—The froth from the pre-flotation plant contains about 4 per cent ash. When electrode coal is being made, this product is four times refloated in the main flotation plant. This means that the froth from the primary flotation cells of 4 per cent ash is fed to the first box and refloated. Then the froth from the first box is transported by an elevator to the feed part of the second box and again refloated, and this is continued through four stages. The ash content is reduced in these four stages successively to 2.5 per cent, 1.8 per cent and finally 1.1 per cent.

Each flotation unit consists of 4 cells; each system (block) consists of 6 units; and there are 6 systems or a total of 36 four-cell units.

The maximum capacity reached with the 36 units was 6000 tons of cleanest coal monthly. Work was continuous during 24 hours, including Sundays, so that the capacity of the plant was $\frac{6000}{24 \times 30} = 8.4$ tons per hour. However, 6000 tons a month was acknowledged to be an exception. The normal rate of production was about 5000 tons per month.

The flotation reagent used was a Beechwood tar oil (Buchenholzteeröl and this was added to the entering feed. Sometimes it was necessary to add a little additional reagent to the following stages.

Besides the slimes from the run-of-mine coal (1 and 2), lump coal could be crushed down to 0.75 mm. to furnish additional feed to the Reinstkohle plant. As the lump coal is selected and, therefore, low in ash, the crushed material had an ash content of about 4 per cent and could be admitted directly to the main flotation plant.

The final froth from the main flotation plant went to vacuum filters (13) and the cake from these filters went to the acid baths (16) for the chemical extraction of the last ash. A cross-section of the vessel is shown in Figure 10.

These acid baths are concrete vessels of about 3 to 4 meters diameter provided with pipes for circulating superheated steam through to the contents.

These concrete vessels are lined with carbon bricks made by Siemens-Plania of Berlin Lichterfelde. These carbon bricks are made of the purest coke produced by the Carl-Alexander plant mixed with pitch and burned at a high temperature by Siemens-Plania.

The carbon bricks are necessary to protect the concrete against the activity of the reagent acid. The acid dissolves the silicious matter of the coal slurry. The part of the steam pipes that is in contact with the acid is also made of pressed carbon bricks. The inner diameter is about 3 inches and the wall thickness is 2¼ inches. Because of the acidity of the water, the rotary drum filters must be lined with rubber, and the cloth on the filter is of artificial resin (plastic). There are 14 of these acid ash extractor units in the plant.

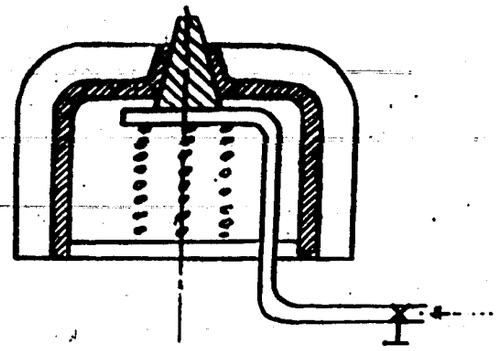

FIGURE 10.

Ash Extraction. A mixture of water, hydrofluoric acid and hydrochloric acid is made in the ratio of 100 parts of water to 1 of HFl and 2 of HCl, and the ratio of water to coal is 2 to 1. The effluent water from the filters (17) is almost neutral as virtually all the acid is consumed in dissolving out the coal-ash matter. By this acid extraction method, the ash content is reduced to 0.5 per cent.

The cake from filter (17) is treated in the water baths (18) to remove the rest of the acid. From here it goes to the next filter (19). The cake from filter (19) is dried in drier (20) and stored in (21). Further on the purest coal (Reinstkohle) is coked in the normal way (22) and is then ready for shipment to the aluminum refinery where it is pulverized and mixed with 30 per cent of pitch to make the electrodes.

The main flotation process is continuous, and the coal stays about one-half hour in the frothers. The acid baths operate on the batch principle, and the slurry stays in contact with the boiling acid for one hour. As shown in Table 8, the yield depends largely on the quality of the seams used.

TABLE 8 - TYPICAL YIELDS OF VARIOUS GRADES OF PURE COAL

Ash %	Seam 1 Yield %	Seam 2 Yield %	Seam 3 Yield %
0.4	20	0	0
0.4 - 0.6	15	10	0
0.6 - 0.8	10	30	0
0.8 - 1.2	30	15	0
over 1.2	25	55	100
			0
			0

Where seam 1 gives a theoretical yield of 75 per cent of coal of an accumulative ash content of about 1.1 per cent, seam 2 would give only 45 per cent, and seam 3 is incapable of yielding any coal of that grade.

