinate with a density D_{70}=0.802 and an extract with a pour point of 20° C. By treating in two stages at 40° C and adding a third stage at -10°C there is obtained as a final result, 40.4% by volume of a raffinate with a density D_{70}=0.794, i.e. about 13% more raffinate than from isothermal treatment at 40° C; to this the two 40° stages have contributed 24.7 vol.% (as a consequence of the resulting change in density of the final raffinate) and the -10° stage has contributed a further 15.7 vol.%. The extract with a density D_{70}=1.009 now has a pour point of -30° C.

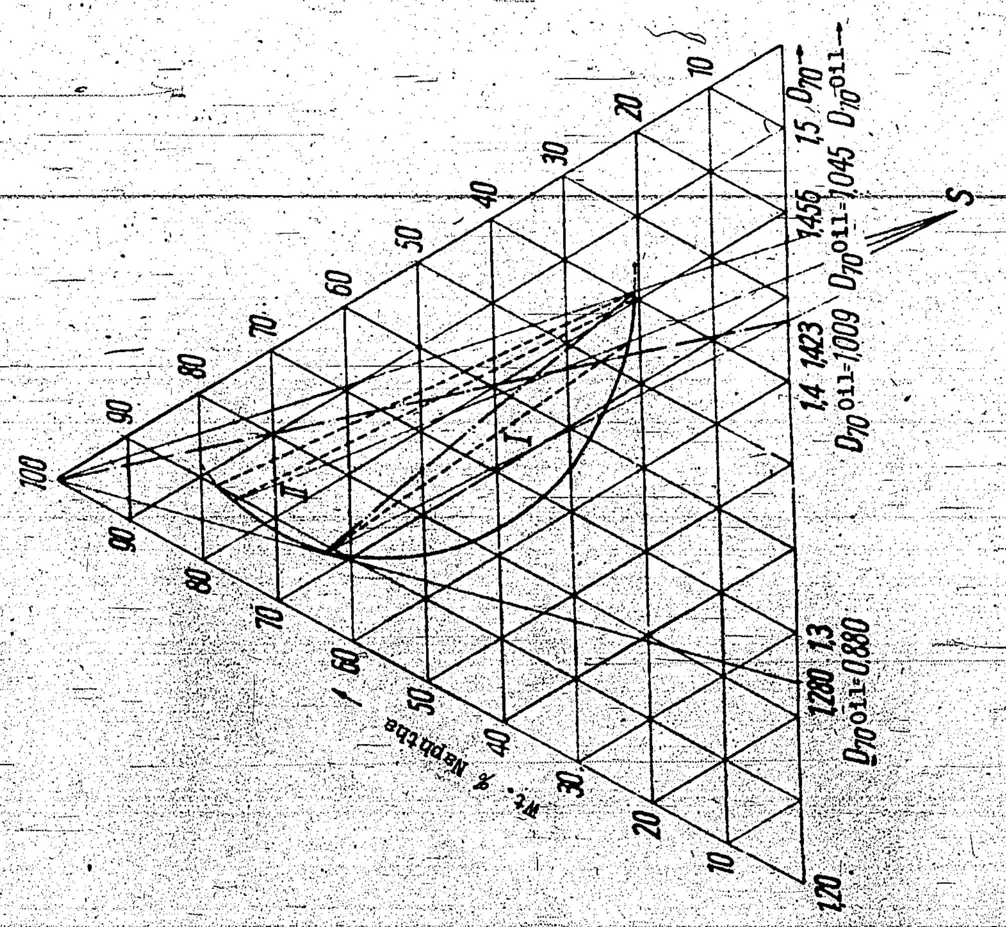
Thereby we have accomplished everything that can be accomplished with L-TC tar using liquid sulfur dioxide as a selective solvent, unless an additional step is added at a still lower extraction temperature, such as -25 or -30° C or even lower. Whether such a procedure is necessary or not is primarily an economic question which depends upon the additional extraction results which might be obtained.

USE OF NAPHTHA TO SEPARATE AN SO_2-EXTRACT FROM A TAR FROM LOW-TEMPERATURE CARBONIZATION OF BROWN COAL.

The part of the raffinate material which still remains in the extract from the extraction at -10°C, is removed by washing the extract solution with naphtha. In commercial operations the wax-free middle-oil distillate is also treated with the naphtha wash and is separated into a raffinate and an extract; as a result the extract relationships are somehwat more striking in this naphtha wash. In the present situation this is disregarded and only the final extract from the -10° stage is extracted with a low boiling naphtha fraction, without first removing the solvent (SO_2). The boundary curve for this part of the total separation procedure is also shown, not at -10° C but instead at 0° C; as a result the density (D_{70}) of the final extract is somewhat lower, i.e. 1.045 instead of about 1.060 at -10° C.

Figure 9 shows the boundary curve of the naphtha wash. This curve lies with the two phase area to the right and the raffinate part of the curve is on top. The base of the triangle represents the density (D_{70}) of the SO_2 - containing solution and the apex the pure solvent - in this case, naphtha. In this extraction procedure the result is a removal of residual raffinate material from the SO_2 - extract.

This naphtha extraction differs from the previously described SO_2 extraction in that the naphtha solvent goes into the raffinate and also in that the charge stock - the final SO_2 - extract dissolved in SO_2 - is introduced in the top of an extraction tower and flows from top to bottom counter-current to the upflowing lighter naphtha; at the lower end of the extraction system the extract of the naphtha wash is discharged and the solvent (naphtha) is introduced, contrary to the SO_2 extraction, while at the upper end the raffinate solution is discharged and the charge stock is introduced. The upper part of the curve represents the raffinate solutions and the lower part the extract solutions. The raffinate with the lowest density is found from the tangent to the curve which passes through the apex of the triangle, while the extract with the highest density lies at the right hand outer end of the lower branch of the curve. In contrast to SO_2 extraction, the use of a large amount of solvent results in an extract of high density and a raffinate which contains a large amount of extract material; the use of a small amount of solvent results in a raffinate of low density and an extract with a large amount of raffinate material. In contrast to the previously described SO_2 extraction, by removal of solvent it is possible to effect a separation of a given raffinate solution into a new raffinate solution (a raffinate with a lower density than that of the charge solution) and an accompanying extract solution (an extract with a corresponding density) and similarly by treating an extract with an increasing amount of solvent the density of the extract can be increased. These special characterists produce the location and form of the boundary curve. In this extraction pure solvent and final extract come together in the lowest stage and at the opposite end of the extraction system (upper part of the extraction tower) the solution of final raffinate in naphtha leaves the system countercurrent to the entering SO_2 solution of the extract, i.e. the charge solution. In order to determine the point S a line is drawn through the point on the base of the triangle corresponding to the



——— Charge-Stock Line, SO_2-Ext. Soln. ——— Line Joining Final Extract and Final Raffinate

-·-·-·- Tie-Lines of Individual Stages

Fig. 9 TAR DISTILLATE FROM L.-T.C. OF BROWN COAL, NAPHTHA WASHING OF SO_2 EXTRACT IN TWO STAGES AT 0°C.

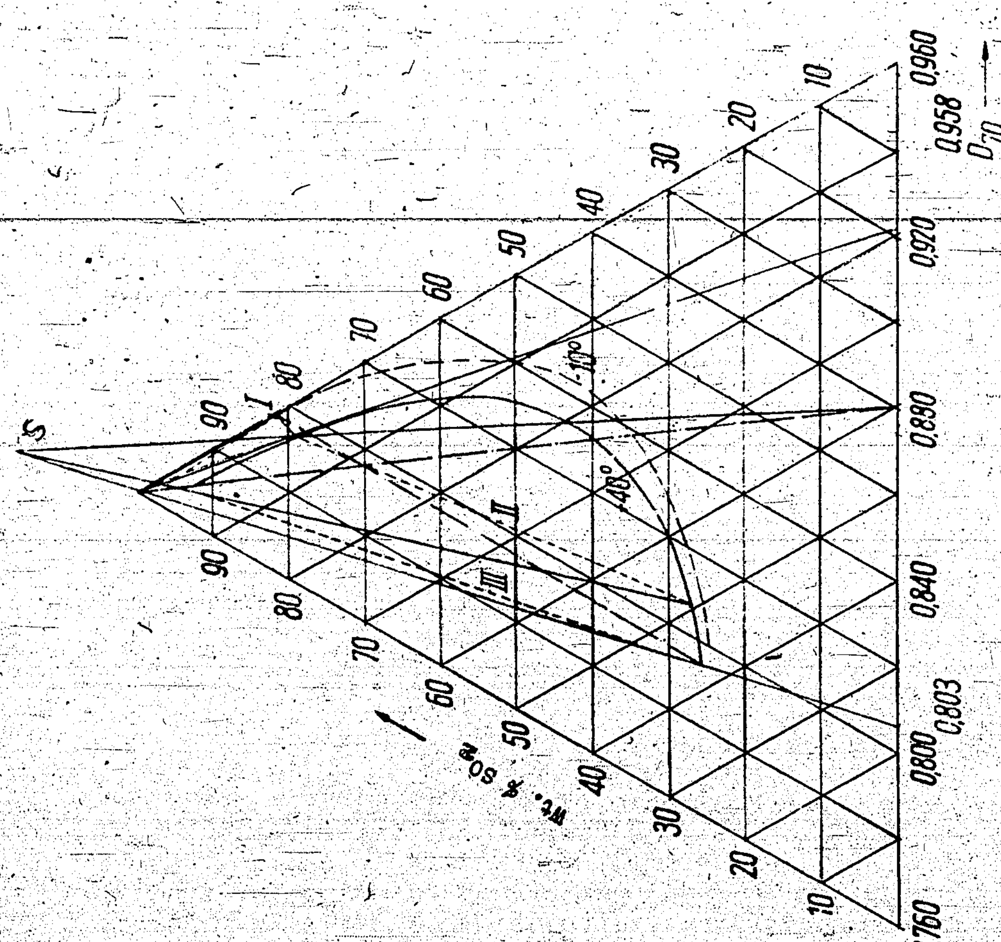
charge stock and the point of tangency on the boundary curve (of a line through the apex), i.e. corresponding to the final raffinate, and a line is drawn through the point corresponding to the final extract and the apex of the triangle (representing the pure solvent). These two lines intersect in the point S.

The point of intersection of the tie-line between the final extract and the final raffinate indicates the amounts of charged SO_2-extract (from the -10° stage of the SO_2 extraction) and of naphtha which have been introduced into the process, and likewise this tie-line is divided by the charge stock line into parts which are proportional to the amount of raffinate and extract solutions. With the aid of the point S, it is possible to determine that this naphtha wash likewise can be carried out in two stages.

By this procedure a final raffinate is obtained with a density D_{70}=0.880 and a final extract with a density D_{70}=1.045. The extract in the charge stock to this step had a density D_{70}=1.009. From these data it can be calculated that this naphtha washing results in a separation into 21.8% raffinate and 78.2% final extract. Since the initial extract charged to this naphtha wash was 59.6% of the initial L-T.C. tar distillate, there should be added to the 40.4% volume raffinate obtained in the SO_2 extraction an additional 13%. This naphtha raffinate is the second and heavier Diesel oil product. These Diesel oil products will be designated by "I" in the following discussion. With a simultaneous extraction of the neutral oil in this naphtha wash and a decrease of the extraction temperature to -10° C., the density of the naphtha raffinate is lower, and the resulting amount of raffinate is increased. The simultaneous use of neutral oil results in the introduction of lower boiling components in the naphtha raffinate.

SEPARATION OF SHALE OIL DISTILLATES WITH LIQUID SULFUR DIOXIDE.

Before we go into a consideration of dewaxing, which is the same for L-T.C. tar and for shale oil, we will consider briefly the boundary curve for the SO_2 extraction of shale oil (Fig.10). This extraction is also carried out in two stages at 40° C., and in a subsequent stage at -10° C. From this extraction is obtained a final raffinate



—— Charge-Stock Line
------ Tie-Lines of Individual Stages
—·— Line Joining Final Raffinate and Extract

Fig. 10 SHALE OIL DISTILLATE, SO_2 EXTRACTION OF THE MAIN FRACTION IN THREE STAGES AT 40°C., 40°C., AND -10°C.

with a density D_{70}=0.803 and a final extract with a density D_{70}=0.958. This corresponds to a raffinate yield of 50.3% from the wax-containing fraction. A complete discussion of the separation of shale oil will be presented later.

SEPARATION OF HARD WAX AND SOFT WAX FROM THE WAX-CONTAINING SO_2 RAFFINATE.

The process of dewaxing will now be discussed. The SO_2 raffinate is freed from solvent (the sulfur dioxide) by vaporizing it. After this treatment it contains 50% or more by weight of total wax; it is therefore a very oily wax slurry, and the following process can be characterized as de-oiling just as well as de-waxing. Simultaneously with the separation of wax, there is effected a separation into hard wax with a melting point of 50-52° C., or 52-54° C., or even higher, as may be desired, and into a soft wax with a melting point of 25-30° C., or even higher and into an oil filtrate with a low pour point. In the separation of soft wax the solvent used is dichloroethane, with or without sulfur dioxide. The separation of hard wax is carried out at 5 or 10° C. depending upon the melting point desired, and the separation of soft wax is carried out at about -20° C. The pour point of the final filtrate will then be about -15° C. or lower. The hard wax is practically oil-free; the amount of wax determined by the method of Holde is 98-99%; the soft wax contains about 10-14% of material with a higher density than corresponds to a pure waxy hydrocarbon. The exact degree of freedom from oil is somewhat inaccurate since there is no sharp dividing line between the low-melting soft wax and the fluid paraffin hydrocarbons.

The requirements which the new uses for wax demand, the synthesis of lubricating oil and the oxidation to fatty acids, vary somewhat from the specifications for wax heretofore used. In order to specify accurately the inspection data for the wax fractions which are to be used for the synthesis processes named, we have been in correspondence with the Norddeutschen Mineralölwerken Stettin GmbH, at Stettin-Pölitz, and with the I.G. Laboratorium in Ludwigshafen and have changed the operating conditions and properties of the resulting wax during the course of many tedious experiments until we have finally obtained samples with the required characteristics.

The hard wax definitely meets all requirements as to freedom from oil, density, molecular weight, boiling range, distillation residue and aniline point. However, it is a somewhat different situation for the total wax and for the soft wax. As an indication of the properties of a wax, the following inspection data will be used as guide:-

Initial boiling point, not under 100° C. at 1 mm pressure (i.e.) about 300° C. at 760 mm);
Final boiling point, not substantially greater than 300° C. at 1 mm pressure;
Density (D_{70}) of the distillation residue which is left at 300° C. and 1 mm, not greater than 0.800;
Aniline point of the total wax, averaging 109-110° C.;
Aniline point of the soft wax, not less than 102°C;
Complete absence of cyclic hydrocarbons for products to be used for synthesis of fatty acids.

By paying sufficient attention to the operating conditions in the dewaxing step, and by the development of a special filter, it has become possible completely to fulfil the specifications just recited. It has been found possible to remove the lower boiling constituents, i.e. boiling below 150° C. at 1 mm and also the constituents with too high a density, which produce a distillation residue at 300° C. and 1 mm pressure, by conducting the de-oiling at about -10° C., or by a dewaxing at this temperature, and these constituents go into the de-oiling filtrate or remain in the de-waxing solution. It is possible, by a proper choice of the de-waxing temperature, to retain the undesired components of the total wax and of the soft wax in the filtrate. If it appears possible that the pour point of the filtrate will be too high by such a procedure and the pour point of the mixture of the two Diesel oil fractions will be above the permissible value as a result of a separation of certain Diesel oil components in the naphtha wash, the wax must be subjected to a solvent de-oiling a second time at a desired temperature, and the resulting filtrate can then be converted into heating oil.

The separation of waxy components by dewaxing the SO_2 raffinate, or by after-treating the total wax or soft wax fractions from the L-T.C. tar (from brown coal) at different temperatures with dichloroethane, depends upon the materials contained in these fractions, and particularly upon the melting points of the wax components, i.e. in this case, also upon the molecular weight. In wax mixtures containing straight-chain paraffins, isoparaffins and cyclic compounds, the melting point is of primary importance in determining the separation conditions, since cyclic hydrocarbons which have the same melting point but a different molecular weight than the paraffin hydrocarbons, will be separated in the same filtrate.

As a result, as we shall learn later, by treating wax which has been obtained at a temperature of -20° C. with dichloroethane at -10° C., the low-boiling (paraffin hydrocarbons) and the highest boiling (primarily cyclic hydrocarbons) components will go into the same filtrate. So from a total wax fraction which has been obtained by dewaxing at -20° C., there can be obtained only soft wax components by an after-treatment at -10° C., and the low-melting components will be brought into solution, including those with a melting point of 20° C.; by after-treating at the -5° C., all soft wax components having a melting point up to about 25° C. will be separated, or in case the former dewaxing temperature has been changed to the temperatures of this after-treatment, these soft wax components will remain in solution.

In the extremely careful and systematic investigation of the fractional separation of wax components with dichloroethane as solvent, we have been able to obtain an indication of the composition and nature of the wax contained in tar from low-temperature carbonization of brown coal as a basis for the development of the de-waxing process. In the meantime, under stimulus of F. Schick, H. Gross and K. H. Grodde in the laboratories of the Deutsche-Erdöl, A G., a very good investigation along a similar line has been carried out and has been published in "Oel und Kohle", which has particularly dealt with waxes and mineral oils and gives an interesting glimpse of the nature of wax (5).

Our investigations which are discussed herein concern only wax present in brown coal and the shale oil. Petrol-

(5) "Oel und Kohle", 1942, pp. 419 ff.

eum wax from various mineral oils which have been investigated by us differ appreciably and comprise only to a small extent straight-chain and branched-chain paraffin hydrocarbons dependent upon the origin of the petroleum. For such petroleum waxes, the fractional separation with dichloroethane does not take place with the same relationships to melting point, molecular weight, density etc. as the corresponding waxes from brown coal.

In the following discussion, there will be presented a fractional separation of this nature for a total wax and a soft wax from tar produced by low-temperature carbonization of brown coal.

Table 1, presents data relating to the total wax from a tar from Hessian brown coal which was separated at a temperature of -15° C. and, as a result, no longer contained the lower melting components of the soft wax. The total wax under consideration was separated into seven fractions and a residue. The fractions which were obtained as a filtrate consist almost entirely of straight-chain paraffin hydrocarbons and, as can be seen, when they are submitted to separation at various temperature levels between -10 and 40° C., this apparently simple material produces fractions corresponding to molecular weights. The isoparaffins have increased in concentration in the residue. The total wax consists of straight-chain hydrocarbons to the extent of 87.4% and undoubtedly the 12.6% residue can still be further separated. The straight-chain hydrocarbons are in a range of molecular weight from C_{17}-C_{26}.

The determination of the molecular weight is unusually difficult for such paraffin hydrocarbons and the rules are valid only for relatively chemically pure materials and such mixtures which do not melt much above 40° C; only for individual materials and by very careful work can reliable results be obtained for those materials with higher melting points. The best process is the freezing point method using benzene as a solvent. The boiling point method generally results in a considerable scattering of values, even for individual substances. With wax mixtures containing hydrocarbons of various molecular weights and correspondingly different melting points and solubilities, a separation of crystals and wax readily takes place in the freezing method and falsifies the results; in the boiling point method, the elevation of the boiling point is very small, since only small amounts of such materials of high molecular weight can be dissolved in comparison with their molecular weights, while still remaining in the valid range of dilute solutions, and as a result, the chances for errors are greater.

TABLE 1.

Fractional Separation By Dichloroethane Of A Total Wax Fraction Of A Tar From Low-Temperature Carbonization Of Brown Coal.

Separation of Charge Stock and Each Fraction with 400 ÷ 200 vol. % $C_2H_4Cl_2$	Charge Stock.	Melt Pt. °C	D_{70}	Aniline Pt. °C	Mol. wt.	N_{70}		Melt Pt. °C	D_{70}	Aniline Pt. °C	Mol. wt.	N_{70}	Remarks
	100 wt. %	49.0	0.776_1	108.7	345	1.432_5							
Temp., ° C.	wt. % Residue						wt. % Filtrate						
-10° C	96.0	50.5	0.775_0	109.3	(383)	-	4.0	26.5	0.793_7	91.3	264	1.440_0	C_{17}/C_{18}
0° C	86.6	51.5	0.775_6	110.5	(392)	-	9.4	34.0	0.780_9	95.3	292	1.434_0	C_{19}/C_{20}
10° C	71.5	53.5	0.774_9	113.3	(418)	-	15.1	40.5	0.778_5	98.3	312	1.433_2	C_{21}/C_{22}
20° C	49.2	56.0	0.774_7	116.8	(439)	1.433_0	22.3	46.5	0.775_0	105.0	323	1.432_0	C_{22}/C_{23}
25° C	34.3	58.0	0.775_8	119.1	(478)	1.434_2	14.9	50.5	0.774_5	110.7	347	1.433_1	~ C_{24}
30° C	25.2	60.0	0.776_6	120.2	(552)	1.433_9	9.1	53.5	0.774_3	113.7	360	1.433_9	~ C_{25}
40° C	12.6	63.3	0.777_6	121.5	(675)	1.434_6	12.6	57.0	0.774_5	117.1	380	1.434_6	~ C_{26}

As a rule, we have so proceeded that we have determined the molecular weights only for the filtrates, and have calculated the molecular weights for the residues. However, even these determinations do not result in values of an accuracy greater than +5%, and even so, are average values obtained from a large number of determinations within a narrow range. For waxes from petroleum oils, values obtained by such methods for determination of molecular weight cannot be considered very accure when used for further understanding of the compositions of these waxes; as a result, it is not possible to say that these determinations of petroleum waxes are inaccurate and inexact within the indicated range.

Table 2 presents the data obtained from a soft wax, obtained from a tar distillate from a brown coal coming from a district in Middle Germany. It has been separated into 5 filtrate fractions and a residue by working at 5 different temperature levels between -20 and 15° C. The first fraction undoubtedly still contains oil. However, the second and third fractions also have lower melting points than correspond to the molecular weights of straight-chain paraffin hydrocarbons and are probably paraffin hydrocarbons with branched chains. On the other hand, the last two fractions and the residue come closer to containing the straight-chain paraffin hydrocarbons C_{18}, C_{19}, and C_{22}.

The relationships can be seen more clearly from the following graphical presentations.

Fig. 11 shows a melting point curve for straight-chain paraffins from C_{15} to C_{60} as a function of the molecular weight. The line which runs more or less parallel with this curve represents the various filtrate fractions from the total wax under investigation; the dotted line between the two represents the residual fractions of the soft wax, the upper part of this latter line corresponds well to the curve for the pure paraffin hydrocarbons while the last two filtrate fractions deviate further therefrom. The melting point of the residues of the filtrate fractions of the total wax deviate increasingly from the curve of the pure paraffin hydrocarbons as the extraction is carried out.

It can be readily seen that a very small amount of isoparaffinic material has a very strong influence upon the melting point since the content of such material is of the order of only 10%. The melting point of the charge stocks have been indicated as circles; it can be seen that the melting point of the total wax lies on the curve of the

TABLE 2.

Separation Of A Soft Wax, From L-T.C. Tar From Brown Coal, By Dichloroethane.