The flotation plant does not actually deliver the theoretical yield, but perhaps 80 per cent of the theoretical yield.

The advantage of the acid extraction method is that the effective yield at 1.1 per cent ash can be actually carried forward to the final de-ashed product of 0.5 per cent ash content. If separation by float- and sink methods to obtain the same end ash content were attempted, the yield would be very much lower.

The tailings from the main flotation plant, still low in ash, were mixed with the fine coal from the jig washers and sold. The tailings from the pre-flotation plant (9) having an ash content of about 40 per cent were mixed with middlings from the jig washers (also about 40 per cent ash) and fired on special Martin stokers.

The production of purest coal at Carl Alexander is stopped at present by bomb damage to the surface works; nor is there any need for purest coal for aluminum production in Germany at the moment. The production of normal coking coal of the plant at present is about 1000 tons per day.

18. Zeche Koenigen Elizabeth

The Koenigen Elizabeth property belongs to Mannesmann, A. G.. There are three shafts (1) the Friedrich Joachim, (2) the Hubert, and (3) the Wilhelm Emil. The special coal preparation plant is located at the Wilhelm Emil shaft. This plant was designed especially to produce super-cleaned coal for the manufacture of carbon electrodes for the aluminum industry. It combined the research effort of the producing company, the specialists of Bergbauverein and the equipment manufacturers, Krupp-Gruson A.G., of Magdeburg and Lurgi Apparatenbaum of Frankfurt. Two drawings showing partially the arrangement of the plant are shown in Figure 11 and Figure 12.

Two general schemes are embodied in this plant; one treating the coal by wet methods and the other by dry methods. The objective of both methods was to arrive at a final ash content of 0.5 to 0.7 per cent without having to resort to acid extraction.

In order to obtain this result, certain seams that contain the largest proportions of very low ash, low gravity float material were selected and special separating methods were developed in an attempt to separate very small grains at low gravities.

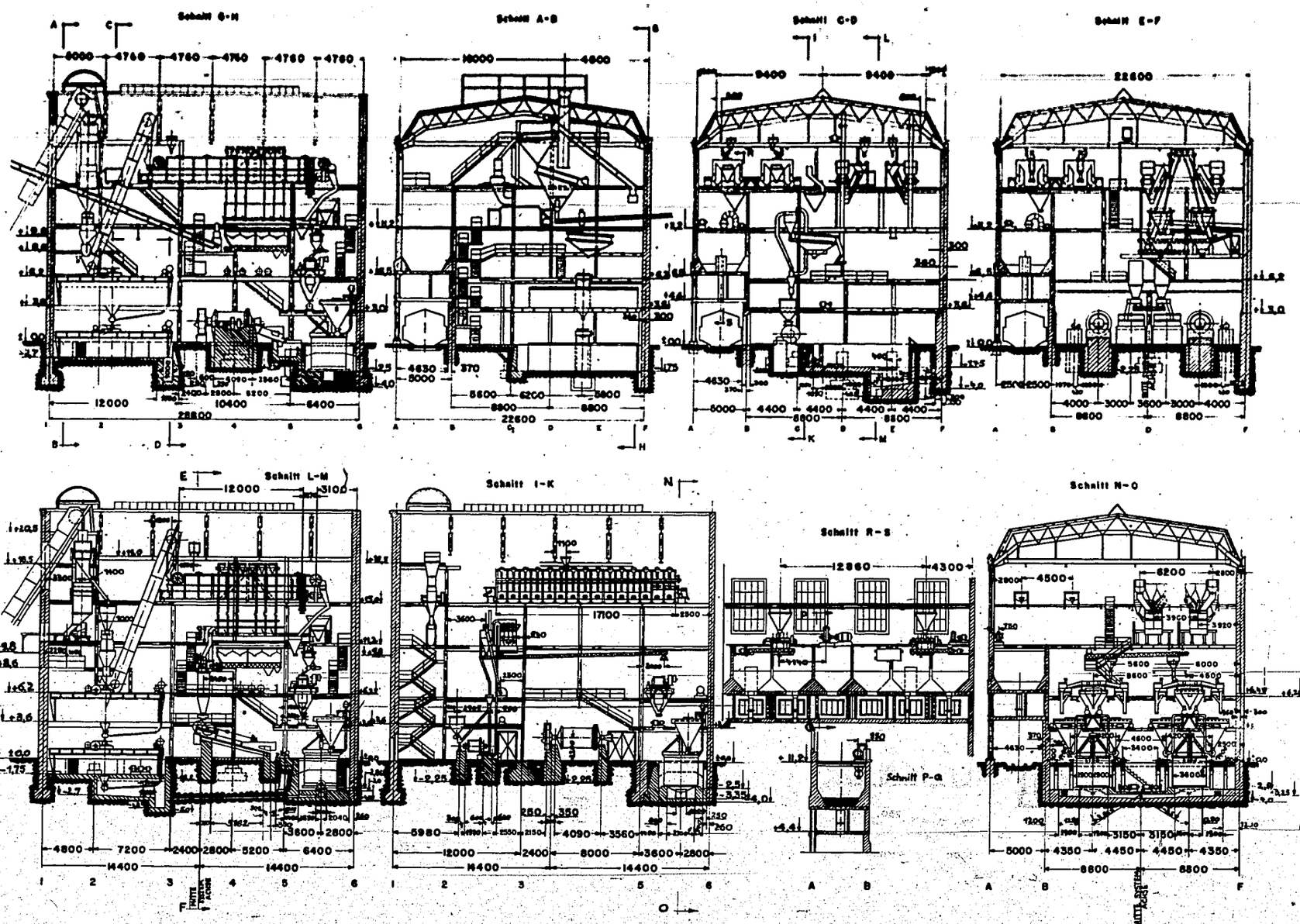

FIGURE II – SOME SECTIONS OF THE REINSTKOHLE PLANT AT KOENIGEN ELIZABETH.