Separation of the Soft Wax, Oil Removal with 400 + 200 vol. % $C_2 H_4 Cl_2$ Temp., °C.	100 wt. % soft wax.	Melt Pt. °C.	D_{70}	Aniline Pt. °C	Mol. wt.	N_{70}	Remarks		Melt Pt. °C	D_{70}	Aniline Pt. °C	Mol. wt.	N_{70}	Remarks
	wax wt. %	30.9	0.768_6	101.2	292	1.430_3		wt. % Filtrate						
-20° C	95.3	31.5	0.768_8	101.5	(294)	–		4.7	12	0.790_4	87.3	256	1.442_0	
-10° C	87.9	32.3	0.768_3	102.2	(294)	–		7.4	20	0.774_0	92.4	296	1.434_0	
0° C	71.6	33.8	0.768_5	103.2	(285)	–	C_{19}/C_{20}	16.3	25	0.771_2	95.8	310	1.432_0	
10° C	43.5	36.7	0.768_2	105.6	(294)	–	C_{20}	28.1	29	0.768_6	99.8	283	1.431	$\sim C_{18}$
15° C	20.5	43.5	0.769_2	108.9	(310)	1.432_0	C_{22}	23.0	32	0.768_5	102.5	288	1.430_3	$\sim C_{19}$

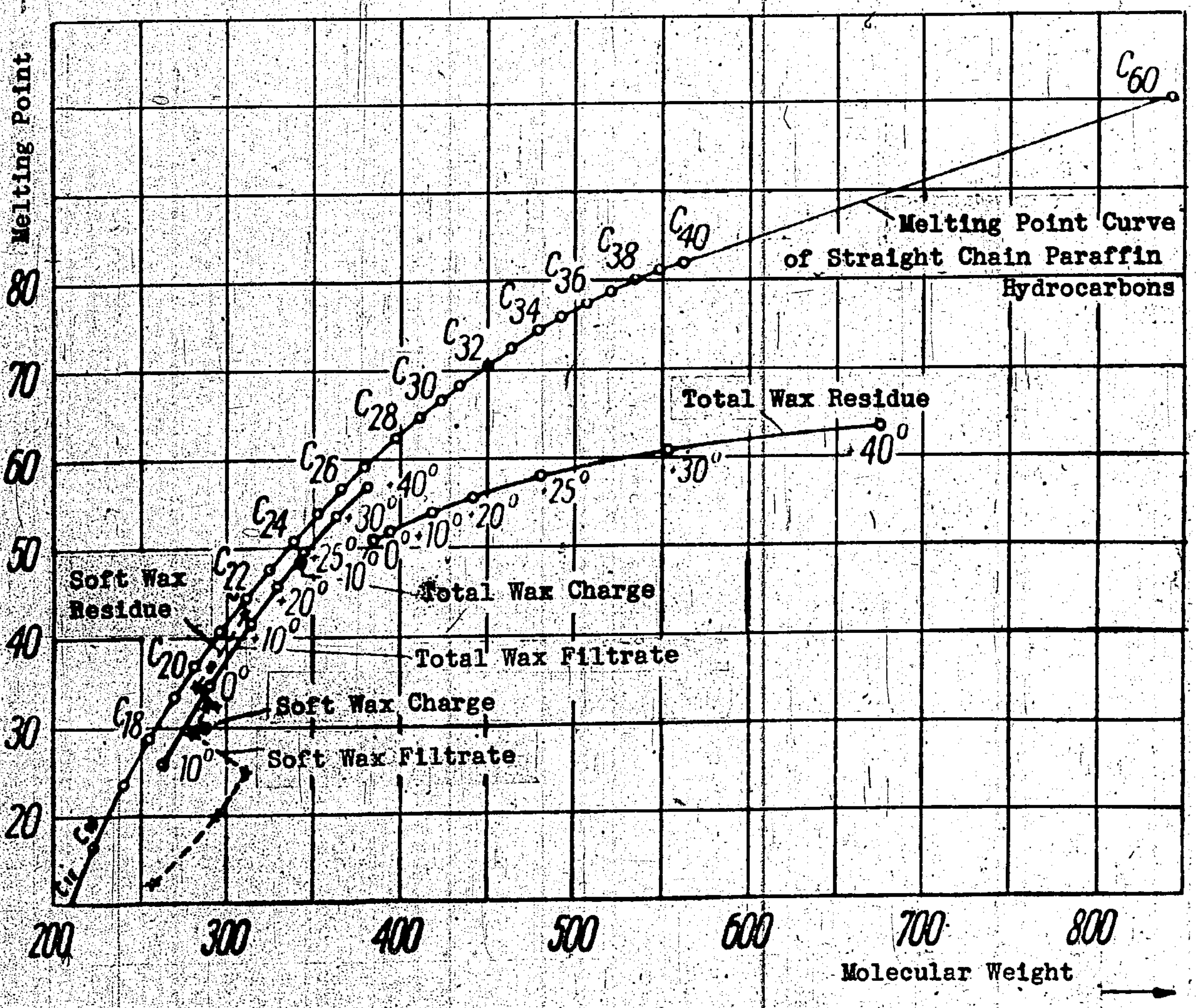


Fig. 11 FRACTIONAL SEPARATION OF TOTAL WAX AND SOFT WAX FROM AN L. T.C. TAR DISTILLATE FROM BROWN COAL

filtrate fractions while after removal of only 4% of the filtrate, the melting point of the first residue is quite a distance from the melting point curve of the paraffin hydrocarbons.

The melting point of the initial soft wax was substantially further from the curve of the straight-chain paraffins, as a result of its high content of non-straight chain paraffin materials.

Fig. 12 shows the aniline points of various filtrate and residue fractions obtained at the various de-oiling temperatures. Both curves of the total wax tend to be directed toward a common point of intersection as the de-oiling is carried to completion, and as the aniline points increase; this point of intersection is reached at a de-oiling temperature of about 65° C. and indicates that the highest possible aniline point for the residual fraction would be about 122.8° C. The corresponding curves for the soft wax exhibit the same tendency and the point of intersection of the two curves appears to correspond to a de-oiling temperature of about 24° C. with an aniline point for the last fraction of about 112.5°C

A second pair of curves show the relationship between molecular weight and aniline point for the total wax. In the manner in which the direction of the curve changes for the residue, it clearly can be seen that the residual fractions are becoming richer in isoparaffins while, in an exactly similar way, the curve for the filtrate shows that it tends to be composed of substantially only straight chain paraffin hydrocarbons. The curves also show that the aniline point is not an indication of the molecular weight since one and the same aniline point corresponds to various molecular weights. (This will be clearly shown in connection with Fig. 13). In the case of soft wax, the curve representing the change of molecular weight of the filtrate fraction as a function of the aniline point passes through a somewhat indefinite maximum point and the corresponding curve for the residue fractions passes through a similar minimum point, and it is for this reason that an evaluation of these has been given up for the purpose of this paper.

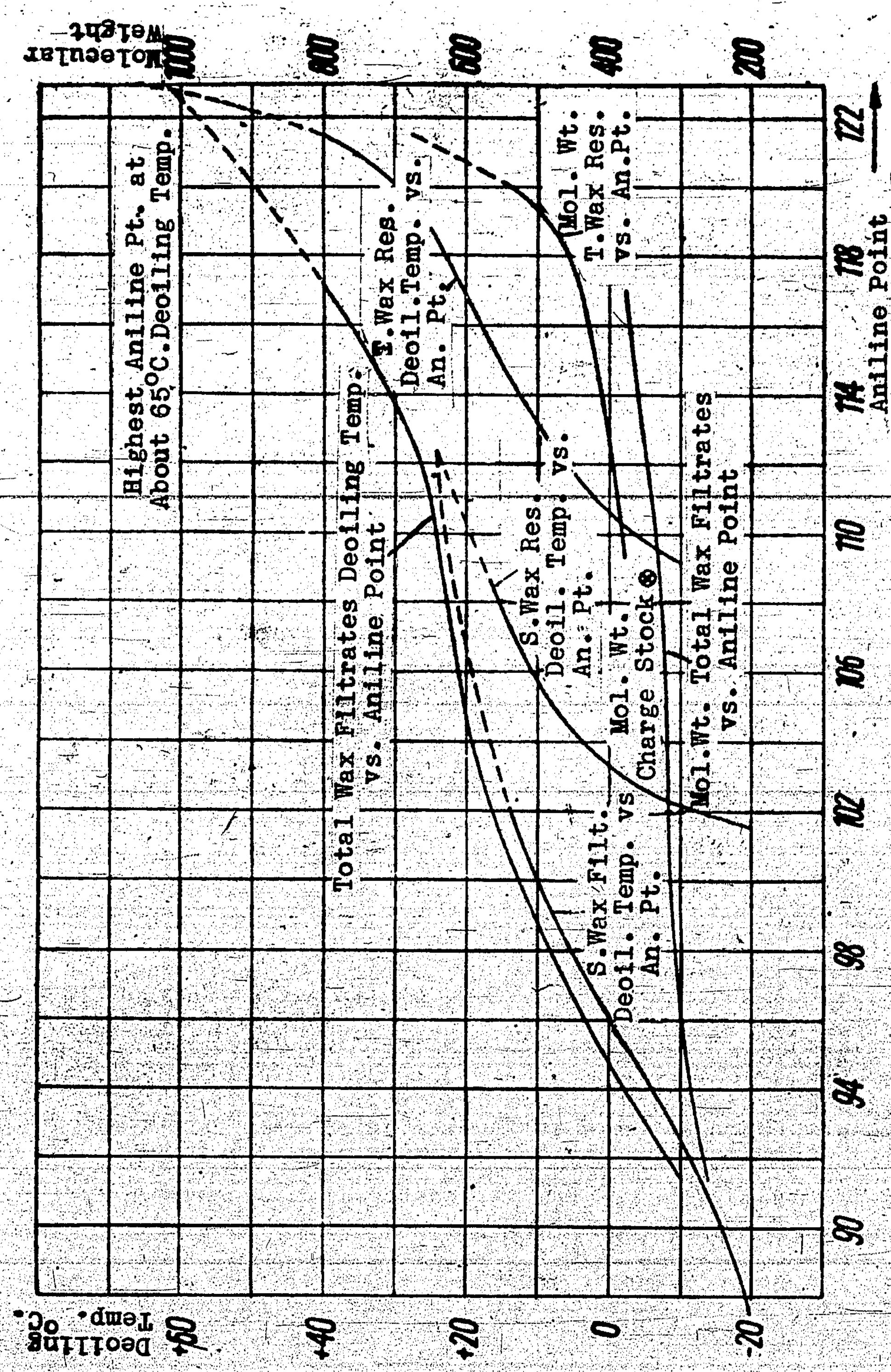


Fig. 12 DEOILING TEMPERATURE AND MOLECULAR WEIGHT vs. ANILINE POINT FOR TOTAL WAX AND SOFT WAX

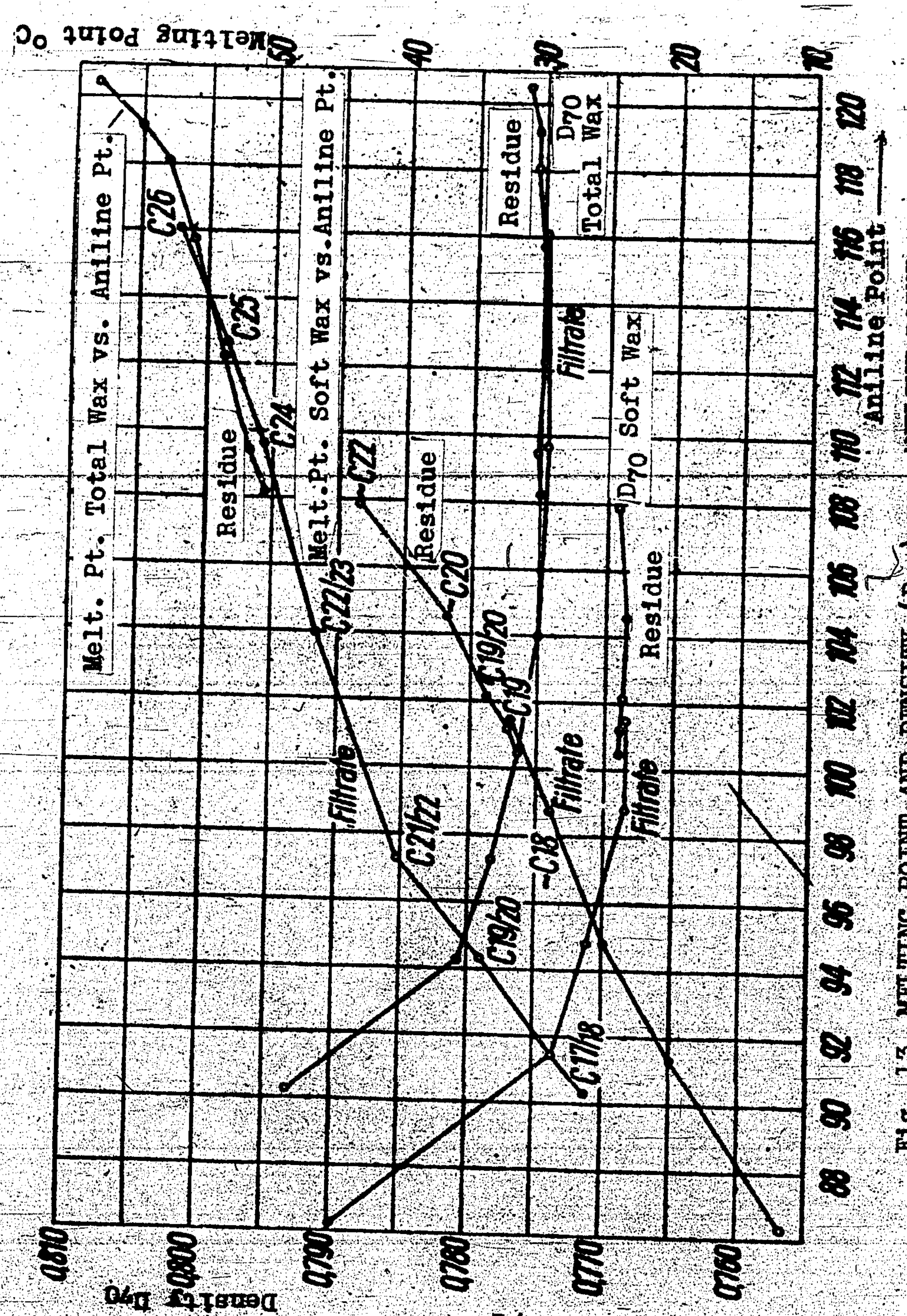


Fig. 13 MELTING POINT AND DENSITY (D_{70}) vs. ANILINE POINT FOR TOTAL WAX AND SOFT WAX

The relationships between melting point and aniline point are presented in Fig. 13. For both types of charge stock, the curves for the filtrate fractions and those for the residue fractions tend to come together. Here also those hydrocarbons which in part tend to be more or less pure in individual fractions have the same aniline points in spite of their differences in melting points.

Of particular interest on the same graph are the curves which present the relationship between density and aniline point. It can be seen that the density of the initial fractions for both types of initial waxes are too high for paraffin hydrocarbons and that the two first filtrate fractions, i.e. representing about 12-14% of the charge stock, must be removed by a suitable regulation of the de-oiling temperature in order that these waxes shall comply with the rules just discussed. For actual operations, this is of considerable significance since the undesired portions which are removed at a low temperature by selective treatment with dichloroethane contain low-boiling components, i.e. all components with too high a density (oily material and cyclic compounds) remain in solution at about -10° C.

The wax obtained from shale oil is quite similar in many of these relationships to the wax obtained from brown coal even though, in general, it appears to be closely related to wax obtained from natural petroleum; shale oil belongs to the class of natural petroleums, without any doubt. The double distillation (once in the low-temperature carbonization process and once in distillation of the resulting shale oil product) results in a great similarity in the behavior of the curves, as is generally also the case for petroleum waxes; as can be seen in Fig. 14, the individual fractions differ appreciably from corresponding fractions in the wax from brown coal in spite of the double distillation. The four first filtrate fractions (Table 3 and Fig.14) have melting points which are too low and have the characteristics of isoparaffins, while only the very last filtrate fraction has the characteristics of a straight-chain paraffin and approaches those of a C_{24} paraffin hydrocarbon. In the case of the residue fractions, the first four residues tend to come ever closer to the melting point curves of pure straight-chain paraffin hydrocarbons, while on the other hand, the filtrate curves and also the positions of the last residues prohibit a conclusion that they are related to straight-chain paraffin hydrocarbons. The high melting point of the last residue, 62° C., and the low molecular weight of 305 are conclusively and clearly an indication of a cyclic

TABLE 3.

Separation Of A Total Wax Fraction From A Shale Oil Distillate

Separation of Charge Stock and Each Fraction with 400 + 200 vol. % $C_2H_4Cl_2$.	Charge Stock.	Melt Pt. °C.	D_{70}	Aniline Pt. °C	Mol. wt.	N_{70}		Melt Pt. °C.	D_{70}	Aniline Pt. °C	Mol. wt..	N_{70}	Remarks
	100 wt.%	45	0.778_8	109.9	343	1.435_9							
Temp., °C	wt. % Residue						wt. % Filtrate						
-10° C	96.6	46	0.779_6	111.3	(344)	1.434_7	9.4	22	0.785_1	96.3	335	1.439_3	
0° C	81.1	47	0.7796	112.5	(344)	1.433_2	9.5	27.5	0.780_9	100.8	339	1.434_9	
10° C	63.7	50	0.779_9	115.2	(344)	1.433_2	17.4	34	0.779_9	105.3	346	1.434_8	
20° C	43.8	53.5	0.780_5	117.2	(342)	1.431_9	19.9	40	0.7786	107.9	349	1.434_9	
30° C	12.9	62	0.785_7	119.0	(305)	1.437_5	30.9	50	0.779_9	113.8	357	1.433_1	

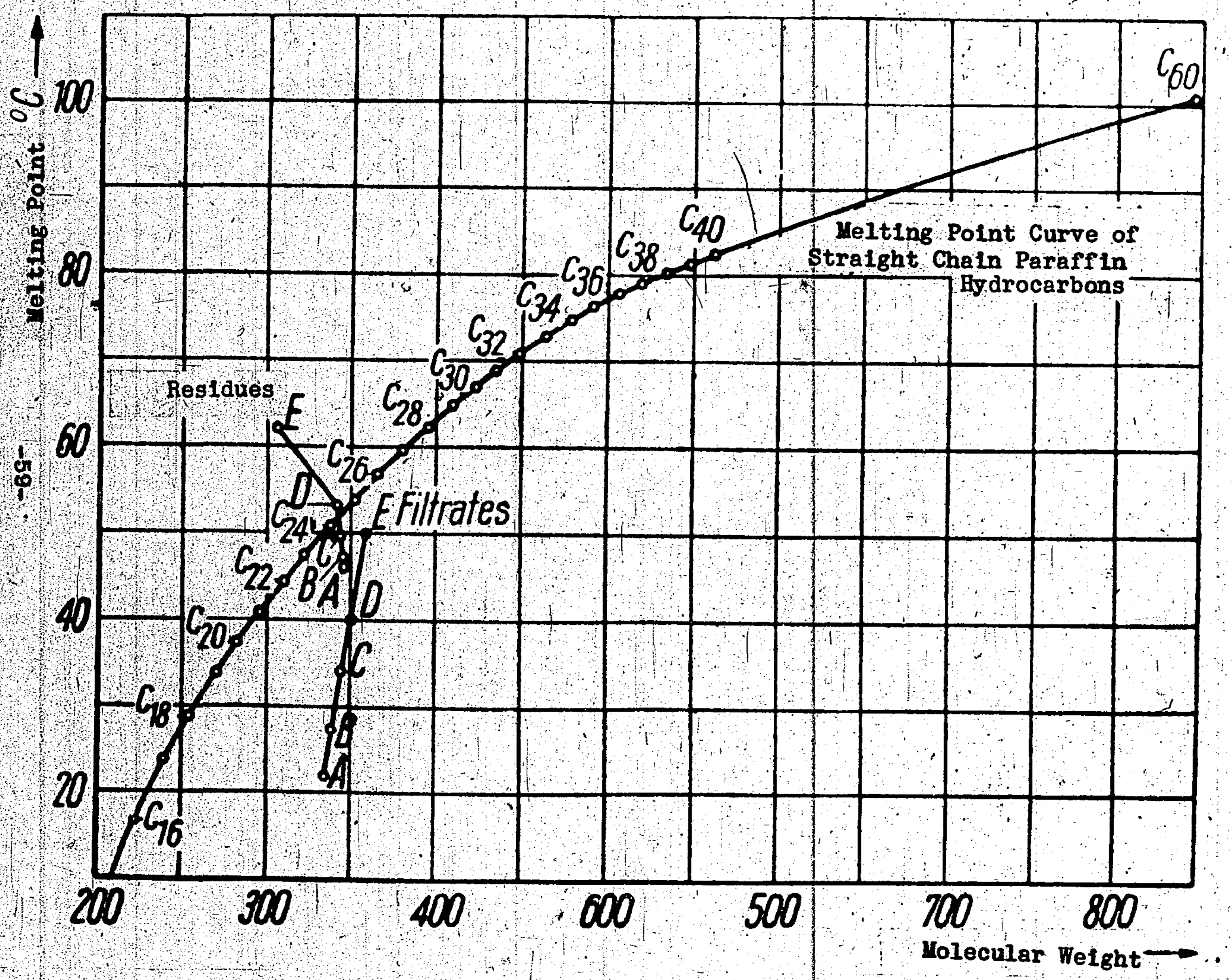


Fig. 14 FRACTIONAL SEPARATION OF TOTAL WAX FROM SHALE OIL DISTILLATE

structure; the high density and refractive index are additional proofs of this.

There is graphically presented in Fig. 15, for wax from shale oil, the relationships of melting point to aniline point, de-oiling temperature to aniline point, and density to aniline point. In general, they show the same relationship as the corresponding curves for wax obtained from brown coal.

From these analyses of various waxes, it can be seen that the wax from brown coal is a very good raw material for oxidation to produce fatty acids because of the high content of straight-chain paraffin hydrocarbons, while the soft wax from brown coal and the wax from mineral oil should be better raw materials for the synthesis of lubricating oils as a result of their high contents of isoparaffin hydrocarbons, and also of the content of cyclic hydrocarbons in the latter material. As far as I am aware, such an evaluation of these raw materials has not previously been made because of the lack of knowledge of the composition of these various waxes.

FLOWSHEET FOR SEPARATION OF TAR FROM LOW-TEMPERATURE CARBONIZATION OF BROWN COAL WITH YIELD DATA FOR THE INDIVIDUAL PRODUCTS.

We shall now pass to a presentation of technical data. A simplified flowsheet for the separation of L-T.C. tar is given as Fig. 16, which illustrates the important operating steps.