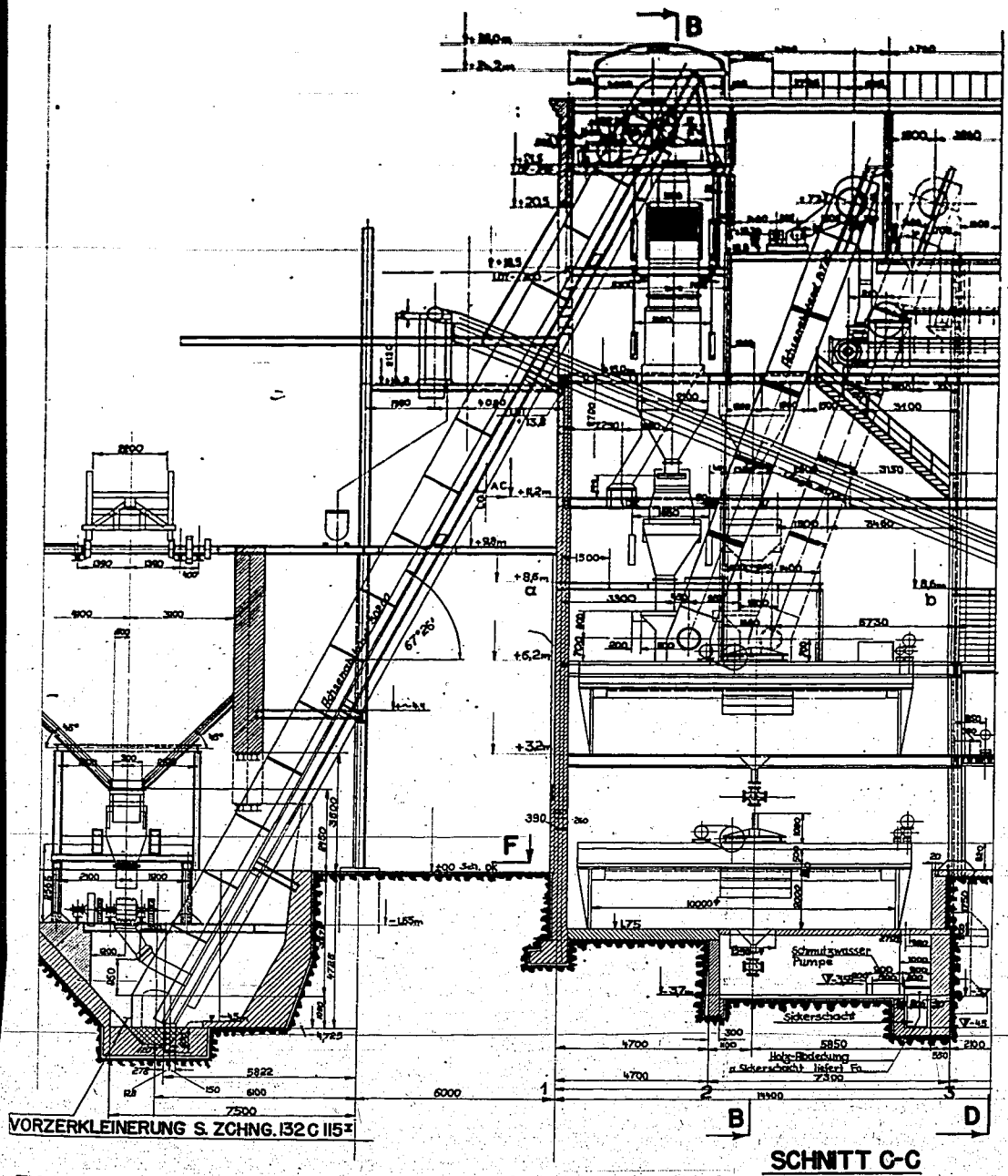

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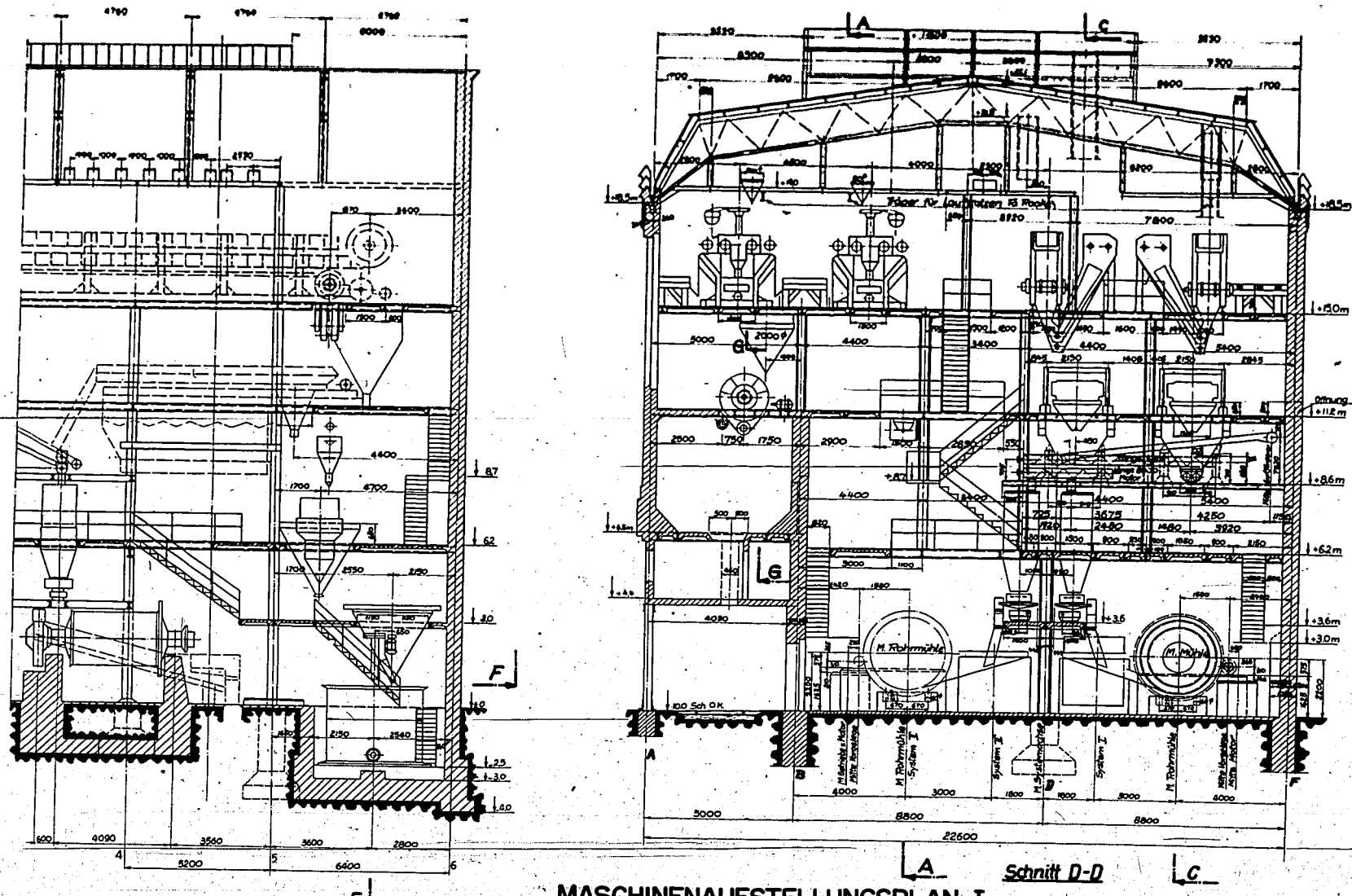
FIGURE 12 - GENERAL LONGITUDINAL SECTION OF REINSTKOHLE PLANT AT KOENIGEN ELIZABETH

PART I



MASCHINENAUFSTELLUNGSPLAN I
EINER REINSTKOHLE-HERSTELLUNGS-ANLAGE

Belastungsangaben s. Zchg. II F 723 II

ZECHE KÖNIGIN ELISABETH, SCHACHT WILHELM.

FIGURE 12 - GENERAL LONGITUDIAL SECTION OF REINSTKOHLE PLANT AT KOENIGIEN ELIZABETH PART II

The wet process centers around the Laminarström heavy media wash box devised by Dr. Vogel to attempt to separate grains as small as 1 mm. in a very finely pulverized magnetite suspension, whereas the older heavy media separators of Troop and de Vooys had heretofore handled only material down to 5 mm. size.

The dry method, proposed by Lurgi Apparatenbaum, centers around the treatment of 1½ mm. x 0.1 mm. grains by electrostatic separators.

Complete plant equipment to operate by these two methods had been installed at Koenigen Elizabeth, but the electrostatic separators had not yet been placed in operation, and the second Laminarström plant had worked only experimentally when the plant was partially demolished by bombing.

Operation was to concentrate on coal from the widely known Finefrau seam operated extensively in the Ruhr and in the South Limburg field of Holland as well.

A flow sheet of the Reinstkohle plant is shown in Figure 13, page 53. The feed to the plant is hand-picked coal broken to pass a 60 mm. bar screen. The 60 mm. x 0 feed coal delivered to the plant at the rate of approximately 12 tons an hour is crushed and sized over 8 mm. cloth on an inclined mechanical vibrating screen (1); the 8 mm. x 0 undersize from this screen is then dedusted over an identical screen with 3/4 mm. cloth. The oversize of the first screen (8 mm.) is returned to the crusher which operates thus in closed circuit to deliver the entire feed finally at 8 mm. x 0 size. The screens are 3 meters long x 1½ meters wide.

The sized feed coal of 8 mm. x 3/4 mm. or 10 mm. x 3/4 mm. which amounted to about seven and one-half tons per hour, 62.7 per cent of the raw feed, was handled in one Vogel Laminarström washer.

The Laminarström washer is a rectangular box 18 meters long by approximately 1 meter wide and 1 meter deep placed in a horizontal position. A slow-moving scraper line traverses the upper part of the box. This scraper line consists of two strands of matched roller chain which operates entirely above the liquid in the box but carries pivoted rectangular scraper flights that dip into the liquid on the lower run traveling from the feed end to the discharge end of the box. In this part of the run, the scrapers are held in a vertical position by outriders on either side of the attachments that secure the scrapers to the sidebars of the chain. The return run of this scraper line is above the box and clear of the contents.

In the bottom of the box is an entirely separate drag chain that conveys the sink material to the discharge end. Both scraper lines travel at such a velocity as to traverse the 18 meters length of the box in 3½ minutes.