The wax-containing tar distillate is pumped into the plant with a piston pump and mixed in a circulating pump with the penultimate extract solution of the SO_2 extraction. The mixture is then cooled in a cooler to about -10° C. whereby there is a formation of two phases and wax crystallizes out. The phases are separated in a centrifuge whereby the final extract of the SO_2 extraction is separated, which is ultimately sent to the naphtha wash, while the wax-containing raffinate phase is passed to an extraction tower (the previously mentioned two-stage tower) wherein it is further extracted with liquid sulfur dioxide, isothermally at 40° C., as previously discussed. The resulting extract solution is used for the first extraction of the distillate charge stock, as just mentioned. The raffinate solution containing wax goes to a vaporization apparatus where the sulfur dioxide is separated in three

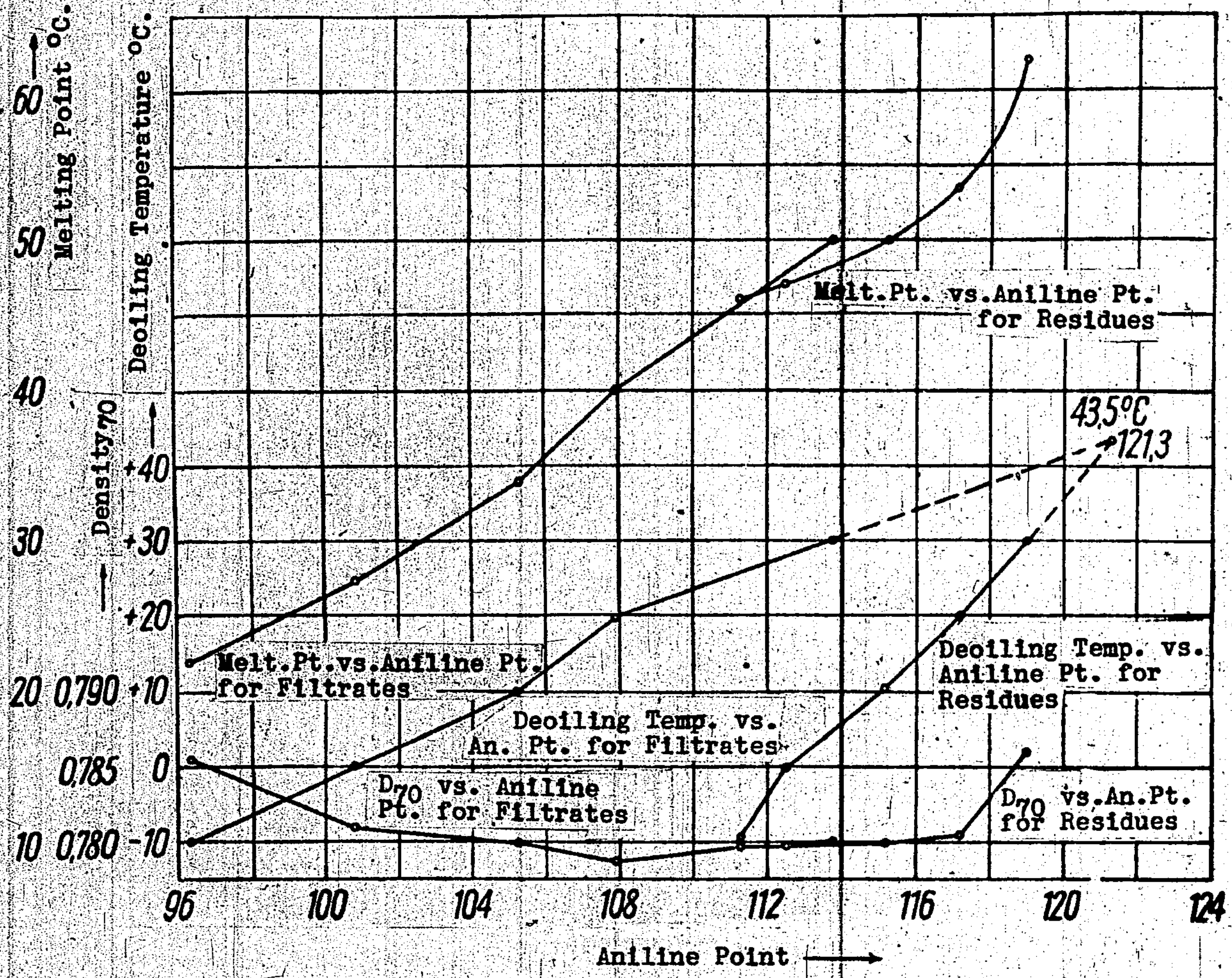


Fig. 15 MELTING POINT, DEOILING TEMPERATURE, AND DENSITY vs. ANILINE POINT FOR TOTAL WAX FROM SHALE OIL

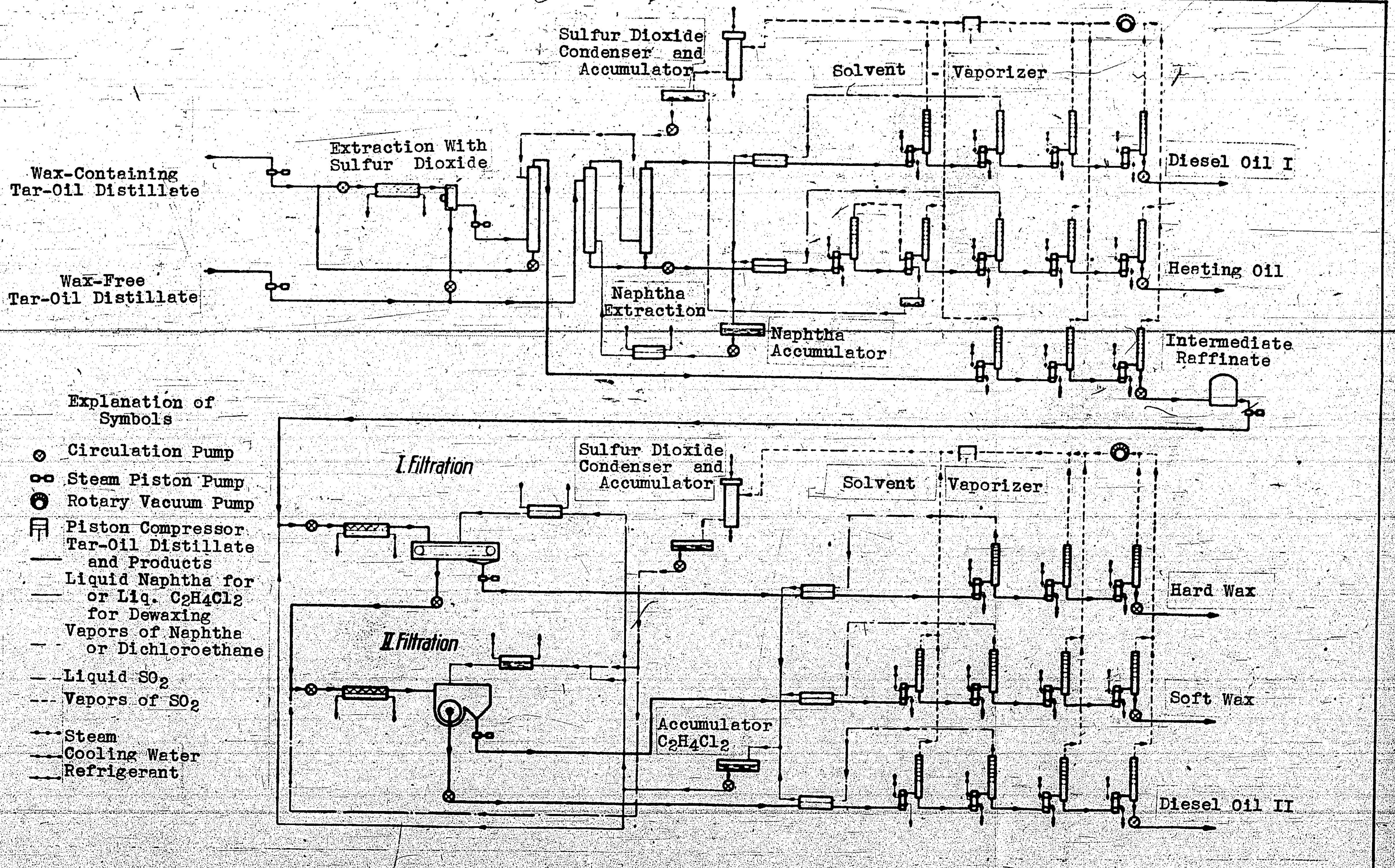


Fig. 16 FLOW SHEET FOR A TAR SEPARATION PLANT ACCORDING TO THE EDELEANU PROCESS

stages. This SO_2 raffinate is accumulated in a tank and is passed from there to the de-waxing step.

The extract solution from the centrifuge, which is the final extract of the SO_2 extraction, is passed at the centrifuging temperature and without separation of the SO_2 in admixture with the wax-free middle oil fraction to the naphtha wash. The mixture flows counter-current to naphtha from top to bottom in an extraction tower at -10° C. The desired naphtha-containing raffinate solution is discharged from the top of the tower and is subjected to an after-washing in a second tower with SO_2 to remove the last traces of creosote. This raffinate from the naphtha wash, containing the components of Diesel Oil I, is passed to a vaporization plant. It is first heated in a pre-heater in heat-exchange with condensing naphtha vapors, and then freed from SO_2 and naphtha in four stages.

The extracts from the naphtha wash obtained from the two extraction towers, and containing a small amount of naphtha and a lot of SO_2, are combined and treated to remove naphtha and SO_2 in a manner similar to that just described for the raffinate, except that five stages are used. It is worthy of note that the SO_2-vapors produced in the first vaporization are used to heat the second condenser-pressure vaporizer. The extract, freed from solvent, is a finished heating oil.

Each of the vaporization plants for the raffinate has a condenser-pressure vaporizer, while on the other hand, the vaporization plant for the extract has a high-pressure vaporizer and a condenser-pressure vaporizer. The naphtha is vaporized from the naphtha-containing solution in the subsequent vaporizer and, utilizing its heat of condensation and a part of its sensible heat for heating, it is condensed in a preheater and collected in a naphtha accumulator from which it is recycled to the process. Then follows the low-pressure SO_2 vaporizer, from which the SO_2 vapors are brought to the condenser pressure by means of a compressor and also the SO_2 vapors from the vacuum vaporizer are brought to the condenser pressure by a rotary vacuum pump and a compressor. These SO_2 vapors are liquified in the condenser and collected in an SO_2 accumulator for re-use in the process.

The wax-containing SO_2 raffinate which has been obtained from the SO_2 extraction and collected in an accumulator is passed to a de-waxing plant, diluted with dichloroethane, and cooled to the filtration temperature for hard wax in a scraper chiller. The separation of the hard wax takes place in a specially-designed continuous band filter in which the filter cake is washed free from oil with pure solvent.*

* See discussion starting on page 11 of this report. JPJ.

The hard wax so obtained is freed from dichloroethane in a three-stage vaporization plant. The filtrate solution passed from the continuous band filter contains a small amount of liquid SO_2 and is passed through a low-temperature cooler to a drum filter in which the separation of the soft wax is effected at about -20° C. As a washing liquid is used the cold solvent mixture having a similar composition; the used washing liquid goes back into service for dilution of the SO_2 raffinate. The soft wax is passed to a four-stage vaporization plant in which it is freed from the solvent. The wax-free filtrate solution flowing from the drum filter is also freed from solvent in a four-stage vaporization plant and is the final Diesel oil II.

The vaporization of the mixture of dichloroethane and SO_2 takes place in a manner analogous to that used for the mixture of haphtha and SO_2 in the extraction part of the process.

The products which are discharged from the process are submitted to an after treatment, with the exception of the heating oil. The Diesel oil components and the soft wax are clay-treated and the hard wax is treated with sulfuric acid, and subsequently with clay in order to give it a white color.

The following tables present the results and yield data from treatment of L-T.C. tar and of shale oil.

In Fig. 17 is presented the process for separating an L-T.C. tar from a brown coal obtained from central Germany. The raw tar, consisting of tar from the precooler, tar from the electric precipitator and middle oil is subjected to a two-stage distillation, at atmospheric pressure and under vacuum, and separated into a small amount of naphtha and water, a **wax-free middle oil fraction, a wax-containing fraction**, and a distillate residue. The wax-containing fraction is subjected to a redistillation in order to produce a white hard wax. The two distillation residues - from the first distillation and from the redistillation - are coked to produce electrode coke, and the resulting cracked oil, which contains colored material, is mixed with the raw tar prior to the initial distillation.

The wax-free and the wax-containing fractions are separated by means of selective solvents into Diesel oil, heating oil, hard wax and soft wax, as already discussed.

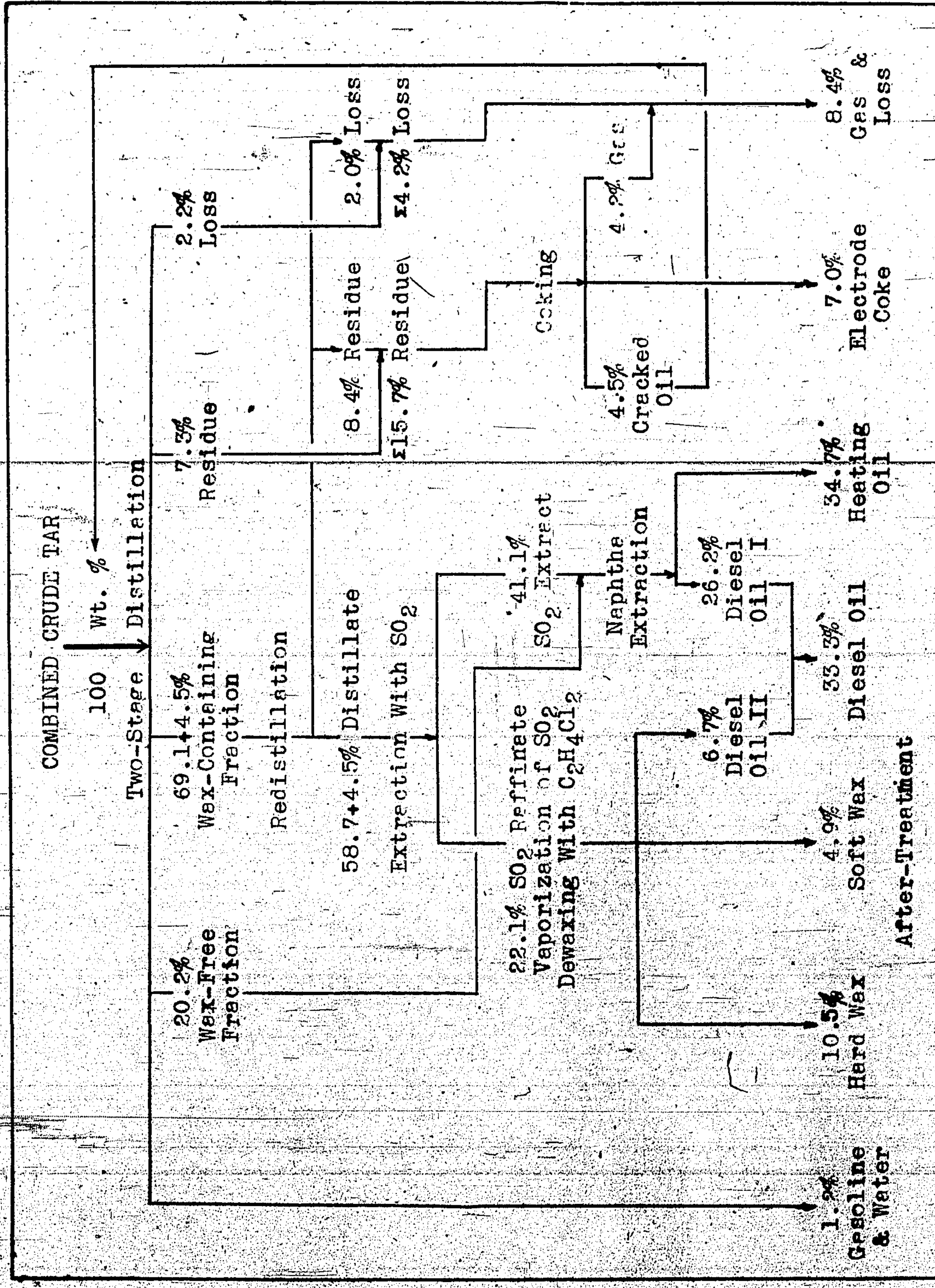


Fig. 17 SEPARATION OF TAR, FROM LOW-TEMPERATURE CARBONIZATION OF BROWN COAL, BY DISTILLATION AND TREATMENT WITH SELECTIVE SOLVENTS

By this procedure, the following products are obtained from 100 kgs of combined crude tar:

Naphtha and water	1.2 kg.
Hard Wax	10.5 kg.
Soft Wax	4.9 kg.
Diesel Oil	33.3 kg.
Heating Oil	34.7 kg.
Electrode Coke	7.0 kg.
Gas and Loss	8.4 kg.
	100.0 kg.

TREATMENT OF SHALE OIL

A similar treatment of shale oil is shown in Fig. 18. In this instance, a shale oil has been obtained from the Puertollano oil shale in Spain, which has been quite thoroughly investigated; however, the treatment discussed herein is basically the same for L-T.C. tar from oil shale from other sources.

The combined crude shale oil is also subjected to a two-stage distillation; the resulting distillate can be treated more easily than the L-T.C. tar distillate produced from brown coal. The method of treatment has already been discussed.

The Diesel oil obtained by distillation is a very good Diesel oil, judging by its pour point and its other properties. Only the principal fraction of 68.5% by weight is treated with liquid sulfur dioxide whereby it is separated into about equal amounts of raffinate and extract, and the results of experiments on this material agree completely with the conclusions deduced from the tie-lines of the graphical presentation. The filtrate produced by de-waxing the raffinate contains Diesel oils and lubricating oils of various viscosities ranging from spindle oil to aviation lubricating oil. This recovery of such lubricating oils is the principal difference as contrasted with treatment of L-T.C. tar from brown coal. The automotive lubricating oil has a viscosity of 12° E. at 50° C. and can be further separated into two parts of an oil having a viscosity of 6° E. at 50° C. and one part of an oil having a viscosity of 18° E. at 50° C.

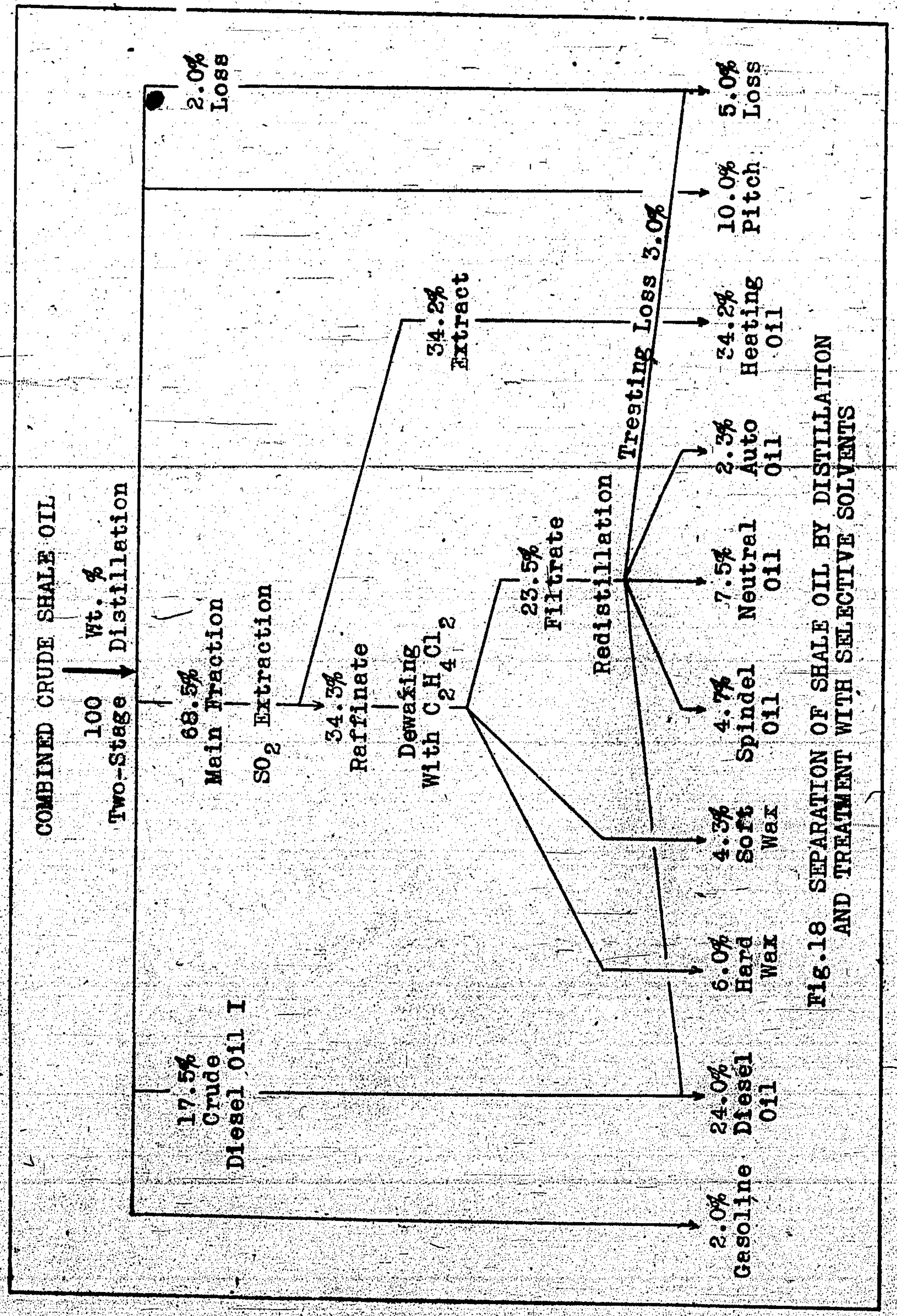


Fig.18 SEPARATION OF SHALE OIL BY DISTILLATION AND TREATMENT WITH SELECTIVE SOLVENTS

The following table gives an indication of the products which are obtained from the combined crude shale oil:

Naphtha	2.0% by wt
Diesel oil	24.0
Hard wax	6.0
Soft wax	4.3
Spindle oil	4.7
Neutral oil	7.5
Automobile Lub. oil.	2.25
Heating oil	34.20
Pitch	10.0
Combined Loss	5.05
	100.00% by wt.

NUMERICAL RESULTS FROM THE SEPARATION OF VARIOUS CRUDE TARS PRODUCED BY LOW-TEMPERATURE CARBONIZATION OF BROWN COAL AND PROPERTIES OF THE DIESEL OILS AND HEATING OILS SO PRODUCED.

Table 4 shows the results obtained from the treatment of L-T.C. tar from brown coals produced in various districts of Germany.

As is shown in the first column, there are some such tars from central Germany which produce up to 50% and more Diesel oil and correspondingly smaller amounts of heating oil, but there are only a few sources of brown coal which give such an L-T.C. tar; the heating oil obtained from tar No. I could be still further refined whereby the yield of Diesel oil would be greater and the density of the heating oil so obtained would be above 1.0. In general, it should be said that the distillation portion of this separation of the crude L-T.C. tar was carried out in experimental apparatus which, in comparison with commercial installations, led to high distillation loss and also to high values for the amount of distillation residue. As comparisons with commercial installations showed, better results could be expected in commerical practice.

Just a few more words should be added relative to the properties of the products obtained by these various procedures for separating L-T.C. tar.

TABLE 4.

Crude Tar Separated Into	Tars From Central Germany I	II	III	IV	Hessian District	Sudeten District	Tar From Pressure Gasification
Gasoline	2.0	2.5	1.5	1.8	2.7	1.5	(topped)
Hard Wax	11.5	7.7	12.3	14.0	7.6	3.5	5.9
Soft Wax		6.0	6.4	6.8	3.6	2.0	
Diesel Oil	47.6	36.5	29.2	32.7	29.8	25.1	19.2
Heating Oil	17.4	24.3	34.0	30.0	39.8	33.9	63.4
Residue	16.5	18.0	12.6	10.2	10.1	27.7	9.4
Dist. Loss.	5.0	5.0	4.0	4.5	6.4	6.3	2.1

According to the schematic procedure, two Diesel oil components are obtained, one from de-oiling the SO_2 raffinate and the other from naphtha washing the SO_2 extract. The first produces a material with a cetene number between 60 and 75, according to the nature of the tar distillate which is available for treatment. A cetene number for the Diesel oil obtained from the naphtha wash is lower and lies between 35 and 45. The cetene number of the mixture of these two components averages between 48 and 55 for L-T.C. tars from central Germany, and about 40 for tars from the Sudeten district. The average density (D_{70}) of the mixtures of Diesel oil lie between 0.800 and 0.850, and the viscosities at 20° C. at less than 2° E. The selective separation can be so conducted that a greater total yield of a Diesel oil having a viscosity of 4° E. at 20° C. can be obtained. The upper heating value of these Diesel oils lies between 10,600 and 10,800, and the lower heating value is about 10,000 Kcal/kg. The specifications which were set by the Reichs Department of Commerce and by the Army and Navy General Staffs were met in all details.

Table 5 brings together data on the finished Deisel oils produced from L-T.C. tar produced from the various brown coals listed in Table 4.

The heating oil produced by our methods of working could be used as naval fuel oil and corresponds to the specifications set for such material. Most important: it should be noted that the density lies above 1, and the lower heating value was never below 8500 Kcal/kg. The coking number lies between 1.4 and 2.5 and always remains under the stipulated maximum value of 3.0.

The pour point can be lowered to below -20° C. without any difficulty, although a pour point of 0° C. was stipulated. The creosote content depended upon the creosote content of the charge stock; a decrease in the creosote content of the finished heating oil was not stipulated in the specifications which has been set.

Conclusions.

It should not be supposed that the separation process which has been discussed was carried out on a commercial scale without any difficulties. Not only are tars produced by the low-temperature carbonization of brown coal very

TABLE 5.

	L-T.C. Tars From Central Germany				Hessian District	Sudeten District	Tar From Pressure Gasification
	I	II	III	IV			
D_{70}	0.815	0.837	0.857	0.868	0.840	0.876	0.845
Viscosity °E/20	1.7	1.57	1.71	2.07	1.6	2.0	1.64
Pour Point ° C	-15	-17	-16	-21	-18	-22	-10
Creosote Content	<0.5	0	0.5	0	0.5	—	—
Cetane Number	58	55	55	48	46.5	40	50
Upper Heating Value kcal/kg.	10 800	10 580	10 640	-	10 690	10 100	—
Corresponding Heating Oils							
D_{70}	0.996	1.030	1.025	1.029	1.006	1.039	1.020
Viscosity °E/50	3.5	2.57	3.1	3.18	1.97	5.67	1.85
Pour Point °C	-25	-25	-27	<-25	-20	-13	<-30
Creosote Content	29	50	36	28	55	34	53
Lower Heating Value kcal/kg.	8 750	8 560	8 600	8 700	8 580	8 660	—

different from natural petroleums, but they also differ among themselves very much. In addition, they often show a great sensitivity to the oxygen of the air which can cause precipitation of material.

These difficulties were overcome as they arose. The SO_2 raffinate as produced today is a very light-colored product and is quite easy to de-wax. The heating oil, in which the total creosote becomes concentrated and which amounts to 30-60% of the final extract, depending upon the creosote content of the charge stock, is especially stable and is miscible in all proportions with other heating oils. The properties correspond to the specifications made by the Navy. The only new apparatus which was used was the closed continuous band filter which was a completely new development. Here also there were great difficulties at first in commercial practice, but these were overcome by cooperation with the builder of this equipment, the Maschinenfabrik Buckau R. Wolf A.G. which, earlier, had also developed the drum filter with us.

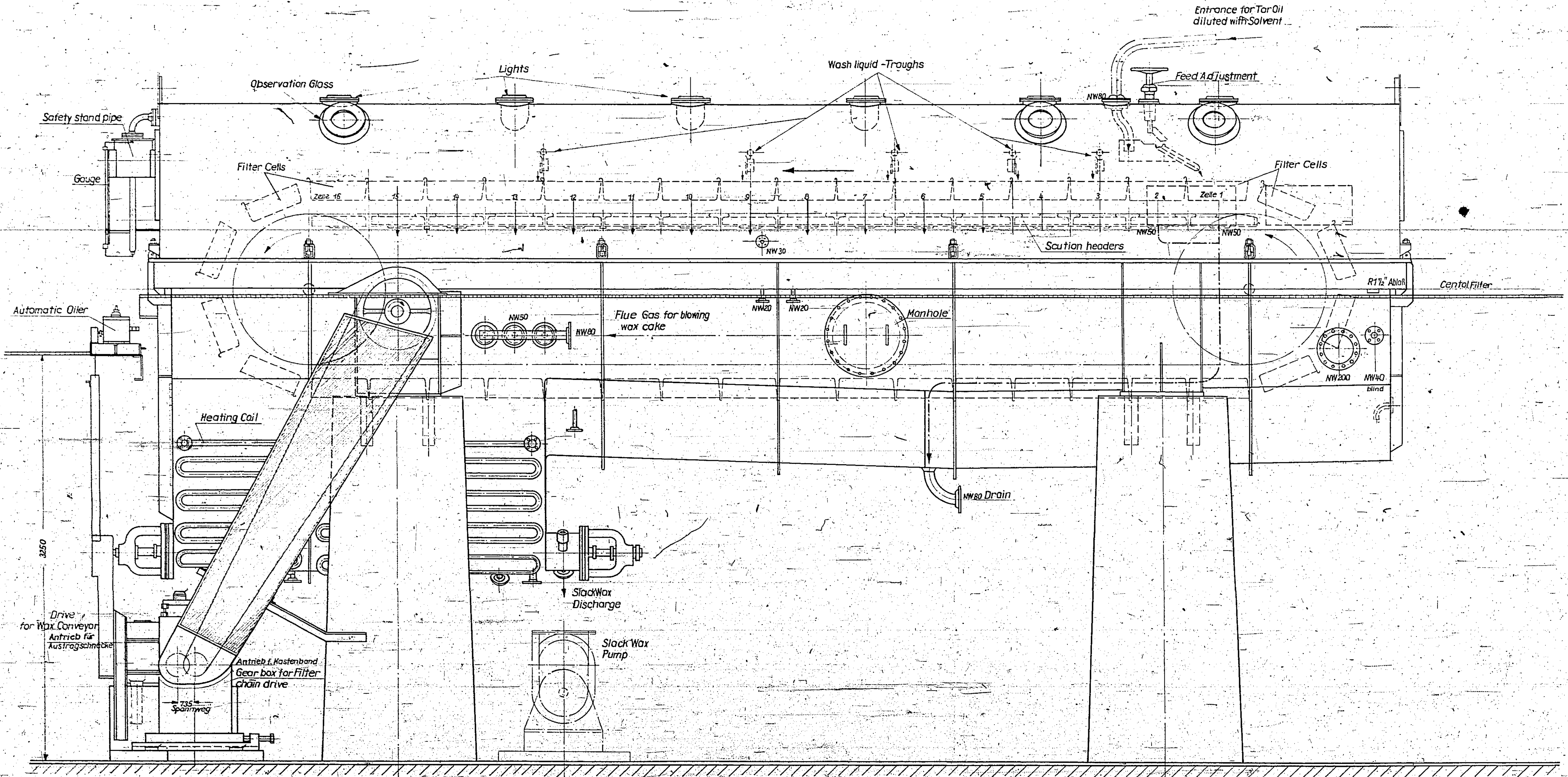
Today, the filtration by use of the continuous band filter is the most striking part of the whole apparatus and operates almost entirely without any further difficulties.

The wax, especially the hard wax, is obtained in a particularly oil-free state and in higher yields than was possible by previous methods of operation; in spite of this, however, it is fully comparable, in all its properties, with the material formerly obtained, and particularly is it possible to secure a good color by the use of appreciably smaller amounts of sulfuric acid and clay in the after-treatment. Specifications as to melting points can be varied quite widely and any demands made by consumers for special products can be easily satisfied.

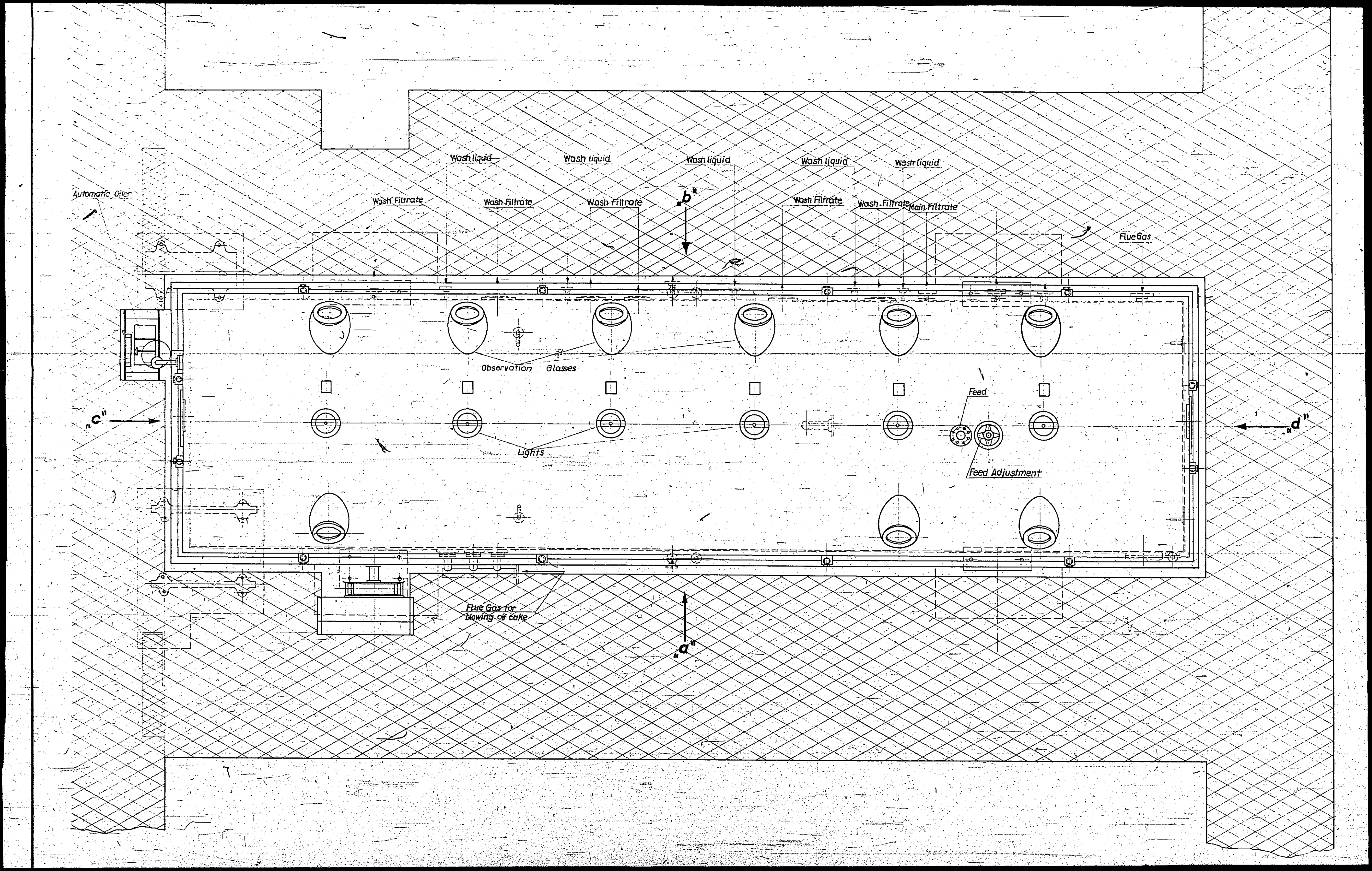
This brings the presentation to an end. I have tried to give a resume of the fully-developed subject of refining with selective solvents, and especially the separation of tar produced by low-temperature carbonization. It was not possible to select less background material without running the risk of overlooking important points.

This work and development was a cooperative project of the major part of the chemical and technical staff of Edeleanu. It is impossible to mention the names of all who contributed, but mention should be made of Dr. Karl Fischer for the chemical part, and Dipl. Ing. Alfred Hoppe for the technical part. The Deutsche Erdöl A.G. erected a large pilot plant at their Rositz works, capable of treating 50 tons/day and the completion of the research was greatly aided by the results obtained in this pilot plant; all interested parties are hereby thanked for their help and cooperation.

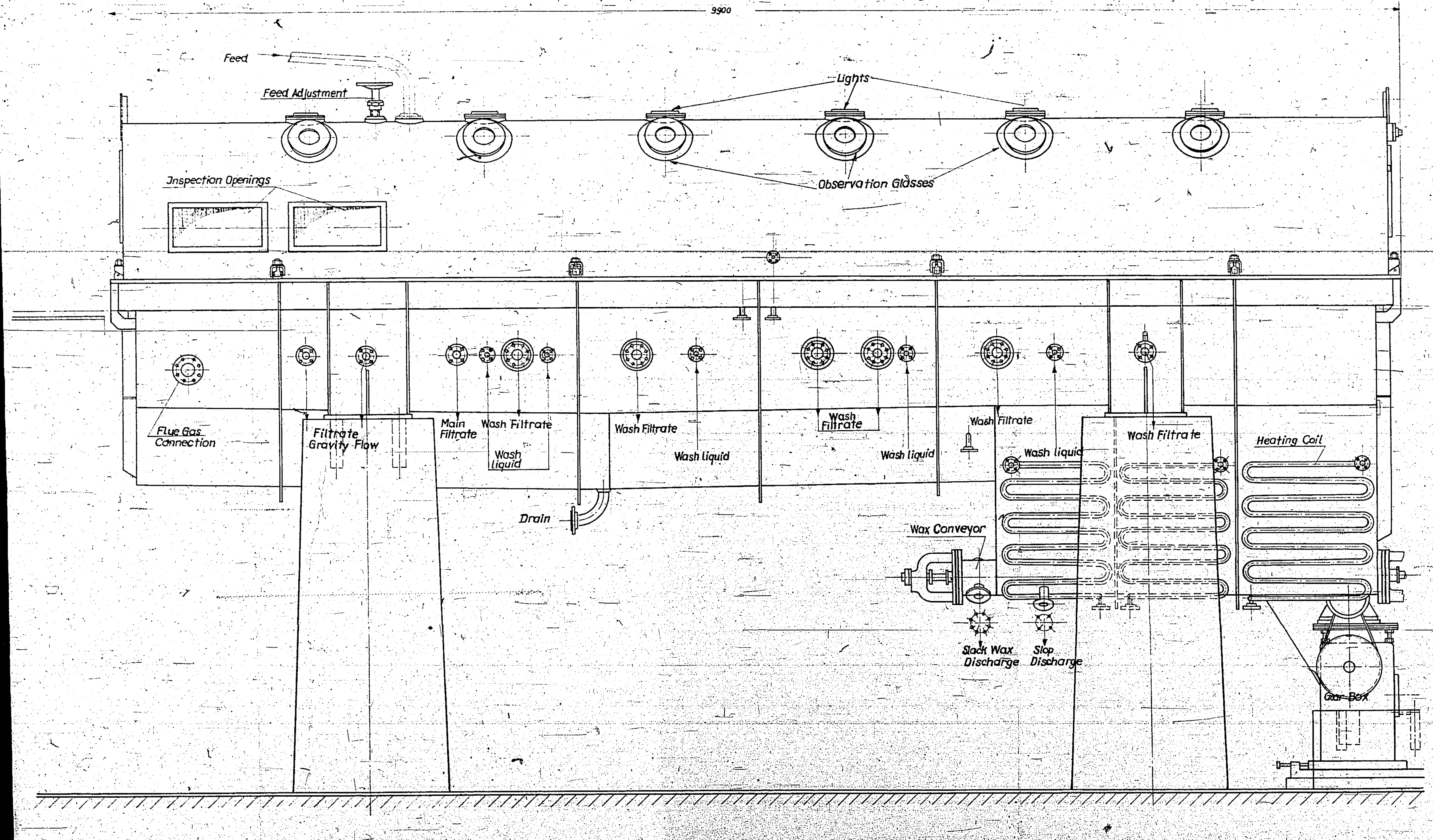
Ansicht „a"

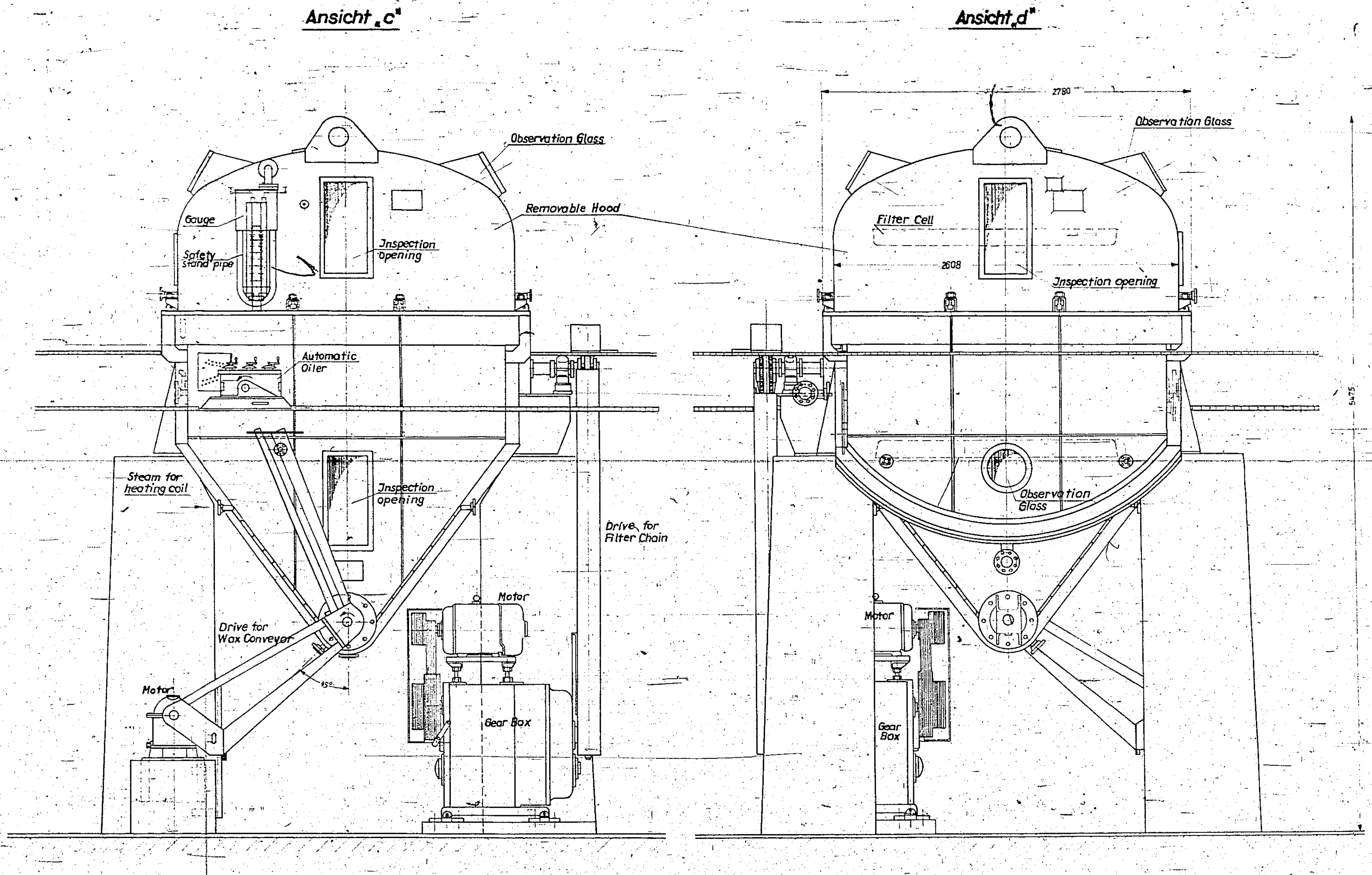


Entrance for Tar Oil diluted with Solvent
Observation Glass
Lights
Wash liquid -Troughs
Feed Adjustment
NW80
Safety stand pipe
Gauge
Filter Cells
Zelle 16
15
14
13
12
11
10
9
8
7
6
5
4
3
2
Zelle 1
Filter Cells
NW50
NW50
NW 30
Scution headers
R1½" Ablaß
Centol Filter
Automatic Oiler
NW50
NW80
Flue Gas for blowing wax cake
NW20
NW20
Manhole
NW200
NW40 blind
Heating Coil
NW80 Drain
3250
Slack Wax Discharge
Drive for Wax Conveyor
Antrieb für Austragschnecke
Antrieb f. Kastenband
Gear box for Filter chain drive
735 Spannweg
Slack Wax Pump


Wash liquid
Wash liquid
Wash liquid
Wash liquid
Wash liquid
Automatic Oiler
Wash Filtrate
Wash Filtrate
Wash Filtrate
„b"
Wash Filtrate
Wash Filtrate
Main Filtrate
Flue Gas
Observation Glasses
Feed
„c"
„d"
Lights
Feed Adjustment
Flue Gas for blowing off cake
„a"

Ansicht „b"

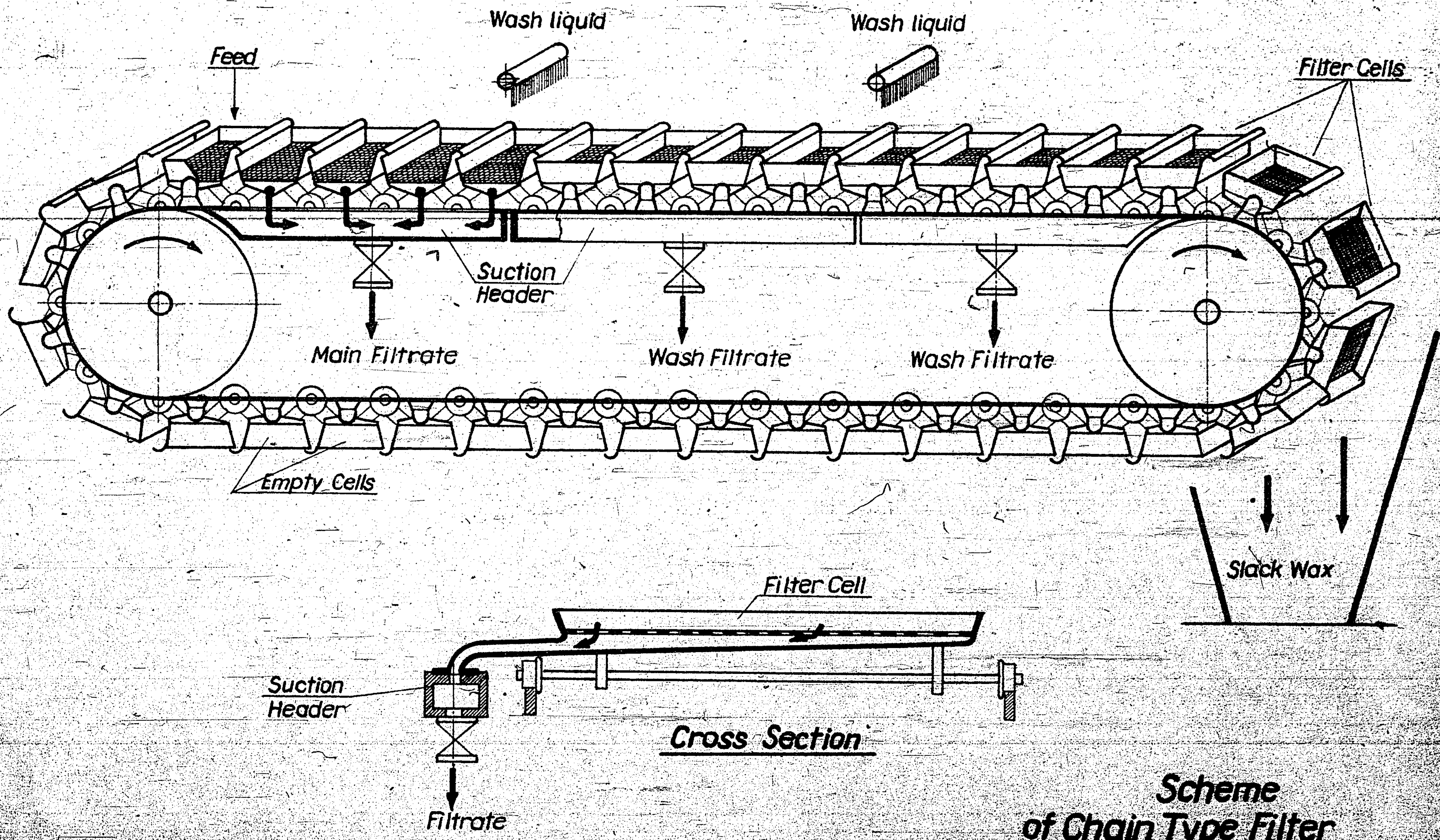

9900
Feed
Feed Adjustment
Lights
Observation Glasses
Inspection Openings
Flue Gas Connection
Filtrate Gravity Flow
Main Filtrate
Wash Filtrate
Wash liquid
Wash Filtrate
Wash liquid
Drain
Wash Filtrate
Wash liquid
Wash Filtrate
Wash liquid
Wash Filtrate
Heating Coil
Wax Conveyor
Slack Wax Discharge
Slop Discharge
Gear Box



	Tag	Name	Edeleanu Gesellschaft m.b.H. Berlin	
Entworfen Gezeichnet Geprüft	 18. 1. 46			
Maßstab 1:20			R.Wolf Bandzellenfilter 1,8 m breit mit 40 Zellen, je 0,78 m²	AS. 12450 10-10690

Chain Type Cellular Filter

Scale: 1:20



Scheme of Chain Type Filter

30.1.46. Kr

Edeleanu-Ges. m.b.H.
Berlin-Schöneberg
Martin-Lutherstr. 61-68

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ITEM No. 30
FILE No. XXX—12

Classification Cancelled,
by authority of
The Joint Chiefs of Staff,
by Col. E. W. Gruhn.

COPY No. 188

RESTRICTED

SCHAUMKOHLE
AND
DR. HEINRICH SCHMITT-WERKE K.G.

Jones
Taylor
Williams

RESTRICTED

COMBINED INTELLIGENCE OBJECTIVES
SUB-COMMITTEE

RESTRICTED

SCHAUMKOHLE (FOAM - COAL)

and

DR. HEINRICH SCHMITT - WERKE, K.G.

7 - 11 July 1945

Reported by

J.P. JONES, U.S.A.
R.A.A. TAYLOR, British
F.A. WILLIAMS, British

on behalf of

British Ministry of Fuel and Power

and

U.S. Technical Industrial Intelligence Committee

15 August 1945

CIOS Target Nos. 30/220 & 30/221
Fuels and Lubricants

COMBINED INTELLIGENCE OBJECTIVES SUB-COMMITTEE
G-2 Division, SHAEF (Rear) APO 413

RESTRICTED

8 p.