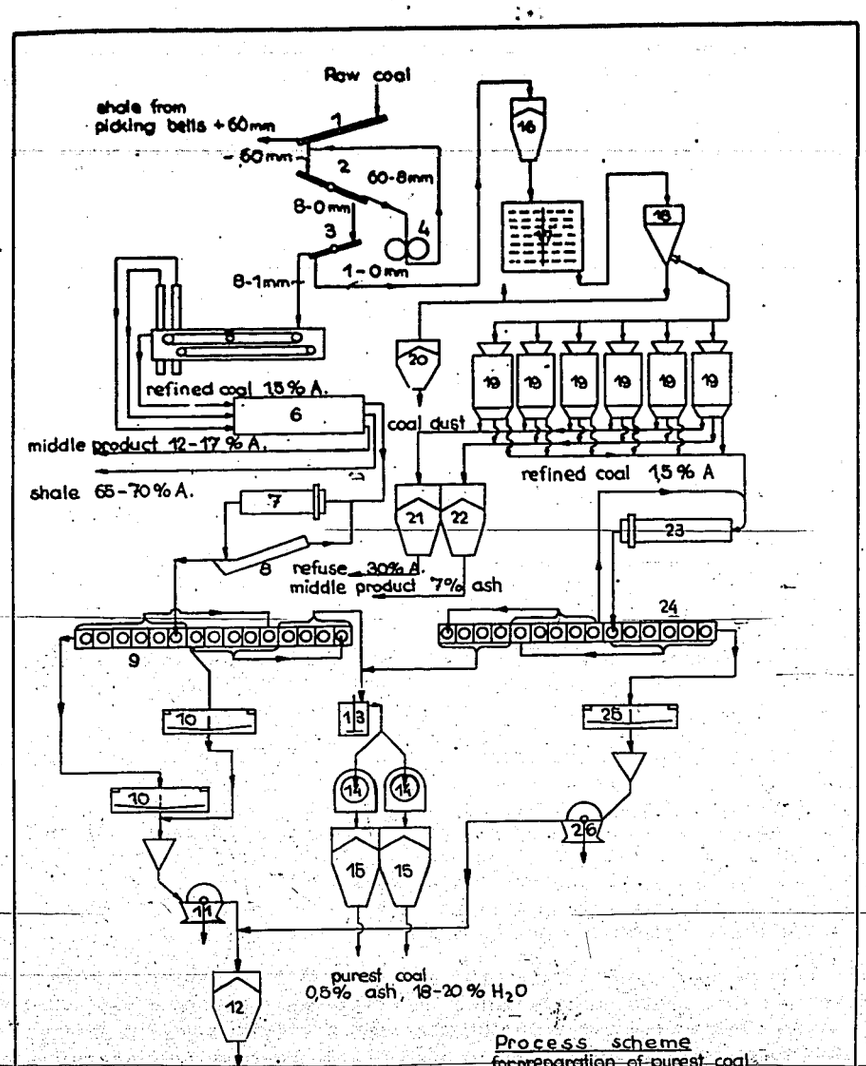


FIGURE 13 - FLOWSHEET OF SPECIAL REINKOHLE PLANT AT KOENIGEN ELIZABETH

The separating medium, a suspension of magnetite in water, flows through this box at a very slow rate. The theory of control of the separations is that the suspension solids of known size consist and controlled degree of dispersion at the moment of entering the box at the feed end will settle at a predeterminable rate during the interval in which the stream traverses the length of the box; and, hence, the effective specific gravity at the point of final separation of the load particles will be precisely determined, taking into account the settlement of the medium. This is presumed to be a more precise control condition than can be obtained by use of the so-called "stable" suspensions that are not perfectly stable, but a slight differential between top and bottom gravities in the box is ignored.

The function of the top scraper line, as conceived by the inventor, is to hold the top layer of the flowing stream in place and induce a more uniform slow rate of travel so that all parts of the top layer, divided up into inter-scraper sections, move at the prescribed rate throughout the length of the box.

The suspension is delivered to the feed end of the separator box by a series of return pipes purporting to start predetermined proportions of the medium in several superimposed layers of the stream in the box so as to further safeguard the uniform flow and the lamination of the moving contents of the stream.

The specific gravity of the feed suspension was controlled by a mechanical sampling and weighing device that diverted samples from the return line to a sample receptacle carried on a scale beam.

The operation was reported to have been based on a feed suspension gravity of 1.30 which at the delivery end of the apparatus resulted in a three-product separation. Due to interim differential settlement of the suspension, the top layer product discharged as pure coal carried 1.3 per cent ash, the bottom layer discharged by a refuse drag carried 86 per cent ash, and the intermediate layer discharged as a middling product carried 10 per cent to 14 per cent ash. The yield of pure coal was approximately 5.6 tons per hour.

The refuse and middling products dropped into separate submerged Redler elevator boots and the solid material was elevated and discharged to the rinsing screens by a two-compartment inclined Redler elevator with two chains in each compartment.