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Personnel of Investigating Team

D.S.Fraser) U.S.Petroleum Administration
J.P.Jones) for War

R.A.A.Taylor)British Ministry of Fuel
F.A.Williams) and Power

Schaumkohle (Foam - Coal)
and
Dr.Heinrich Schmitt - Werke,K.G.

Introduction:

Dr.Heinrich Schmitt is a German physical chemist who has specialized in making products from synthetic resins for about the last 15 years. In 1939 he formed the firm of Dr. Heinrich Schmitt - Werke, K.G., and a subsidiary company, Dr.Heinrich Schmitt, G.m.b.H., to exploit his inventions in this field. These involved primarily production of a frame for portable typewriters by injection molding and producing articles from resin-impregnated wood. During the war the firm had worked on making driving-bands for using small calibre shells in guns of larger calibre, with appreciable success. Starting in October, 1944, H.Schmitt had worked on the development of "schaumkohle"(foam coal)which is a porous mass of granular coal cemented with phenolic resin. The investigating team was interested primarily in this last development.

Two brothers of Heinrich Schmitt, Dr.Ludwig Schmitt (primarily a mathematician and physicist) and Dir.Julius Schmitt (a director of his brother's firm, and primarily a salesman with little technical knowledge), were interrogated at Berchtesgaden, Germany, on 7 to 9 July, 1945, where they were living with their families (and the family of Dr.Heinrich Schmitt) at Haus Göhlstein. Dr.Heinrich Schmitt was interrogated at the Seventh Army Interrogation Center, Augsburg (Bavaria), Germany, on 10 and 11 July, 1945.Werner Fleck, an engineer recently in charge of a drawing office for Skoda at Prague, concerned with the planning and development of fighter aircraft (and an associate of a Dr.Sänger, who is a specialist in this line) was also interrogated just outside of Berchtesgaden on 7 July 1945, with respect to experiments on the use of Schaumkohle for jet propulsion.

The two Schmitt brothers in Berchtesgaden stated that they had been interrogated on June 6, 1945 by Lt. Col. Griffen and Peer of the Intelligence Corps and on June 12, 1945 by Capt.Stratford and Dr.Porter. A report (16 pages) prepared for the first interrogators contained extravagant claims but no factual information, and the information contained in the present report was obtained by requiring a factual report and by subsequent interrogation.

Preparation of Schaumkohle:

Since schaumkohle has not been produced commercially, but only on a relatively small experimental scale, only general statements could be obtained with respect to its manufacture. As raw material there may be used anthracite, bituminous coal, brown coal or coke, or waste coal or fines from spoil-tips at coal mines. Experiments had been made with Ostrau coal (a young bituminous coal from Bohemia), Kladno brown coal (sudetenland), bituminous coal coke, and coke breeze from a variety of mixed coals from the gas works at Heidenau, near Dresden, Saxony. Preferably, granules having a diameter raning from about 0.5 to about 2.5 mm. are used. As a cementing material, it is preferred to use a water-soluble phenolic resin which hardens at a temperature of 160 to 200°C., in an amount between about 4 to 10% of the coal. Resins which have been used are phenol and cresol resins such as Neoresit of the Nowack A.G.in Bautzen, Saxony, and those produced by Abbert and Co. in Biebrich, near Wiesbaden. If it is necessary to reduce the viscosity of the resin solution to make it workable, enough water, or other suitable solvent is added to give a suitable solution.

The indicated preferred manner of manufacture is to add the resin solution to the stirred granular mass until the proper amount has been added. The resulting material is then molded in any suitable manner, no great pressure being needed other than to assure absence of large voids. The molded material is then dried at about 100°C. until most of the water is vaporized (both the water in the resin solution and that in the original coal particles)..

This results in the formation of a porous structure.The temperature is finally raised to a maximum of about 160 to 200°C., so that the resin is irreversibly hardened. The apparent specific gravity of the resulting product was in the range of about 0.4 to 1.2.

The resin used is the cementing and binding agent, and the procedure of manufacture is such that a porous mass results, with the resin concentrated primarily where the edges and corners of the granules touch each other. A highly porous coal is generally unsatisfactory as a raw material because the individual granules absorb too much resin. An amount of resin in the upper part of the indicated range must be used with the small coal granules. It was stated that an undesirable product resulted:

(a) If too much resin is used.

(b) If instead of resin another substance that does not properly harden irreversibly is used; for example, water-glass, cerinol (a quick-hardening binder for cement) sulphite liquor, oils, or pitch, etc.

(c) When a substance is chosen that hardens before the water is evaporated.

(d) If chemicals are admixed that decompose the above hardening material.

(e) If the coal is tamped and pressed too hard into the mould.

For some uses it was found desirable to incorporate a combustion promoting chemical in the schaumkohle. About 1% of iron oxide was stated to be one of the best of such materials, although a similar amount of calcium carbonates, or other calcium salt, appeared to be almost as good. For very rapid combustion, or ready ignition, about 1 to 3% of an oxidizing agent such as potassium nitrate or perchlorate, or powered sulfur, could be used.

It was alleged that various catalysts for reactions other than those of combustion could also be included (i.e. for hydrogenation) but there was no experimental background for this. Brief details of preparation were stated to be in German patent applications SCH 130,110,IVc/39b, filed November 18, 1944, and SCH 130,279,IVc/39b, filed December 28, 1944. These patent applications also include information on using solid granules of other materials to form "foamed" bodies.

It was alleged that no cost estimates relative to schaumkohle had been made. However, it can be readily seen that the use of even 4% of a phenolic resin would result in a relatively expensive fuel, in addition to labor costs.

Uses of Schaumkohle:

Schaumkohle had been considered for use as a fuel in gas-producers for automobiles and as a propellant for rockets and jet propulsion. It was more or less porous, depending upon the size of the original coal particles, and air or other gas can be passed through a molded body of it.

A. For Gas Producers:

Three experimental runs had been made in a "Zeuch" gas producer, where blocks of schaumkohle replaced the brown coal briquets normally used. The greater reactivity of the schaumkohle resulted in a higher temperature and the grates were burned out. It was claimed, however, that operation was satisfactory otherwise and that a somewhat increased amount of producer gas was available when the vehicle was operating under increased load. Heinrich Schmitt also alleged that the tubes filled with schaumkohle described on page 6 were useful in gas producers. One of the claims made in connection with the use of schaumkohle for this purpose was that it provided a convenient way of handling and transporting granular coal.

However, several small samples of schaumkohle blocks, cubes about two inches on an edge, were obtained; these appeared somewhat friable and it was noted that an appreciable amount of coal granules were produced by the abrasion resulting from handling and carrying them.

B. For Jet Propulsion:

In April 1945, the Avia works near Prague, a Skoda firm, had made three preliminary experiments on the use of schaumkohle as a fuel in a jet propulsion unit, under the supervision of the previously-mentioned Werner Fleck. It was planned to suspend a hollow, cylindrical, suitably molded mass of schaumkohle in a combustion chamber of an athodyd unit; combustion was to be initiated with a liquid fuel and after the schaumkohle block was ignited, power was to be obtained from this latter fuel alone. It had been calculated that the combustion space should have a cross-sectional area 7 times the area of the inlet, and that experiments should be carried out on the basis of a forward speed (for the unit) of about 210 meters per second. Experiments were carried out in a wind tunnel with air speeds within the combustion space of about 30 meters per second. Only two such experiments were made; the maximum burning rate obtained was about 1 mm. per minute, and since it had been determined that the coal would have to burn at a rate of at least about 5 mm. per minute, in order to obtain the necessary power, the flight engineers did not think the results were encouraging. Although the Schmitt brothers made great claims as to the physical stability of their schaumkohle moldings, Fleck reported that in these tests the block disintegrated well before it had been completely consumed by combustion. However, the ash sloughed away readily and appeared to be free from unconsumed combustible material.

The ending of the war obviated any further work along this line, although a third molded block of schaumkohle had been prepared and transported to Berchtesgaden. This was a cylinder about three feet long and 20 inches in diameter, with iron reinforcement and air passages running parallel with the cylinder's axis.

Development of Schaumkohle:

According to information given by Dr.Heinrich Schmitt, he was ordered to go to Prague in October 1944 by an agent of Geilenberg and there, along with others, was commissioned to produce a material comprising a tube of resin-impregnated wood containing coal together with a sufficient amount of an oxygen carrier to be capable of furnishing all the oxygen required for combustion of the coal. None of those present was given any explanation of the ultimate use of such a material. Schmitt indicated to the team that, as a physical chemist, he thought the idea was somewhat fantastic, but he felt compelled to follow his instructions. After his workers had prepared tubes for this purpose the proposed filling material was not delivered. This circumstance, together with his earlier doubts as to the feasibility of mechanically combining coal with a sufficient amount of an oxygen carrier, led him to attempt to produce a porous mass of coal (in the tube) to which a stream of air would have ready access. His experience with phenolic resins prompted him to try them as binders for granular coal, with almost immediate success. In this manner a tube, having walls 6 mm. thick, 8 cm. in diameter, and 55 cm.long, was filled with a porous solid fuel, leaving 5 cm. unfilled at one end and 10 cm. at the other. When the coal was ignited and a stream of air passed through (counter to the course of the combustion at a rate up to 4 liters per second, under a pressure of 0.2 to 0.4 atmospheres) the entire amount of coal could be burned, without disintegrating or dispersing, and the outside of the tube would remain cool enough (sic) to be held in the hand, whereas a thin-walled metal tube would have been melted. The schaumkohle could either be formed in the rube using the same resin as was used to impregnate the wood, forming the schaumkohle and molding the wooden tube at the same time,or the tube and schaumkohle could be prepared separately. Apparently, the tube did not tend to burn through.

Driving Bands for Subcalibre Shells:

It was stated that the use of a driving band to adapt a small shell to a gun of larger calibre was covered by a French patent issued during World War I. However, when such a band is made of metal, it often flies to pieces and endangers the gun crew. Heinrich Schmitt stated that at the end of 1943, he persuaded Dr.Ing.Morhard of the Skoda works to experiment with such driving bands made from resin impregnated wood. A large number of such bands were made to adapt an 88 mm. shell to be fired from 105 mm. gun, and a considerable number of firing tests were made, with dummy shells, on the artillery ranges at Hillersleben, near Magdeburg, extending into 1945. It was claimed that the range of an 88 mm. shell could be increased from about 8 km. to about 16 km., and that the driving bands disintegrated into such fine, light pieces that there was absolutely no danger to the gun crews.

A brief statement of the preparation of these driving bands was obtained from Ludwig and Julius Schmitt. A strip of wood (preferably beech) about 0.3 to 0.5 mm. thick was soaked in an aqueous solution of a water-soluble phenolic resin, partially dried, wrapped around a suitable form, and pressed in a mold while being heated. A pressure of 200-250 kilograms per square centimeter was used, a temperature of about 140 to 150°C., and a time of about 1 minute per millimeter of thickness. The rough moldings were then machined to the proper dimensions.

The Firm of Dr.Heinrich Schmitt-Werke,K.G.:

According to a statement by Heinrich Schmitt, this firm was registered in 1939 in the Trade Register of Frankfurt-on-Main with a capital of 1,610,000 RM. The sole manager is Dr.Heinrich Schmitt with a share capital of 810,000 RM. Other shareholders are (a) Handels - u. Verkehrsbank A.G., Hamburg, share capital 250,000 RM.,with a claimed capital of approximately 700,000 RM., (b) Dr.Dimar v.Kemecke, share capital 500,000 RM.,(c) Dr.Erich Kussmann, solicitor, share capital 50,000 RM, since retired. The address of the company is Frankfurt A/M, Steinweg 9.

The company has been primarily concerned with production of typewriters from synthetic resins according to processes and designs patented by Dr.H.Schmitt with an unrestricted territory for manufacture within the framework of the company's organization. The company has claim only to the production rights. The further arrangements for manufacture have to be carried on by the subsidiary company, Dr. Heinrich Schmitt, G.m.b.H. which exercises its rights over production by a separate license. The share capital of the G.m.b.H. is 50,000 RM. of which the private company holds 50%.

As far as could be learned, the development of the driving bands and of the schaumkohle could also be considered as having been carried out by this firm.

When the documents of the Heinrich Schmitt-Werke K.G. were being examined, some that were removed seemed to have a bearing on Schaumkohle but it seemed on closer investigation that this was not so. These were chiefly progress reports of work done under what is apparently a code-name Leistungssteigerung in der Zementindustrie (increase of output in the cement industry), a title that appears to be irrelevant. The work is concerned with the production of a porous combustible material, the composition of which does not seem to suggest that the material can be a fuel per se. The purpose of the work does not seem to be revealed. The work was divided into two groups - one the Stadthagen section under Flauck, the other the Geretsried section under Crebert.

J.P.Jones

R.A.A.Taylor

F.A.Williams

Copy 1

ITEM No. 22
FILE No. XXVII-85

Classification Cancelled,
by authority of
The Joint Chiefs of Staff,
by Col. E. W. Gruhn.

COPY NO. 145

RESTRICTED

MISCELLANEOUS CHEMICALS
I.G. FARBENINDUSTRIE A.G.
LUDWIGSHAFEN AND OPPAU

Kern, Murray, Sudhoff

RESTRICTED

COMBINED INTELLIGENCE OBJECTIVES
SUB-COMMITTEE

RESTRICTED

✓I.G. FARBENINDUSTRIE A. G.

LUDWIGSHAFEN AND OPPAU AM RHEIN

MISCELLANEOUS CHEMICALS

5

19-30 June 1945

Reported by:

J.G. KERN.... CWS, Hq ETOUSA
R.L. MURRAY.. CWS, Hq ETOUSA
R.W. SUDHOFF. CWS, Hq ETOUSA

27 July 1945

CIOS Target Nos. 22/1(F) & 22/1(o)
Miscellaneous Chemicals

COMBINED INTELLIGENCE OBJECTIVES SUB-COMMITTEE
G-2 Division, SHAEF (Rear) APO 413

RESTRICTED

95 p.

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PERSONNEL OF INSPECTION TEAM

J.G. KERN	CWS,Hq ETOUSA
R.L. MURRAY	CWS,Hq ETOUSA
R.W. SUDHOFF	CWS,Hq ETOUSA

I.G. FARBENINDUSTRIE A.G.

LUDWIGSHAFEN AND OPPAU AM RHEIN

MISCELLANEOUS CHEMICALS

1. INTRODUCTION

The I.G. plants at Ludwigshafen and Oppau were visited from June 19th through June 30th. Most of the principal men were interviewed, some of them many times. In general, they were very cooperative. Their organization for handling investigators was excellent.

Both the Ludwigshafen and Oppau plants were badly damaged by more than 100 air-raids. The Ludwigshafen military government has estimated that 70% of above ground structures and equipment, and 30% of what is below ground level, have been seriously damaged. This estimate seems reasonably accurate.

At the maximum, the employees numbered 32,000. About 8,000 are working at present. Most of the plant is completely shut down, although part of the ammonia and nitric acid plants have been started up again. They are very short of coal but some is now coming in by rail from the Saar. A great deal of cleaning up and repairing is in progress.

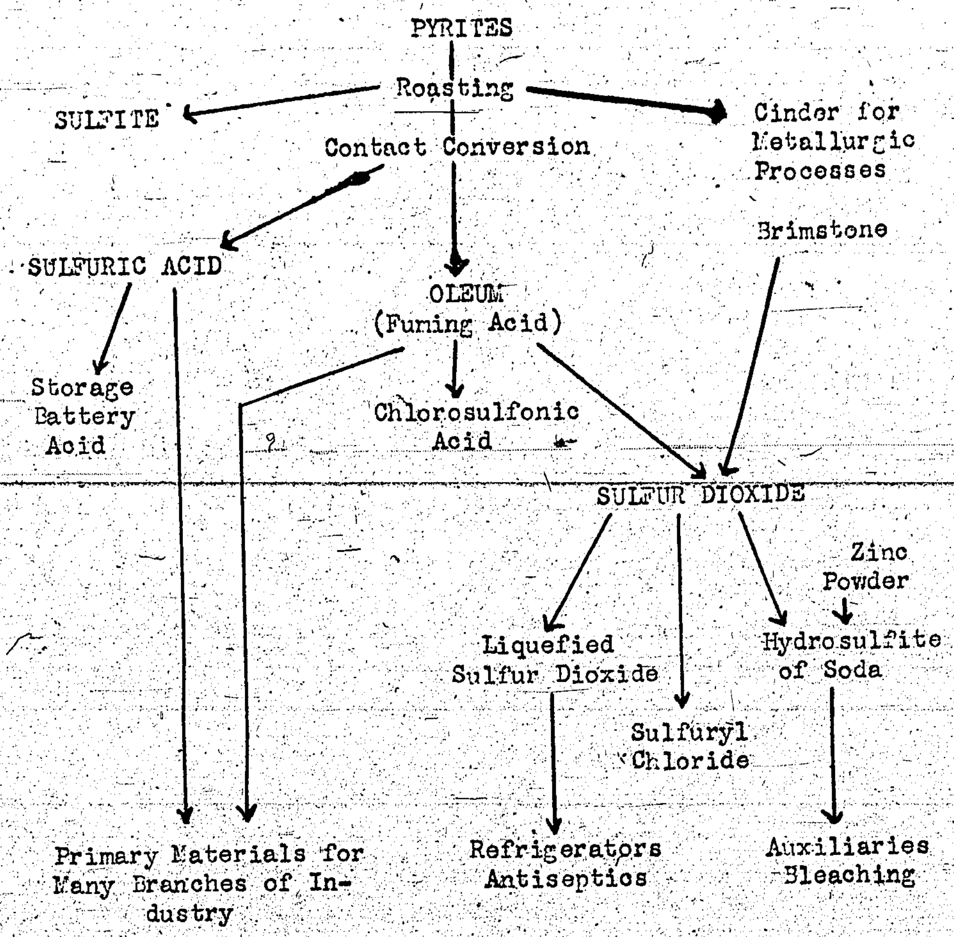
A large room on the 3rd floor of the main office building has been fixed up as an exhibit. Eighteen large charts, showing the groups of products manufactured and their derivation, are hung on the walls of this room. Copies of these charts will be found at the end of this section. Many tables are covered with samples of their products, and articles made from or with the aid of them. This was a first class exhibit and was very helpful in orienting the investigating team.

Research and developments at Ludwigshafen and Oppau have had a profound influence on the growth and activities of the I.G. and while there were newer and larger plants put up by the I.G., some of them stemmed from developments, and were due to the personnel at Ludwigshafen and Oppau. This fact made the investigation of these two plants and the interrogation of their personnel of unusual interest.

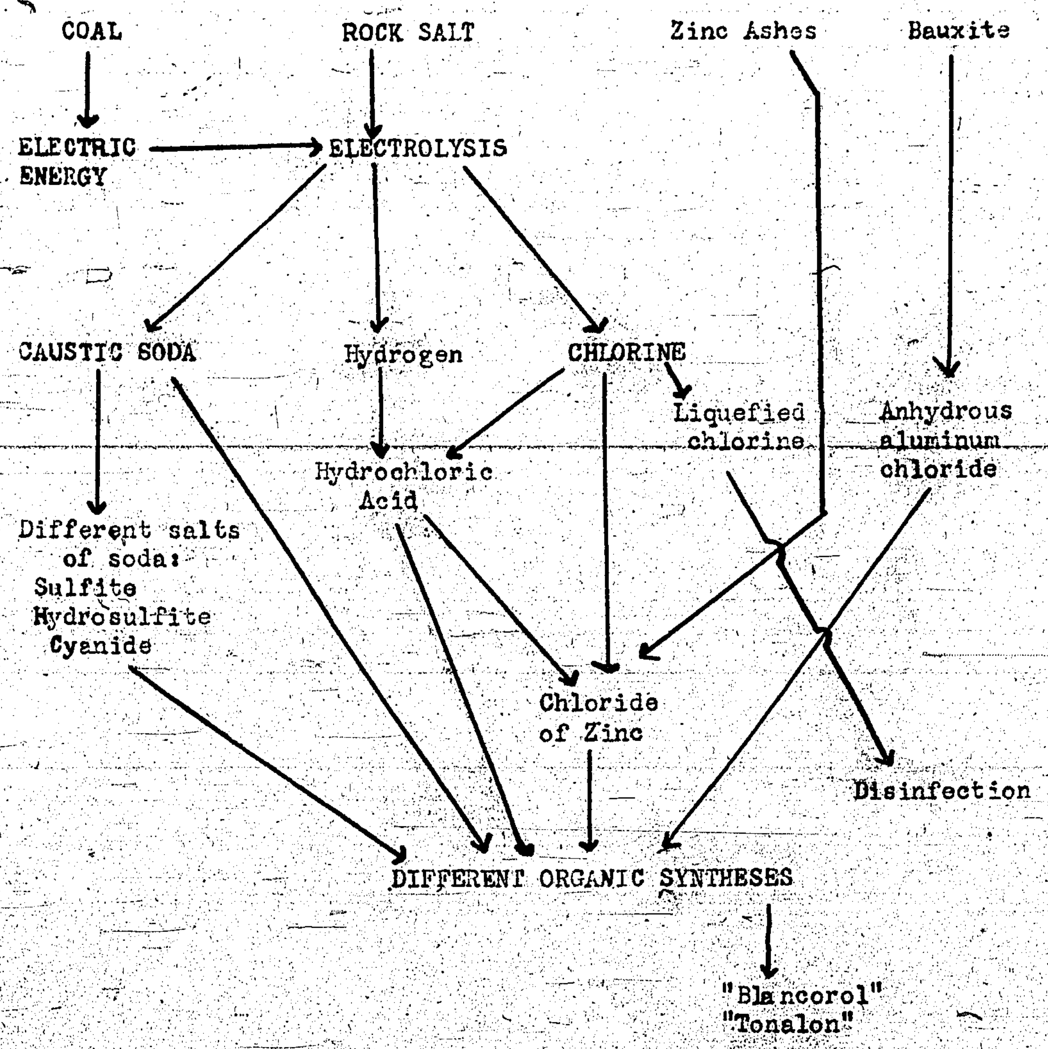
Production capacities (with the plants fully repaired) for some of the more important products of Ludwigshafen and Oppau were stated to be as follows:

	Metric tons per year
Sulfuric acid	180,000
Alcohol synthesis - methanol	43,000
butyl crude	144,000
Calcium carbide	96,000
Plastics (polystyrene - igelite - buna igamide - oppanol, etc.)	60,000
Solvents and synthetic resins	48,000
Auxiliaries	39,000
Caustic soda	34,000
Chlorine	30,000
Oil plant (crude)	30,000
Tannery agents	16,000
Paraffin oxidation	12,000
Dyestuffs (total)	9,260
Lanusa	1,200
Nitrogen (basis 100% N_2)	274,000
Calcium nitrate	120,000
Nitric acid	73,000
Sodium nitrate	37,000
Ammonium sulfate	154,000
Urea	37,000
Calnitro	330,000 to 402,000
Nitrophoska	290,000

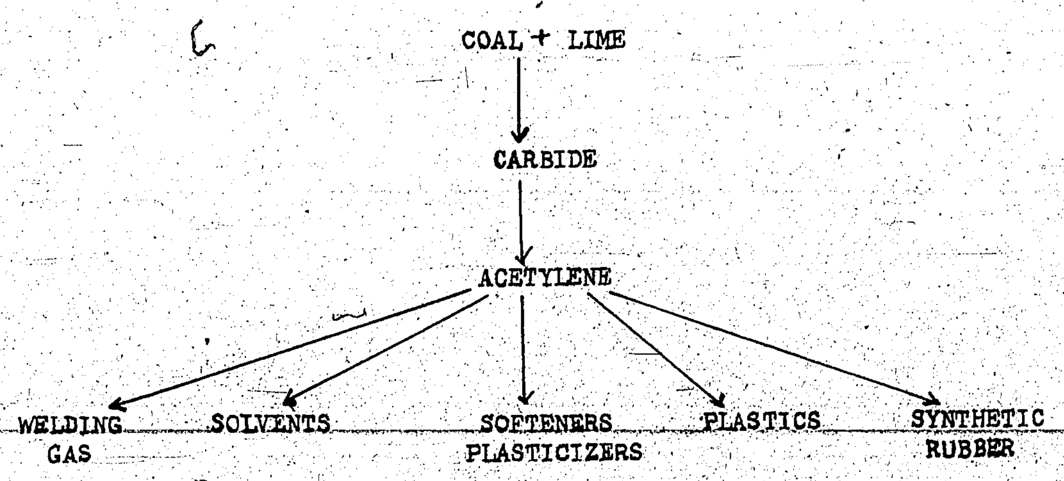
SULFURIC ACID GROUP



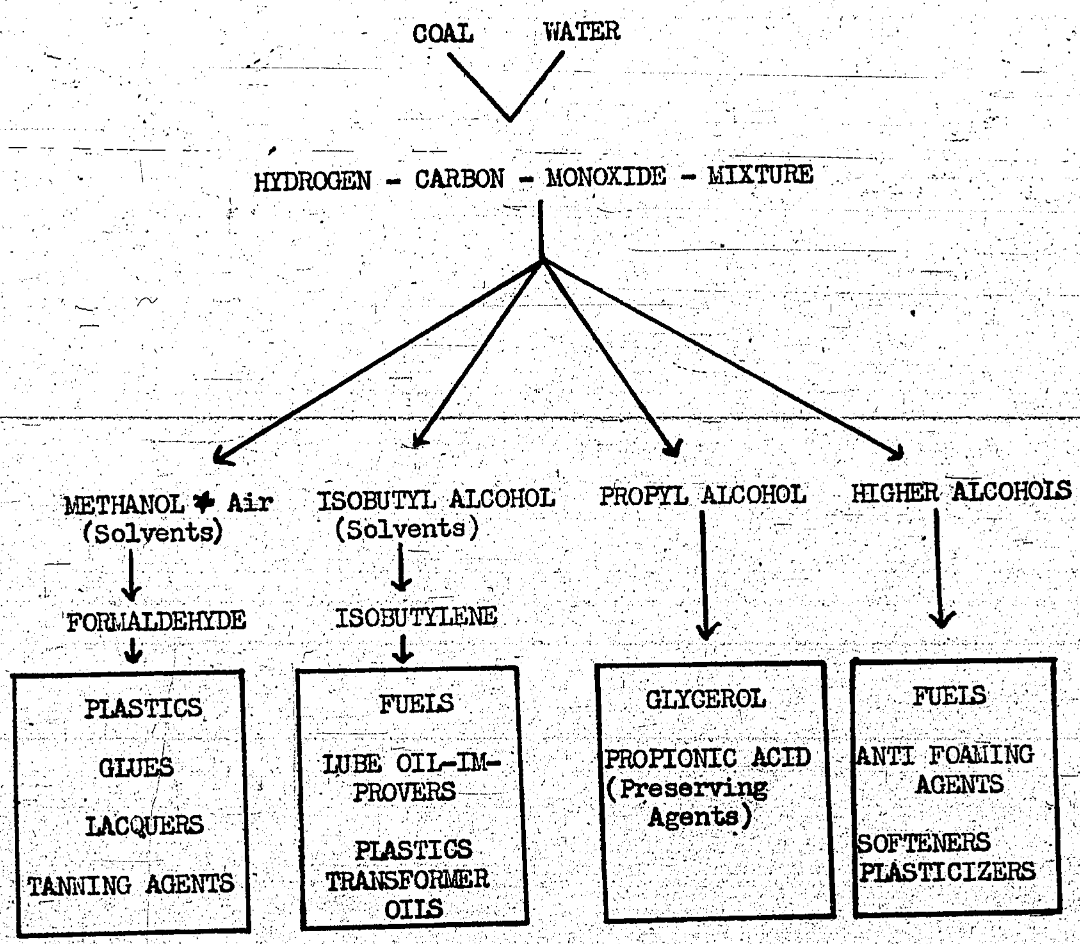
CHLORINE GROUP



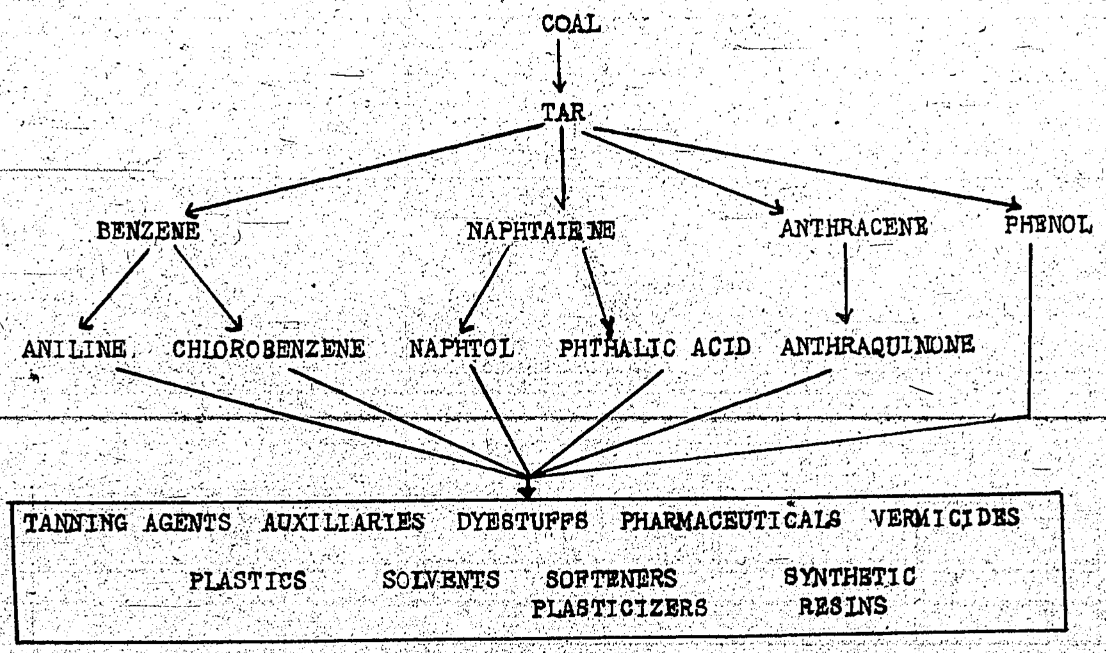
ACETYLENE CHEMISTRY



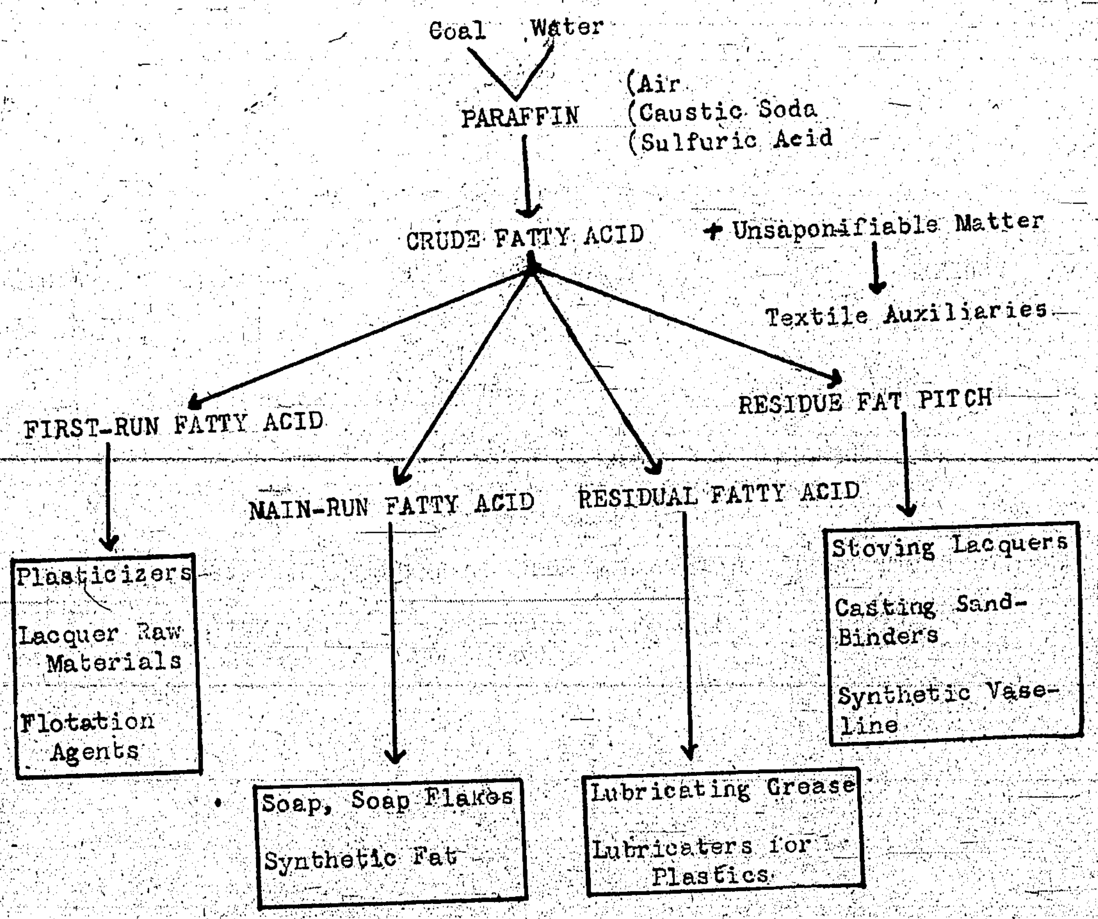
ALCOHOL SYNTHESIS



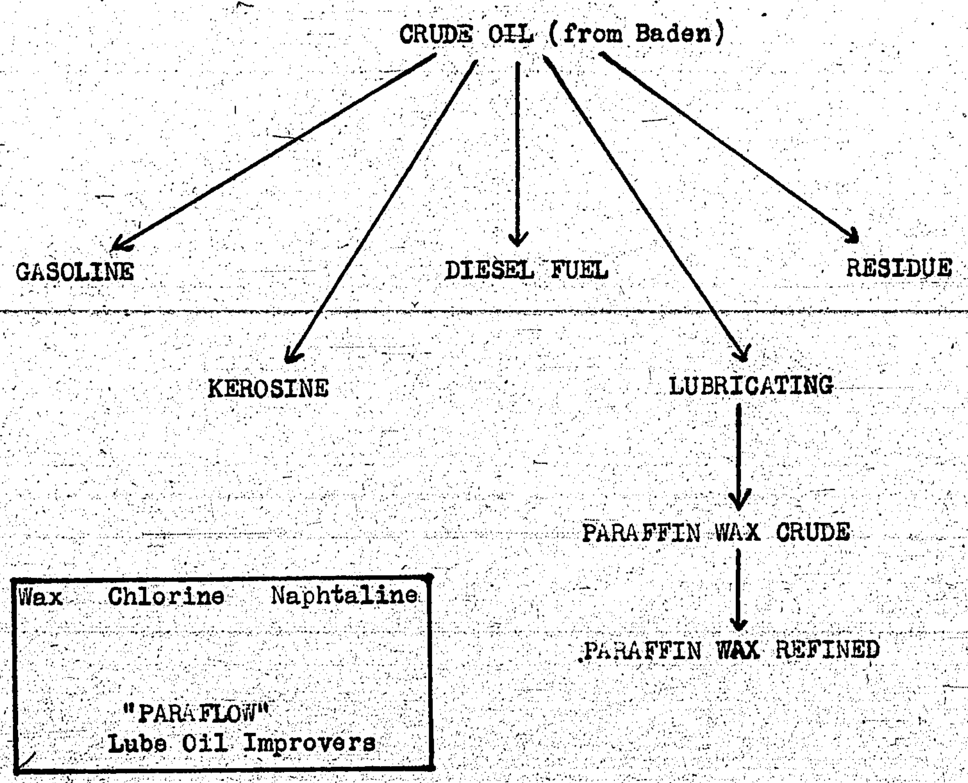
TAR CHEMISTRY



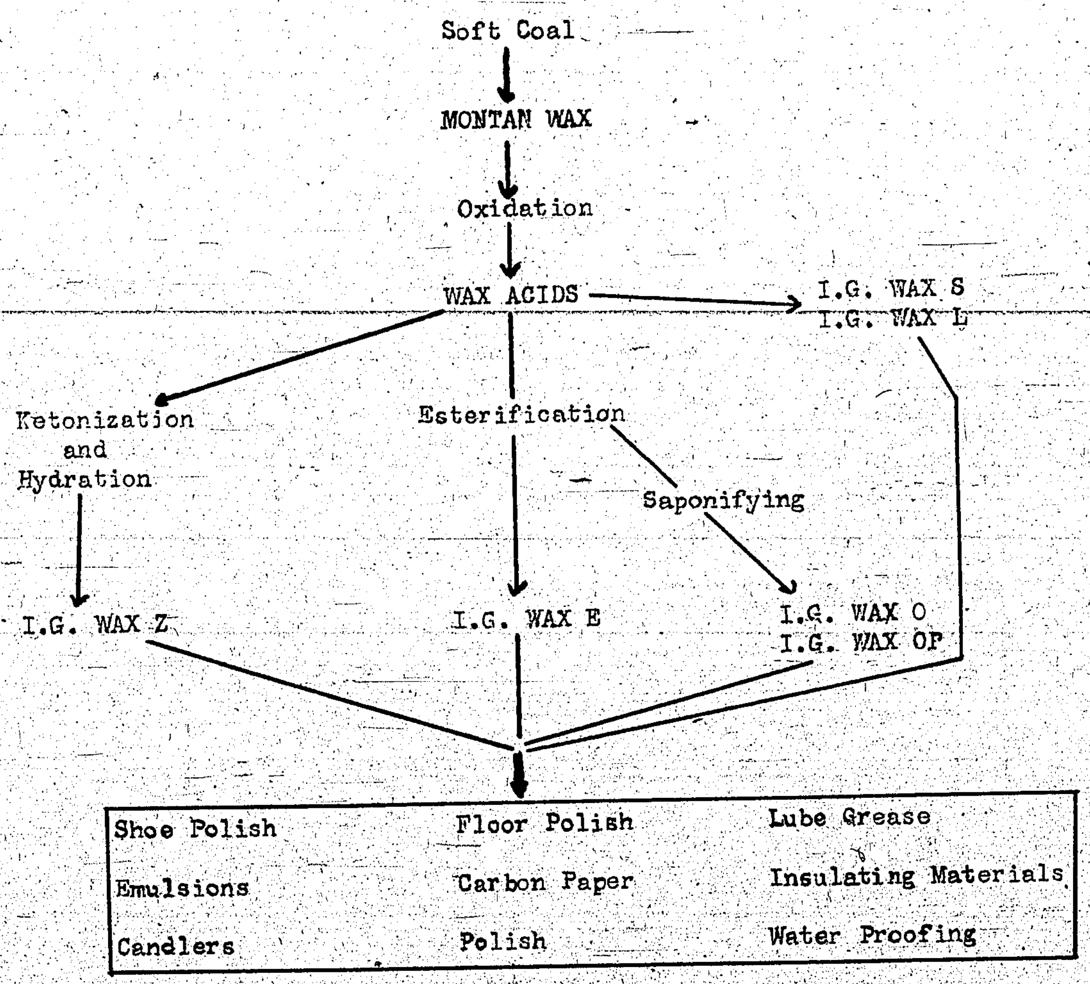
PARAFFIN OXIDATION



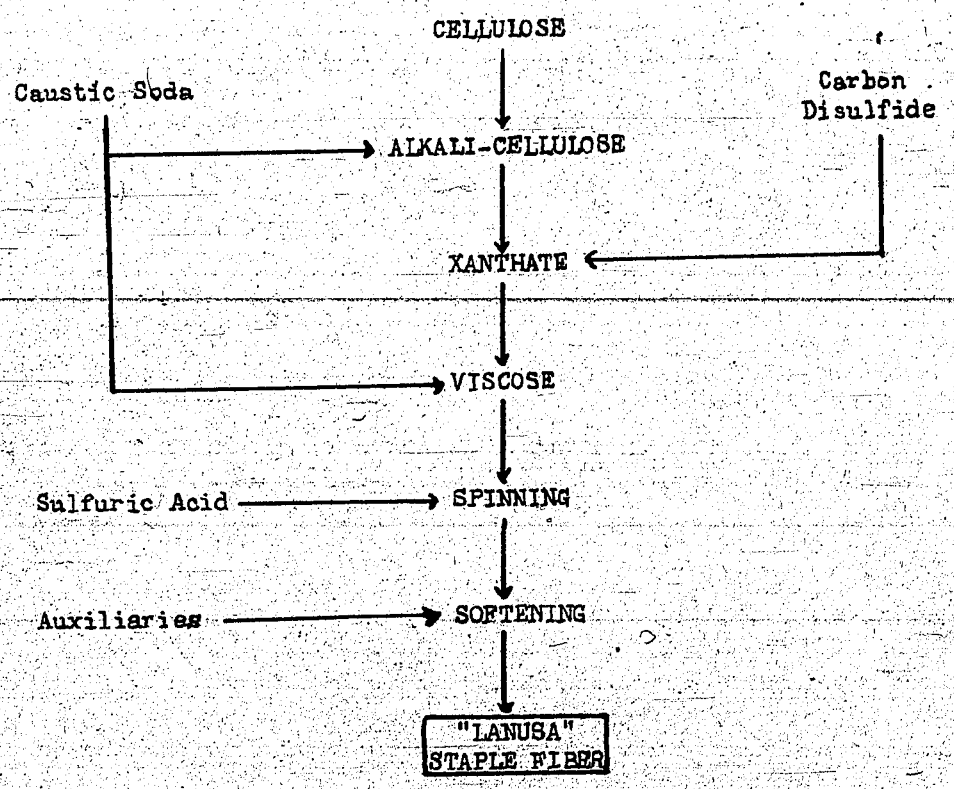
OIL PLANT



SYNTHETIC WAXES



MANUFACTURING
OF "LANUSA" STAPLE FIBER



PLASTICS

POLY-CONDENSATION PRODUCTS			POLYMERIZATION PRODUCTS		
UREA FORMALDEHYDE ↓	PHENOL FORMALDEHYDE ↓	DICARBONIC ACID DIAMIN ↓	HYDROCARBONS	ESTERS	ETHERS, AMINE, etc.
Amino Plastics	Phenolic Plastics	Polyamid	Ethylene Styrene Butadiene Isobutylene	Vinyl Chloride Acrylic Ester	Vinyl Ester Ethylenimine Vinyl Carbazol
"Pollapas" "Kaurit" "Plastopal"	"Luphen"	"Igamid	"Buna" "Oppanol" "Polystyrol" "Lupolen"	"Igelit" "Acronal"	"Igevin" "Polymin" "Luvican" "Oxydwachs"

SYNTHETIC
TANNING AGENTS

INORGANIC

ALUMINUM COMPOUNDS	CHROMIUM COMPOUNDS
"Blankorole"	Chromium Alum

ORGANIC

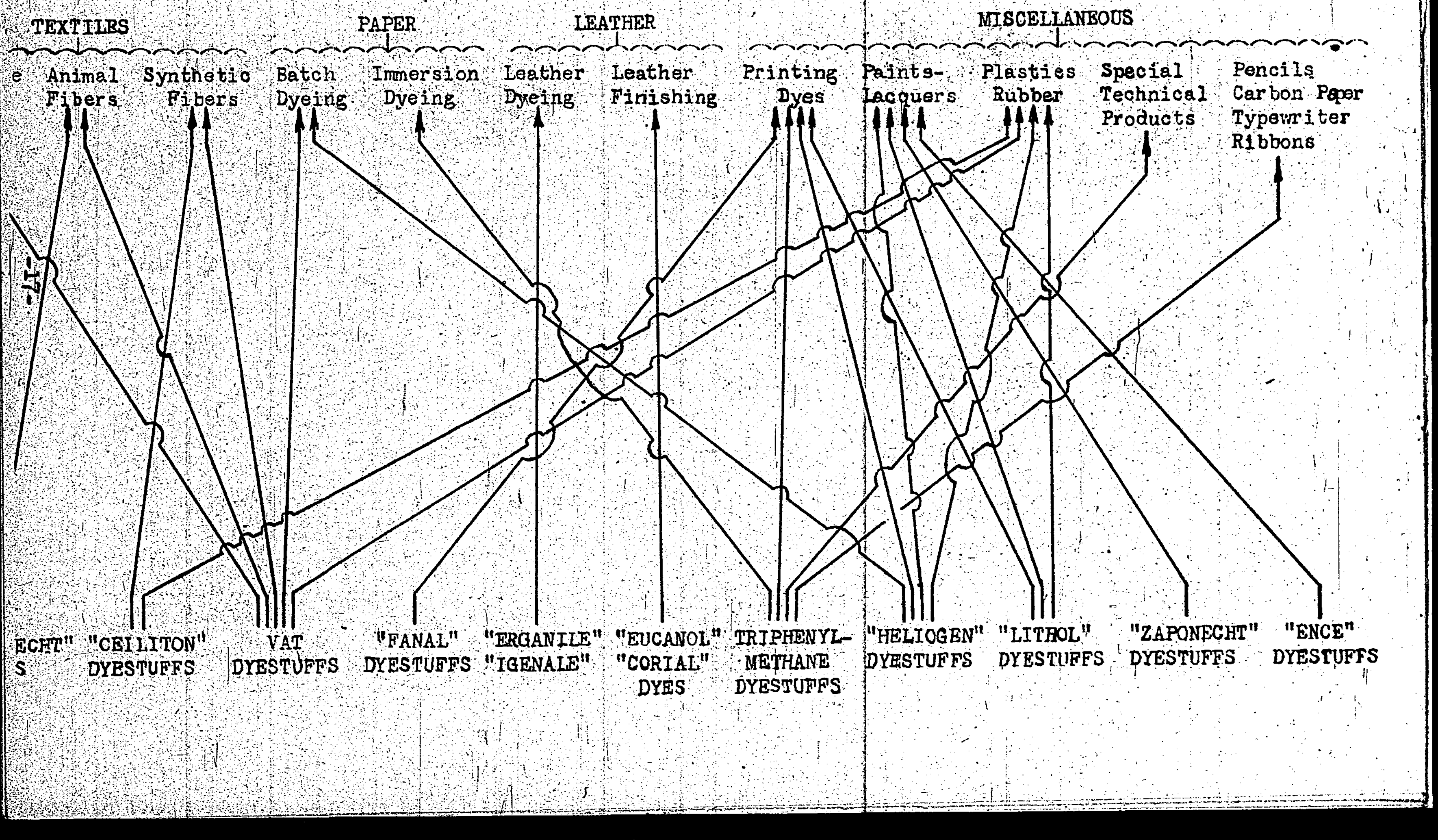
PHENOL AND NAPHTOL DERIVATIVES	COMPLEX METAL COMPOUNDS
"Tannigane"	"Ferrigane"

SOLVENTS, PLASTICIZERS AND SYNTHETIC RESINS

HYDROCARBONS	ALCOHOLS	KETONES	ETHERS	ESTERS	CONDENSATION RESINS	POLYMERIZATION RESINS
Hexahydrobenzene	Methanol	Cyclohexanon	Glycolether	Glycolacetate	"KM Resins"	"Acronale"
	Propanol	Methylcyclohexanon	Polyglycols	Phthalic Acid Esters	"Synthetic Resins AW 2"	"Igevine"
	Butanol			"Plastoles"	"Phthalopale"	"Vinoflex"
	Glycol				"Plastopale"	
	Glycerol				"Luphene"	
	Cyclohexanol				"Alkydale"	