All three products: (1) pure coal, (2) middlings, and (3) refuse, are rinsed on one horizontal Schieferstein Resonance screen divided longitudinally into three compartments.

This screen is 8 meters long clothed with 0.25 mm. wedge wire in short sections of 1 meter length divided into steps with about 5 cm. drop between steps.

The layer of coal on the screen has a depth of 5 to 8 cm.. The screen is driven by an eccentric at 900 RPM by a 12 HP motor. The steel screen supports have an inclination of about 45° giving a substantial rise on the forward stroke.

The suspension is recovered by a magnetic separator. The suspension containing coal and shale slurry is fed to a rubber belt running over a magnetic drum pulley. The magnetite adheres to the belt and the water flushes away the non-magnetic coal and shale particles. Further on, the magnetite on the belt is demagnetized by alternating current and washed off into the storage tank.

The middlings of the Laminar box with about 15 per cent ash was added to the dry screened raw fines for briquetting purposes and the refuse was sent to the pit heap. The pure coal with 1.3 per cent ash content was milled in a ball mill (7) in closed circuit with a rake classifier (8) to return the oversize (over approximately 0.75 mm.) to the mill. The small particles under 0.75 mm. are delivered to the flotation plant (9). The Mineral Separation type frother reduces the ash content from 1.5 per cent to 0.7 per cent, the final froth product is treated in a froth destroyer (13) and then dewatered by the filters (14).

Figure 14 is a quantitative flow diagram of typical operation.

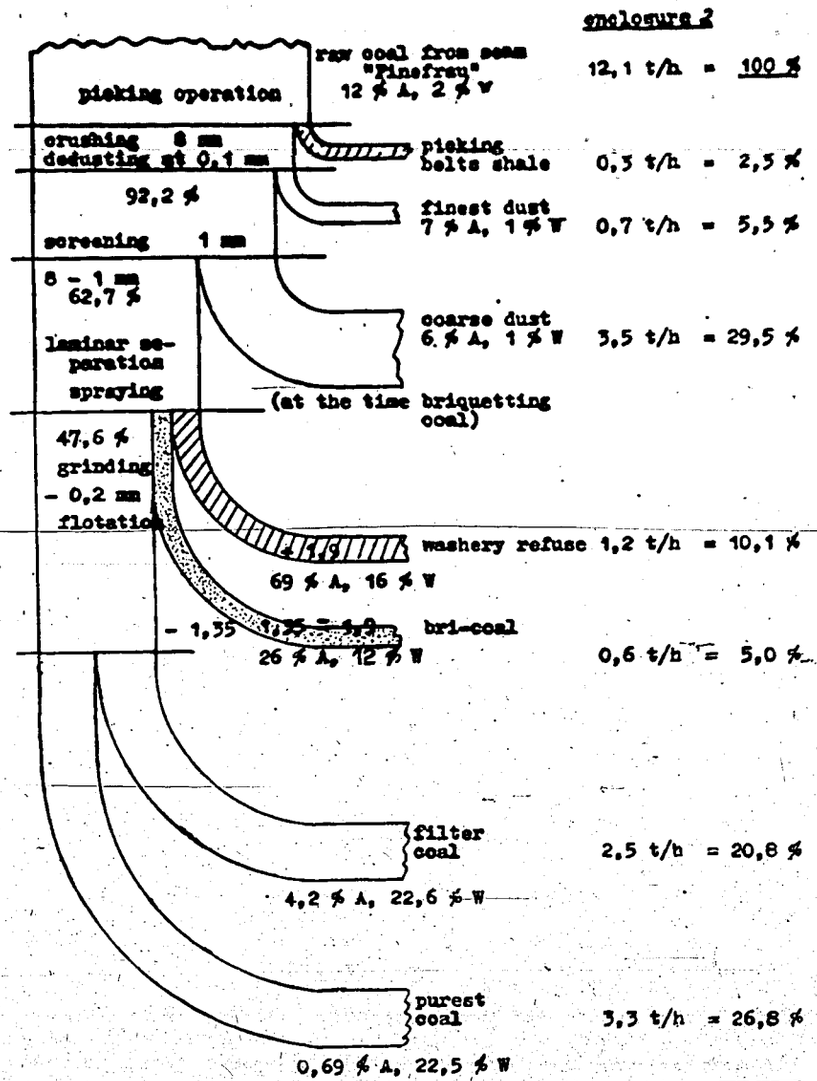
These data, furnished by Dr. Meyer of Bergbauverein, are representative performance data obtained during experimental operation of the first unit.