DYESTUFFS

for

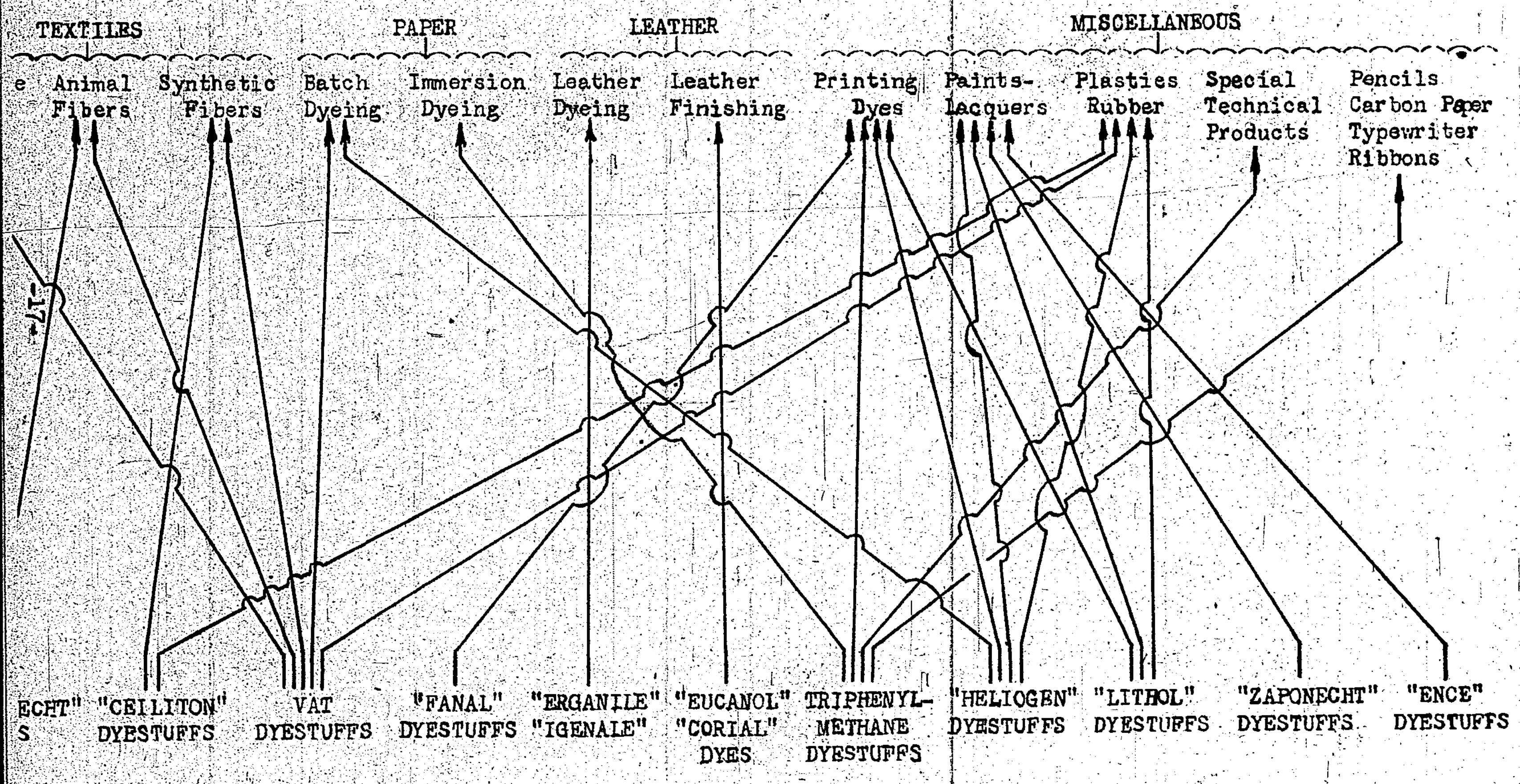


SOLVENTS, PLASTICIZERS AND SYNTHETIC RESINS

HYDROCARBONS	ALCOHOLS	KETONES	ETHERS	ESTERS	CONDENSATION RESINS	POLYMERIZATION RESINS
Hexahydrobenzene	Methanol	Cyclohexanon	Glycolether	Glycolacetate	"KM Resins"	"Acronale"
	Propanol	Methylcyclohexanon	Polyglycols	Phthalic Acid Esters	"Synthetic Resins AW 2"	"Igevine"
	Butanol			"Plastoles"	"Phthalopale"	"Vinoflex"
	Glycol				"Plastopale"	
	Glycerol				"Luphene"	
	Cyclohexanol				"Alkydale"	

DYESTUFFS

for



AUXILIARIES

AUXILIARIES FOR GENERAL USE

Wetting	"Nekal"
Water Softening	"Trilon
Emulsifying	"Emulphor"
Scouring	"Igepal"
Bleaching	"Blankit"

DYEING AUXILIARIES

Levelling	"Peregal"
Penetrating	"Palatinechtsalz"
Reserving	"Katanol"
Reduction	"Hydrosulfit"
Stripping	"Decrolin"

TEXTILE PRINTING AUXILIARIES

Antifoaming agent	"Schaumverhütungsmittel"
Thickening	"Colloresin"
Dyest. Dissolving	"Eulysin"
Discharging	"Rongalit"

WOOL and WORSTED INDUSTRY

Carbonizing	"Leonil"
Oiling	"Servital"
Milling	"Cyclanon"
Water Repelling	"Ramasit"

COTTON INDUSTRY

Boiling	"Ludigol"
Mercerizing	"Leophen"
Water proofing	"Persistol"
Finishing	"Appretan"

MANUFACTURING OF RAYON AND STAPLE FIBE

Softening	"Soromin"
Sizing	"Lumitol"
Desizing	"Lenokal"
Anti-Crush Finish	"Kaurit"

LEATHER AND FUR INDUSTRY

Soaking	"Mollescal"
Liming	"Schwefelnatrium"
Greasing	"Derminol"
Desouring	"Espropansaure"

BASICS FOR DETERGENTS

ALKALIES	Caustic Soda Ethanolamine
PARAFFIN OXIDATION PRODUCTS	Soap Fatty Acids First Run Fatty Acids Residual Fatty Acids
SULFONATES	Fatty Alcohol Sulfonates Fatty Acid Condensation Products
POLYETHERS	"Emulphore"

PHARMACEUTICALS, DISINFECTANTS AND VERMICIDES

PHARMACEUTICALS

Laxatives	Phenolphthalein
Protective Ointments) Skin Protecting Soap)	"Dermolan"
Sugar for Diabetics	"Sionon"
Wax for Dental Purposes	"Zahnwachs"

PRESERVING AGENTS

Margarine	Benzoic Acid
Glues	Betanaphthole
Fodder Fermentation	Formic Acid
Bread	Propionic Acid
Wood	Zinc Chloride

DISINFECTANTS

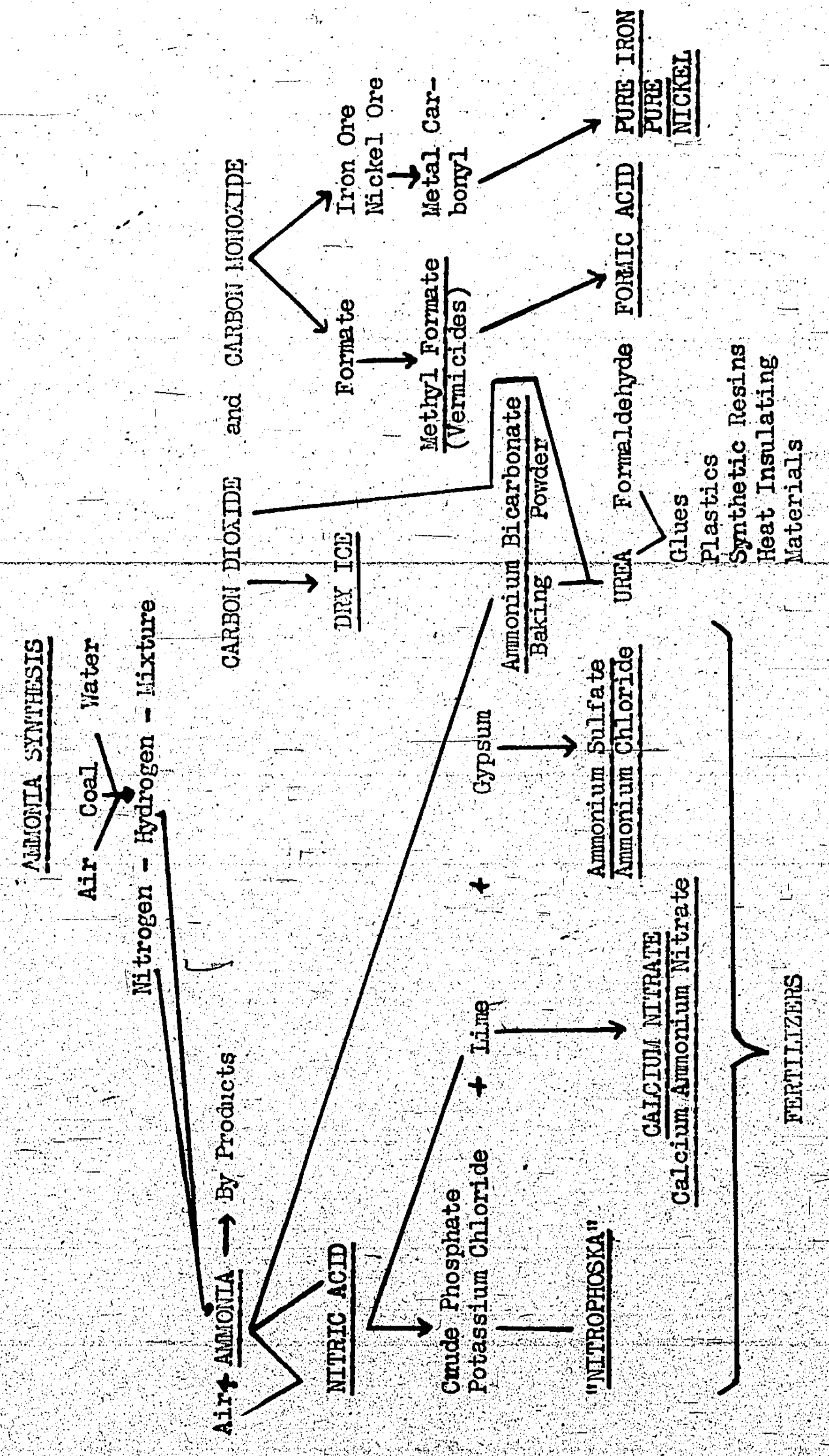
Drinking Water	Chlorine
Anti Epidemics	Hypochlorites
Body Disinfection	"Zephirole"
Room Disinfection	(Sulfur Dioxide (T-Gas

VERMICIDES AND ANTIPARISITES

Vine and Fruit-Tree Parasites	("Calcit" (Arsenate of Lead
Potato Bug	Calcium Arsenate
Corn Bug	Methylformate
Moths	Paradichlorobenzene
Parasites	"Lauseto"

BUILDING MATERIALS AND AUXILIARIES

Heat Insulating Materials	"Iporka"
Light Weight Bricks	"Iporit"
Fly Ashes Bricks	
Setting Retarders for Plaster of Paris	"Retardan"
De-shelling Agent	"Enschalon"
Gasket Material	"Oppanol"
Adhesives for Vernier and Plywood	"Kauritleim"



2. INORGANIC DIVISION

a. Chlorine Plant

(1) Brine Department

Salt was received by Rhine barges. It was unloaded at the dock and transferred to wooden tanks on cars. After transportation to the chlorine plant the salt was sluiced and dissolved out of the cars, the resulting brine being pumped to a series of steel tanks lined with Oppanol and brick. These tanks were 15 to 20 ft. in diameter by about 30 ft. tall. The brine was treated in these tanks with sodium and barium carbonate and then filtered in several very large pressure filters. These were special leaf filters installed within pressure tanks 8 to 10 ft. in diameter by about 8 ft. deep, capable of standing 7 to 8 atmospheres pressure. The brine was forced through the leaves of these filters under the above pressure. The filters had to be cleaned out each day and each filter tank was equipped with a heavy removable head (same **diameter** as the tank) which was serviced by an overhead crane. These filters represented a big investment and were far more costly than usually used for brine filtration. The filtration of chlorine plant brine under such a high pressure was of interest.

The depleted recycle brine was evacuated, blown with compressed air and treated with sodium bi-sulfite in an extensive plant constructed of acid proof equipment throughout. After treatment the chlorine free recycle brine was added to the raw brine treating tanks referred to above. Great care was obviously taken to have a feed brine for the cells, with a minimum content of calcium, magnesium and SO_4.

(2) Horizontal Mercury Cells

The plant had a single large cell room with a rather elaborate cellar (10 ft. head room) under the entire floor area. All cell pipe lines were located in this cellar. There were installed in the cellroom 403 horizontal mercury cells divided into 2 circuits of 148 cells each and one circuit having 107 cells. The cells were of different sizes, some having a normal rating of 6000 and others 8000 amperes. Both had been operated at 8000 amperes for some time due to the need for production. The following information was obtained in respect to these cells:

	Electrolyzer		Anodes			
Amps. Rating	Width	Length	No.	Length	Width	Thickness
1. 6000	0.5	5.0	28	.50	.175	.060
2. 8000	0.7	4.5	25	.68	.175	.060
3. 12000 *	1.1	5.0	28	.50 (2)	.175	.060

A feature of these horizontal cells was that the rubber lining of the electrolyzer covers the entire electrolyzer bottom except for circular openings about 15 cm. in diameter positioned longitudinally on the center line of the electrolyzer and spaced approximately a half meter apart. The mercury made contact with the steel electrolyzer bottom through these holes in the rubber lining. This is quite different from the mercury cells previously seen, in which the rubber was carried only a short distance onto the steel bottom along the sides. The operators at Ludwigshafen seemed to definitely prefer their design.

The mercury traversed the 5 meter long cell in 35 seconds. Graphite consumption was stated to be 2.3 kg per 1000 kg of electrolytic product equivalent to about 10 lbs of graphite per short ton of chlorine. Cathode current density was stated to be 2350 to 2800 amperes per sq. m. Mercury loss was uncertain but was said to average about 4% per year. The mercury price used was 15 RM per kg.

(3) Chlorine Cooling, Drying, Compression and Liquefaction

The chlorine coolers were somewhat novel. The hot wet gas passed lengthwise in series through 4 rubber lined steel boxes each about 1 m by 1 m by 2 m long. Each of these boxes contained six stoneware coils. River water flowed in parallel through the 6 stoneware coils in the 3rd box and so on through box number 2 and number 1. The water flow was thus in series parallel and countercurrent to the flow of chlorine. It was stated that these coolers never plugged up and were extremely satisfactory. The chlorine entered the coolers at 70°C and left the last box at about 20°C in winter and 40°C in summer. Lower temperatures could have been obtained by using refrigerated brine but Ludwigshafen preferred to use more H_2SO_4 than to refrigerate, because they had an adjacent contact sulfuric acid plant and the diluted drying acid could be fortified very cheaply with contact SO_3.

The drying was done with 95% H_2SO_4 in the normal manner, three rubber and acid proof brick lined towers approximately 2 m outside diameter by 5 to 6 m high being used.

After drying, the chlorine gas was compressed to 7 to 8 atmospheres pressure in two stage reciprocating compressors, lubricated with H_2SO_4. Each compressor had a capacity of 30 tons a day of liquid chlorine or 45 tons a day of compressed gaseous chlorine. The compressors were driven by 100 KW motors, at a speed of 80 RPM. They were made in accordance with I.G. designs by the Esslingen Machinen Fabrik. Chlorine gas at 30°C was cooled to 0°C by direct contact with evaporating liquid chlorine, before it entered the first stage which compressed it to 1.7 atmos. Leaving the first stage at 90°C the gas was cooled to 30°C in an intercooler with alpha monochloro-naphthalene which in turn was cooled with river water. A second injection of liquid chlorine then cooled the gas to -10°C before it entered the second stage where it was compressed to 7 to 8 atmos. The gas left the second stage at 90°C and was cooled and liquefied by river water in banks of steel coils.

(4) Miscellaneous (Horizontal Cell Plant).

The capacity of the chlorine plant at Ludwigshafen (before the enlargement later referred to) was stated to be 30,000 tons a year or 82 tons a day.

The labor requirements for the chlorine plant (before the enlargement) were said to be as follows:

	Supervisors	Shift Men	Day Men	Total
Brine Dept.	2	12	3	17
Rectifiers	1	3	1	5
Cell room	2	39	16	57
Miscellaneous	-	-	2	2
TOTAL --	5	54	22	81

Cell room includes cell operation and repair, plus chlorine cooling and drying and hydrogen handling. Chlorine compression and liquefaction which was in another building was not included. It required at least 10 additional men.

At an average of 54 hours per week and including 10 men for the liquefaction plant the foregoing is equivalent to 8.6 man hours per long ton of chlorine.

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* There were only a few of these cells. The electrolyzer of this cell is made up of two of the 6000 amp cell electrolyzers placed side by side with two rows of anodes. Dr. Honsberg stated that it showed real promise.

The analysis of the chlorine gas was stated to be as follows:

CO_2	0.8 to 1.0%
H_2	0.6 to 0.8%
O_2 and N_2	Nil
Cl_2	98.6 to 98.2%

The NaOH solution (when the cells were operating at 50% NaOH concentration) was stated to be:

NaOH	50.00%
NaCl	.032
Na_2CO_3	.036
Na_2SO_4	.0035
$NaClO_3$	.026
Fe	.0005
Al	.0004
Cu	.0001
SiO_2	.0013
Hg	.00005 to .0003

Ba, Ca, Mg not detectable

According to Dr. Pfannmüller, the cost of a 30,000 tons a year mercury cell chlorine plant excluding power generation and miscellaneous facilities usually available, was approximately 14,000,000 RM with Hg at 15 RM per Kilo.

(5) New Rotating Vertical Mercury Cell

Ludwigshafen had nearly completed a 20,000 ton a year enlargement of their chlorine plant when it was shut down by bombing, shortage of coal and the occupation. This enlargement included an extension to the cell room in which 84 - 24,000 ampere cells of a new design were being installed. This cell was known as the vertical cell. It had been under development at Ludwigshafen for several years and an earlier version of it (said to be considerably less satisfactory) had been installed at Heydebreck and Hüls two years or so ago. Dr. Honsberg stated that the only cells at these two plants were the earlier version of the vertical cell.

This installation of 84 vertical cells of the newest design had progressed substantially in the enlarged cell room at Ludwigshafen, 28 of them being in place and nearly ready to operate with much progress made on the installation of the remainder. The new vertical cells were rated at 24,000 amperes although one of them had been in experimental operation for several months at 40,000 amperes. The particular advantage of this vertical cell was its large capacity per unit of floor space. At its rated capacity it required only about 19 sq. meters of floor space (including aisles) per 1000 kg of chlorine per day. This compares with over 60 sq m for the 16,000 ampere horizontal mercury cells at Höchst and still more for the lower amperage horizontal cells. Even the 14 meter long 28,000 amp horizontal cells developed at Höchst required something over 50 sq m per 1000 kg of chlorine a day.

To facilitate a visualization of the description which follows reference is made to the attached photographs. The cell consists of a steel drum or rotor 0.60 m in diameter by about 0.50 m in width mounted on a horizontal shaft. This drum carries 5 circular cathode plates at right angles to its axis, each plate being 1.85 m in diameter and spaced equidistant from each other. The drum with the 5 circular plates is enclosed within a steel housing which is split horizontally into three sections. The top section has sloping sides, the central section is roughly square sided and the bottom section is curved to conform to the circular cathode plates. All but the bottom section are rubber lined and the sections are flanged and bolted together. The drum with the 5 circular cathode plates was rotated at 7 RPM by means of a .55 kw motor and V belt drive. Six sets of graphite anodes are supported from the cell housing through connectors. Four of these anodes are disposed between the 5 cathode plates whereas two of them are outside the cathode plates, one on each side. These anodes are stationary and are not adjustable laterally to compensate for wear. The anode assemblies are separated horizontally at 3 places to facilitate circulation of the brine. The separation space is 20 mm.

The bottom of the cell housing was filled with approx. 1300 kg of mercury to a height about 2 cm above the bottom of the rotor. The curved cell bottom had built-in partitions between the rotating cathode plates and extending close to the top surface of the mercury, for the purpose of cutting down the total volume of mercury. These partitions nearly filled the spaces between the lower portion of the cathode plates corresponding to the spaces filled by the graphite anodes above the surface of the mercury.

Purified and nearly saturated hot brine (70°C - 310 gpl) was fed in through the cell housing at one end just above the surface of the mercury. This brine filled the entire housing above the mercury to within about 4 cm of the top where it overflowed (after depletion of its NaCl content to about 260 gpl). The chlorine gas passed out through this overflow pipe which was only partially filled with the outflowing brine, from which it was readily separated.

A vertical direct connected centrifugal pump (0.8 kw motor) was located just outside the cell. The HgNa amalgam (0.15% Na) flowed into it, and was pumped at a rate of 200 kg per minute to the top of a vertical cylindrical tank, called the decomposing "tower." This is about 0.5 m diameter by 1.0 m high. It is filled to within 15 cm of the top with pieces of graphite (roughly 5 mm cubes). The amalgam entered the bottom of the tower through a pipe which rises to a point about 10 cm below the top of the tower at which point the pipe ends in a special return bend fitting which caused the amalgam to flow vertically downward into the graphite packing. Distilled water flowed into the tower by means of a pipe connected on the side just above the bottom. This water passed upward through the tower counter-current to the down flowing amalgam, and overflowed through the side of the tower by an overflow pipe just above the graphite packing. The flow of water to the tower was so regulated that the NaOH solution (caused by the decomposition of the amalgam by the H_2O) was at the desired concentration, which was stated to be 50% to 70% NaOH. The hydrogen which was also formed by the decomposition of the amalgam (reaction of Na with H_2O) passed out through this same overflow pipe and was readily separated from the NaOH solution. The mercury, its Na content reduced practically to nil, flowed by gravity out of the bottom of the tower and back to the opposite end of the cell.

The current flowed from bus bars on each side of the cell through 96 leads, half on one side and half on the other side of the cell, to the graphite anodes. 72 of these leads passed through the top section of the cell and were not insulated from it whereas the 24 leads passing through the central section were insulated from the section walls. The top section of the cell housing was therefore anodic whereas the central and bottom sections were cathodic. The central section of the housing was insulated from the top section by carrying the rubber lining around the junction flanges and by insulating the bolts which held the two sections together. This junction between the top and central section of the cell housing is about 16 cm above the center of the rotor shaft. The flange between the central and bottom sections is 20 cm below the center of the rotor shaft. Bus bars attached to each end of the cathodic bottom section led the current away to the anodes of the next cell in line. Each cell had two "jumper" switches attached to the anode bus at each end of the cell, for by-passing the current so that the cell could be cut out for repairs without disturbing the other cells.

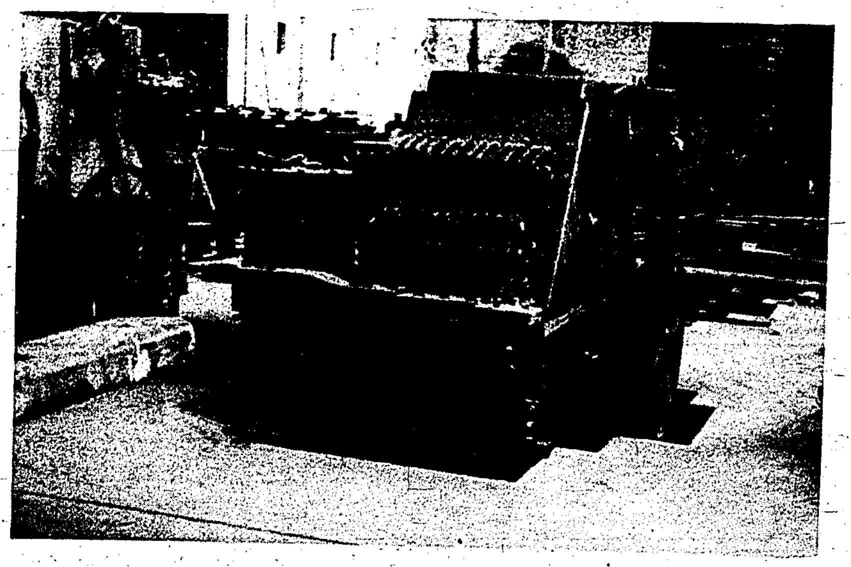
The 5 rotating steel cathodes became amalgamated by passing through the mercury in the bottom of the cell. It was stated that this mercury coating which spread thinly over the entire surface of the steel cathode plates would persist for 24 hours even when no current was passing through the cell. When current was on and the cell in operation, the mercury coating picked up the sodium formed by the electrolysis of the brine, during the cathodes passage through the brine zone. When, due to the rotation, this mercury sodium amalgam passed from the brine zone down into the mercury zone the HgNa amalgam was dissolved in the mercury bath and was supplanted by the mercury in the bottom of the cell which mercury had a lower Na content, because of its circulation through the amalgam decomposing tower. This cycle was continuous.

This vertical rotating cell has not yet been operated for a long enough period of time to thoroughly establish such factors as over-all power consumption, voltage, graphite life and durability of parts, particularly the rubber lining. The chlorine

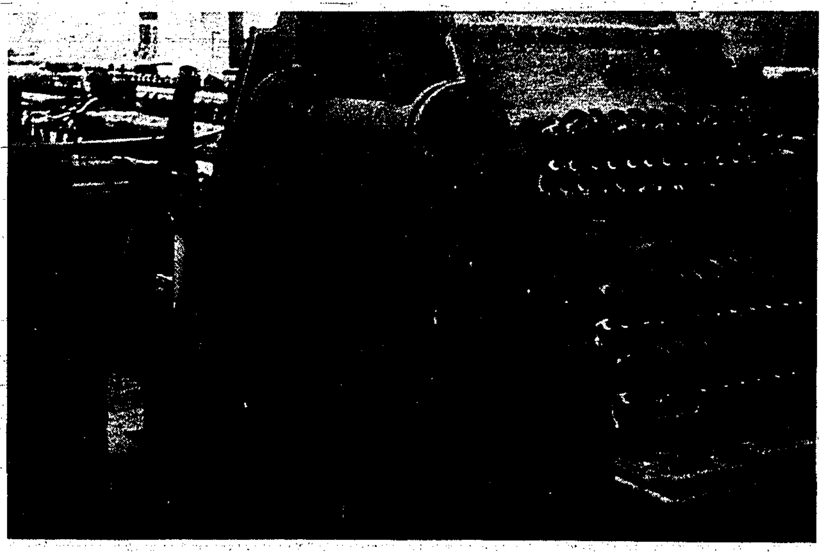
plant superintendent, Dr. Honsberg, as well as Dr. Pfannmüller, were most enthusiastic about it and it must have shown real promise or it would not have been used as the basis for the major expansion of the plant. The operation of an earlier version of this cell as installed at Hüls and Heydebreck is not a fair basis to appraise this improved design, according to Dr. Honsberg. In this connection it is noted here that the cost of making 100 kg of electrolytic product was 13.26 RM at Hüls in 1943, and 17.65 at Heydebreck during the first half of 1944 as compared to an average of 8.26 RM per 100 kg for all the other I.G. chlorine plants in 1943. This is probably an unfair comparison because of other factors.

Dr. Pfannmüller stated that he expected that the voltage of their new vertical cell would be 3.75 at the start and 4.7 at the finish of an anode run. From other sources it was learned that the vertical cells at Hüls had a starting voltage of 4.3 and a finishing voltage of 6.0. Whether the lower anode current density (1700 amperes per sq m as compared to 2500 to 3500 for the horizontal cells) will counterbalance the fact that the anodes are not adjustable to compensate for wear, is yet to be determined. Pfannmüller's estimate on voltage is probably too optimistic. The ampere efficiency was stated to be 92 to 93% which is rather low.

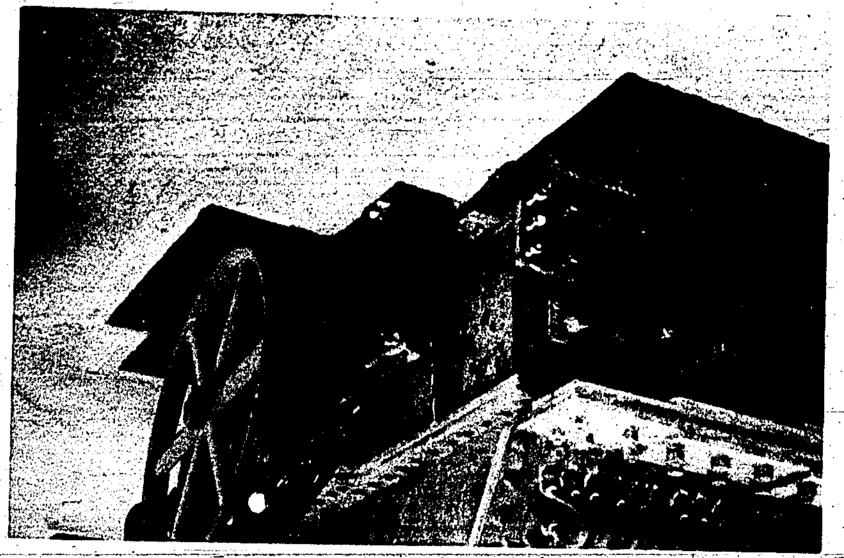
Another slant on this cell was obtained from Dr. Ulrich who was formerly in charge of the chlorine plant at Ludwigshafen. He did not think highly of the cell and expressed the opinion that it had many idiosyncrasies and that it would require at least 5 years continuous operation before it could be stated positively how good the cell really was.



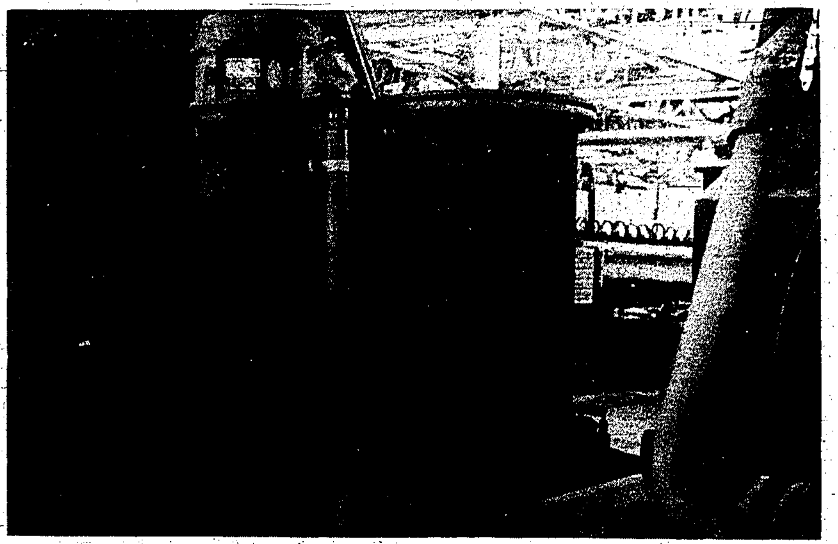
General View of Rotating Vertical Mercury Cell, Showing Amalgam Decomposer (left) and One Anode Bus.



Rotating Vertical Mercury Cell - Close-up Showing Rotor Wheel and Brine and Chlorine Outlet.



Rotating Vertical Mercury Cell Showing Lower Part of Cell and Hole Through Floor.



Rotating Vertical Mercury Cell, Showing Mercury Pump and Decomposing "Tower."

b. Aluminum Chloride

(1) Summary

Aluminum chloride was made at Ludwigshafen from bauxite or from quite pure Al_2O_3 made from aluminum hydrate (Tonerde-hydrat). The bauxite came from the French or Netherlands Indies. The "Tonerde-hydrat" came from Southern Germany. The processes were as follows:

Bauxite Process. - The bauxite was crushed and then dried by direct heating with gas in a fire-brick lined furnace. The dried bauxite containing 55 to 60% Al_2O_3, 1-3% Fe_2O_3 and 1 to 2% TiO_2, was charged to a shaft furnace or chloridizer. Chlorine and CO in equi-molecular amounts were preheated and fed to a contact chamber containing activated carbon which partially converted the gases to phosgene. This passed up through the bauxite in the shaft furnace and reacted to form $AlCl_3$, which was condensed in tall cylinderical condensers. The exit gases were washed with water.

"Tonerde-hydrat" Process. - The "Tonerde-hydrat" was peptized with either HNO_3 or $AlCl_3$ solution, thoroughly mixed in a kneader and then put through an extrusion press. The extruded material was cut off into cylinders an inch or so long and then fed to the same dryer as was used for drying the bauxite. Both the kneader and extrusion press were lined with a corrosion resistant protective coating. From here on, the process was the same as the bauxite process except that the $AlCl_3$ produced was much purer (0.01 to 0.05% Fe) than when bauxite was used and the product did not require re-sublimation.

Yields in the bauxite process were said to be 80 to 85% whereas in the "Tonerde-hydrat" process they were about 85%.

Capacity per Chloridizer

125 tons a month of $AlCl_3$ when operating on bauxite.
140 tons a month of $AlCl_3$ when operating on "Tonerde-hydrat."

A larger furnace had been installed at Schkopau which was said to have a capacity of 250 tons on bauxite and 300 tons on "Tonerde-hydrat."

(2) Chloridizing Step

Dr. Pfannmüller stated that their information was very incomplete as to whether it really was necessary to convert the gases to phosgene before feeding to the chloridizer and he was sure that complete conversion was unnecessary as they had occasionally operated

with very little carbon in the gas contact chamber and the conversion to phosgene must necessarily have been low.

The two chloridizers were steel shaft furnaces approximately 2 m outside diameter by about 12 m high lined with acid proof brick. The shaft was about 1.5 m inside diameter. The reaction temperature was said to be 900°C, but it was also stated that considerable difficulty was experienced in controlling this temperature. The brick lining tended to wear out rather quickly about half way up the shaft where the main reaction occurred and the steel shell of the chloridizer was therefore cooled externally by water or air. The daily chloridizing cycle required about 18 to 20 hours. The chloridizer residue was cleaned out of the bottom of the chloridize every few days, more often when operating on bauxite than on "Tonerde-hydrat."

(3) Condensers

The $AlCl_3$ sublimed up through the shaft chloridizer and over into the top of the first of two long vertical condensers built of steel and equipped with cone bottoms through which the product was packed out. The $AlCl_3$ not condensed in passing down through the first condenser was largely caught in the second condenser up through which it passed to the exit. All ducts were of steel and were equipped with large clean out openings. There were also several manholes in the condensers. It was stated that they had to be pounded occasionally to knock down adhering $AlCl_3$. Rather elaborate ventilating ducts were provided at most of the points where fumes were likely to be present.

(4) Sublimation of Crude Product

The crude $AlCl_3$ produced from bauxite contained 1 to 3% of Fe and 1 to 2% of $TiCl_4$. It had to be purified for some uses. This was accomplished, when necessary, by a sublimation process in which 1500 to 2000 kg of crude $AlCl_3$ plus 40 to 50 kg of finely divided aluminum metal were charged into a molten bath consisting of 600 kg of $AlCl_3$, 20.6 kg of NaCl and 26.0 kg of KCl contained in an externally fired subliming kettle (2 m diam x 3 m deep) equipped with a heavy agitator. The yield of purified $AlCl_3$ was about 80 to 85% and the capacity about 90 tons a month of sublimed product. The $AlCl_3$ so produced contained only about 0.01 to 0.05% Fe.

c. Sodium Hydrosulfite

Sodium hydrosulfite ($Na_2S_2O_4$) was made at Ludwigshafen by the so-called zinc dust process in accordance with the following equations:

$$Zn + 2SO_2 = ZnS_2O_4$$
$$ZnS_2O_4 + 2NaOH = Na_2S_2O_4 + Zn(OH)_2$$

Sulfur dioxide gas was bubbled through zinc dust in water suspension in a well agitated kettle. The zinc dust averaged only about 90% zinc, the balance consisting principally of lead compounds. The resulting ZnS_2O_4 flowed to a second agitated vessel into which caustic soda solution was run. In this vessel the ZnS_2O_4 was converted to $Na_2S_2O_4$. The batch in this conversion kettle was then pumped through filter presses which filtered out the $Zn(OH)_2$ precipitated by the reaction. The filtered solution then flowed to a settling tank for the purpose of further clarification, the settings being returned to the soda treatment kettle. From this tank the batch then flowed to the salting out kettle. The aqueous $Na_2S_2O_4$ solution was kept below 40°C up to the salting-out step.

The salting-out of the $Na_2S_2O_4$ was done with dry NaCl and ethyl alcohol. By raising the temperature to 60 to 65°C during the salting out, the water of crystallization of the $Na_2S_2O_4$ was split off. The $Na_2S_2O_4$ crystals plus the water-alcohol solution then flowed to a Nutsch vacuum filter where the $Na_2S_2O_4$ was filtered off and washed with re-distilled alcohol. The water-alcohol solution was collected in one receiver and the wash alcohol in another.

The $Na_2S_2O_4$ crystals were then dried in a vacuum "paddle" dryer heated by steam to 100°C. The alcohol was recovered from this dryer. Following this drying step several dryer batches were then blended in a mixer to approximately 90% average $Na_2S_2O_4$ content.

The alcohol-water solutions and alcohol washes were accumulated in a storage tank from which they flowed to a still where the alcohol was separated from the water and salts and thus readied for re-use.

The $Zn(OH)_2$ which was precipitated in the second step of the process was worked up as a by-product and sold to rubber fabricators.

A good part of the plant equipment was made of V2A (18-8 stainless). Depending on its quality, 250 kg of zinc dust yielded on the average 460 to 480 kg of 90% $Na_2S_2O_4$ (conc. powder) which was 70% of theory based on 100% zinc. The yield on SO_2 was about 75%. The capacity of the plant was stated to be 900 tons a month.

d. Calcium Carbide and Acetylene Generation

(1) Introduction

The calcium carbide plant at Oppau was visited in company with Dr. Timm and Mr. Heck, the plant superintendent. This modern plant consists of two complete units for the production of calcium carbide and the generation of acetylene gas therefrom. One of the carbide furnaces was about 50% destroyed by bombing; the balance of the plant was apparently in good working order. An addition to the building had been started to house a third unit.

Salient operating data on the units are as follows:

Number of units	2
Capacity per unit .... per year	50,000 tons carbide
	150 tons ferrosilicon by-product
	16,500 tons acetylene gas
Charge:	
Lime - CaO	3,200 kg
Anthracite	750 "
Coke	1,600 "
Yield of technical carbide	3,200 "
Rated capacity per furnace	22,000 KVA
Yield ...... 3,000 to	3,300 KWH per ton of carbide
Acetylene yield - average	285 liters acetylene at ntp per kg of carbide

A detailed description of the process is given in the following:

(2) Production of Carbide

Coke and anthracite coal were crushed to minus $1\frac{1}{2}$" and blended with minus $1\frac{1}{2}$" lime (CaO) received from a nearby plant. The materials were elevated to an overhead storage bin from which they were fed manually to the furnace at a rate sufficient to keep the top of the charge burden about 5' above the level of the molten reaction mixture. The entire top of the furnace was surrounded by a 5' high wire screen barrier and ventilated to take care of dust losses which were discharged to a very tall stack by means of a blower.

22,000 KVA was supplied to each furnace by a three phase system carrying 80,000 to 88,000 amperes per phase. A single transformer reduced the line voltage from 20,000 to the required 110-220 volts.

Three electrodes of the Soderberg type were used per furnace. These electrodes were made in situ semi-continuously. A mixture of coke dust, anthracite, coal dust and tar was kneaded together in a W-P mixer, pressed into approximately 20"x12"x6" bricks which were baked at about 100°C and then loaded into the built-up electrode casing. The casing was made of a steel shell about 14 gauge and was about 1' - 8" wide, 4' - 6" high and 10' - 0" long. The shell was first welded as a belt which was then welded to the top of the preceding section already in place in the furnace. The new casing was filled with the electrode blocks which softened and agglomerated to a solid electrode mass. The entire electrode mechanism, operated hydraulically, was lowered at a rate of about 10 cm per hour as burning of the carbon electrode proceeded. The furnace proper is 21' face by 15' wide by 15' deep and carried a molten carbide mixture to a depth of about 5'. The outer steel shell of the furnace is lined with about 9" of fire brick.

The carbon monoxide gas generated in the reaction was collected in four water cooled brick channels of inverted V shape located outside and between and extending parallel to the electrodes. The top of the V was about level with the top of the charge burden; the bottom was somewhat above the molten charge level. The CO gas was wasted until it was oxygen free and was then cut over to the fuel system where, after washing with water, it was used as boiler fuel.

The carbide product was tapped off every 15 minutes and flowed to a rotary externally water sprayed kiln type cooler about 7' in diameter by 75' long. To prevent corrosion, the first 10' of the kiln was of copper; the balance steel. The molten carbide entering at 2,500°C was cooled to 70°C and delivered as a product, approximately all through 2" mesh, ready for the acetylene generation step. Ferrosilicon produced from the iron in the raw materials plus the iron from the electrode shell was tapped off at a lower level, about once every 24 hours.

(3) Generation of Acetylene

Acetylene was generated in a dry-type unit by reacting the carbide with water sufficient to yield practically dry 95% $Ca(OH)_2$.

Carbide was fed continuously to a weighing feeder and discharged through a double hopper system to a screw feeder which charged it to an approximately 8' diameter by 20' long steel rotary kiln. This kiln contained an inner screen having a diameter about 8" less than the diameter of the kiln. Carbide lumps were retained on the screen while the reacted fines passed through and continued to the discharge end of the kiln. Water entering the far end of the kiln through several spray pipes of different lengths was regulated so as to yield essentially dry lime 95% $Ca(OH)_2$ and maintain a reaction temperature of about 70°C. The acetylene gas leaving the kiln at the entrance end counter current to the carbide was scrubbed with water and pumped to the adjacent plant for use in the production of butadiene, etc. The lime discharging from the kiln carried a small amount of unreacted carbide fines. These fines were removed by a centrifugal separator and recycled to the fresh carbide feed.

(4) Miscellaneous

The following data on German carbide production was obtained at the Heidelberg library:

Capacity 1943 -

Schkopau	30,000 tons per month
Knapsack	25,000
Ludwigshafen	8,000
Auschwitz	4,000
Total I.G.	67,000
Others	78,000
Grand total	145,000 (21 plants)

The other producers named were Piesteritz (presumably operated by I.G.) Wacker-Burghausen, Wacker-Mückenberg, Viag, Lonza, and Degussa.

About 80,000 tons of carbide were converted to acetylene for chemical uses.

Increased production was planned for 1944; 91,500 tons per month for I.G. out of a total of 210,000 tons planned.

e. HCl

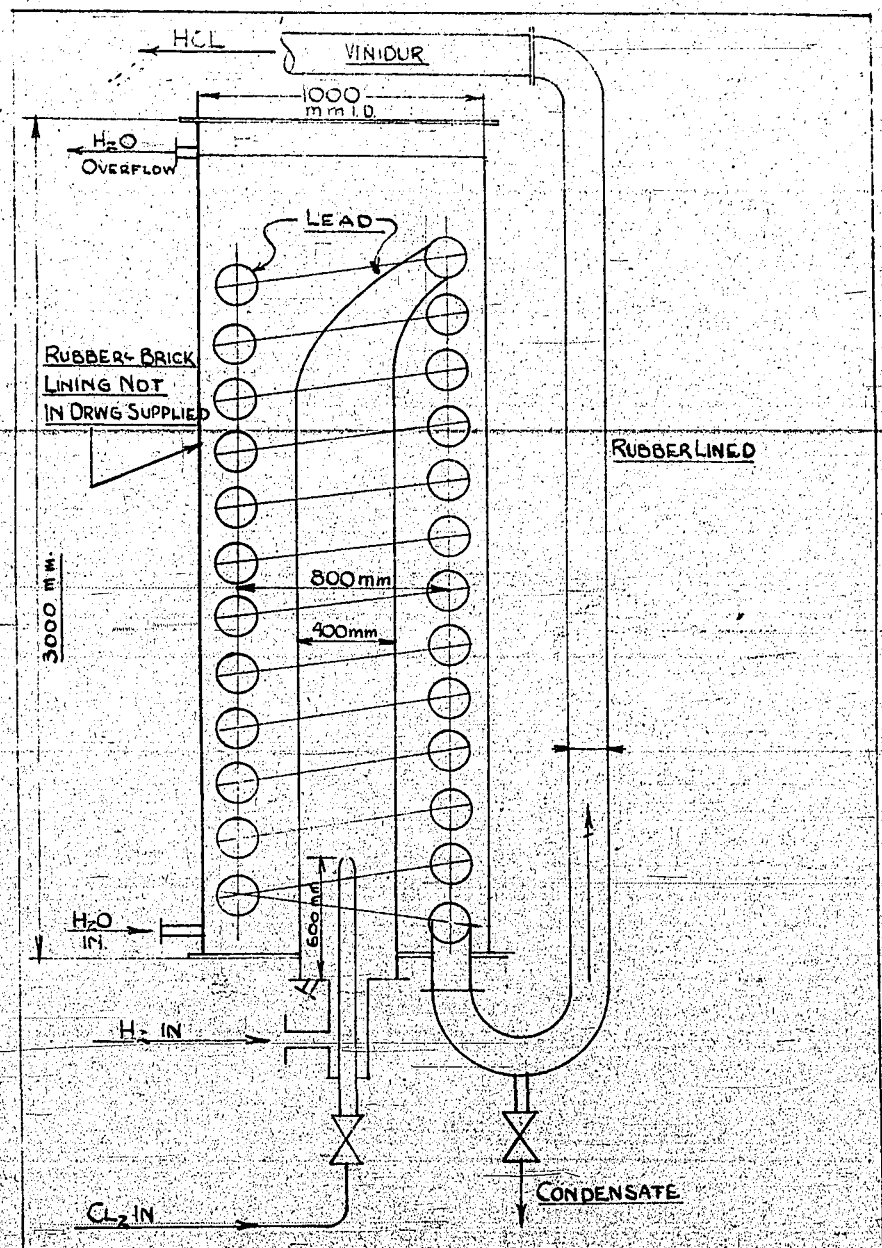
(1) General

A substantial amount of the cell chlorine produced at Ludwigshafen was burned with the hydrogen gas from the cells to produce hydrogen chloride gas. Some of the gas was absorbed in water to make hydrochloric acid (20 to 22° Bé) another portion was dried with sulfuric acid and this dried hydrogen chloride pumped to various parts of the plant for use in other processes or compressed to 60 atm pressure and condensed to liquefied HCl by refrigeration.

The plant was badly damaged by bombing. A new hydrogen and chlorine burner and the method of compressing the hydrogen chloride gas were of interest.

(2) Burning of Hydrogen and Chlorine

Several conventional silica-ware burners were installed. Recently, a new type burner was developed and several of these had been put in and were preferred to the older ones. The new design of burner (see sketch) consisted of the burner itself, a spiral lead coil for cooling the hydrogen chloride gas, and a steel cooling tank surrounding the lead coil.



HYDROGEN-CHLORINE BURNER

The cooling tank was 1 m I.D. by 3 m high. It was lined with rubber and acid proof brick merely as a protection in the event of failure of the lead coil, resulting in acidification of the cooling water. A vertical lead pipe, 0.4 m in diameter by about 2.5 m long, was installed in a vertical position in the cooling tank. It projected through the bottom of the tank a short distance. Chlorine gas was fed through the bottom of this vertical lead pipe through a small vertical pipe ending in a nozzle 0.6 m above the bottom of the lead pipe. Hydrogen gas was admitted through a tee in a larger pipe surrounding the chlorine pipe. This larger pipe ended at the bottom of the lead pipe. The hydrogen therefore filled the lead pipe surrounding the chlorine inlet pipe up to its tip at which point it burned with the chlorine to form hydrogen chloride gas. A small drain was provided in the bottom of the lead pipe for the withdrawal of any condensate which might form.

The 0.4 m diameter by 2.5 m high lead pipe, tapered at its upper end to 120 mm in diameter, which was the size of the spiral lead cooling coil which passed downward through the cooling tank and out the bottom. This spiral lead coil (pipe diameter 120 mm) had 12 turns, the diameter of the turns being 0.8 m.

After passing through the bottom of the cooling tank the gas turned 180° and passed vertically upward for a distance of about 4 m. through a rubber lined steel pipe, after which the pipe changed to one made of Vinidur.

Cooling water entered near the bottom of the cooling tank and overflowed near the top. The temperature of the outflowing water was maintained at 70 to 75°C. No mechanism was in evidence for proportioning and controlling the hydrogen and chlorine.

(3) Hydrochloric Acid Production

Some of the hydrogen chloride from the burners was absorbed in water in steel towers (rubber and acid proof brick lined). The gas passed through these towers in series counter current to the water feed. The acid flowing out of each tower was pumped through cooling coils into the top of the next tower in series.

(4) Hydrogen Chloride Compression and Liquefaction

Some of the burner gas was dried in sulfuric acid drying towers and then pumped to various parts of the plant for use in other processes. A small portion of the dried gas was delivered to a reciprocating 4-stage carbon ring compressor. This compressor had two tandem cylinders operating partly in parallel and partly in series, stages I, I and IV in one and stages I, II and III being in the other.