Electrostatic Separators

In the dry plant, the dedusted coal from screen (3) 1 mm. is fed to the electrostatic separators (19) after being dried in a Büttner Turbine dryer (17). The electrostatic separator plant consists of 6 machines, each provided with 12 separator units in two parallel banks of 6 units, one under the other, in this respect very much like the Johnson separator. The separator elements are 20 cm. in diameter and 2.5 meters in length.

The DC tension amounts to 25,000 volts. This installation has not yet been in operation and only laboratory experimental data were available; but the designers think the dry process will produce about the same product as the wet plant.

enclosure 2



Quantity floating picture

for production of purest coal in the purest coal plant Königin-Elisabeth according to the output obtained in February 1944 (1st stage)

FIGURE 14 - QUANTITY FLOW DIAGRAM OF KOENIGEN ELIZABETH REINSTKOHLE PLANT

19. Preparation of Hydrogenation Fuel

There has apparently been no special technique developed for the preparation of coal to be used in the Bergius process of producing liquid fuel.

Coal was supplied from a number of collieries in the Ruhr district including pits of Hibernia A.G., the state controlled mines, and the Nordstern pit near Gelsenberg.

In some of these plants the coal was washed by the conventional jigging system in which case only the coarse coal was used for hydrogenation and the fines carrying most of the fusain was diverted to the coke ovens.

The most commonly reported ash specification for hydrogenation coal is 4.0 per cent. Although it is considered very desirable, from an operating point of view, to have a lower ash coal, 4.0 per cent was apparently the most desirable specification for economic use of the fuel. The Ruhr coals will, in general, yield a coal of that grade by the conventional methods, but any substantial reduction below that level of ash content entails an uneconomical sacrifice in yield.

In heavy media plants, a clean coal of 4.0 per cent ash is commonly obtained by separation at around 1.45 specific gravity.

In some cases, it is reported that certain seams were worked separately to obtain a preferred coal for hydrogenation, that is, to obtain coal of favorable petrographic characteristics with high hydrogen content, low oxygen. It is important to have a high concentration of the brighter coal constitutents with a low proportion of fusain and opaque matter.

20. The Schieferstein Screen

The Schieferstein Resonance screen is very widely used in the Ruhr area for difficult sizing jobs and for heavy tonnages. It is considered to be more effective than normal shaking and vibrating screens.

A drawing showing the general arrangement of this screen is shown in Figure 15. Shop drawings of one balanced double deck design will be available in the files of Solid Fuels Subcommittee in Washington.

The unique feature of this screen is the Resonance element incorporated into the screen supports and drive arms. A picture drawing of one type of resonance supporting element is shown in Figure 16. These are in effect live rubber shock absorbers mounted between the main screen frame brackets and the fixed structure, as shown in Figure 15, in such a way that on each stroke one resonance element is compressed and the other extended, and on the reverse stroke these stresses are reversed. A somewhat similar element in the drive arms relieves the reactions that would otherwise be transmitted through the drive arms to the drive shaft. When the screen motion is synchronized with the harmonic period of the resonance elements, the machine is operating in resonance. Under these conditions, the energy requirements are very low and reactions transmitted to the supporting structure are at the minimum. A large part of the energy put into the resonance elements is returned to the screen on the reverse stroke.

Each type and model is tested in the works to ascertain the proper relationship of screen motion and resonance elements to arrive at the preferred operating speed and stroke. The screen is in resonance when driven at the speed that gives the maximum length of stroke ascertained by the shop test. A typical test curve showing the relation of stroke length to speed in strokes per minute is shown in Figure 17. In this instance the range of efficient operation would be about 375 to 405 RP

The resonance principle of operation has been applied to heavy mine run shakers and to light high speed dewatering and fine screening sieves. Control of the patents was vested in a syndicate which licensed three manufacturers: i.e., Carlshütte Maschinen and Stahlbau Gesellshaft, Waldenburg; Krupp-Gruson A. G., Magdeburg; and Klöckner-Humboldt-Deutz, A.G Cologne. Shop drawings are being obtained from the Humboldt firm.

The other two plants were not visited, but an interview was obtained with Dr. W. Kluge, formerly associated with Carlshütte, who is at the Branch Office temporarily located in Steele near Essen. An assembly drawing of one Carlshütte model of the Schieferstein screen will be in the file.

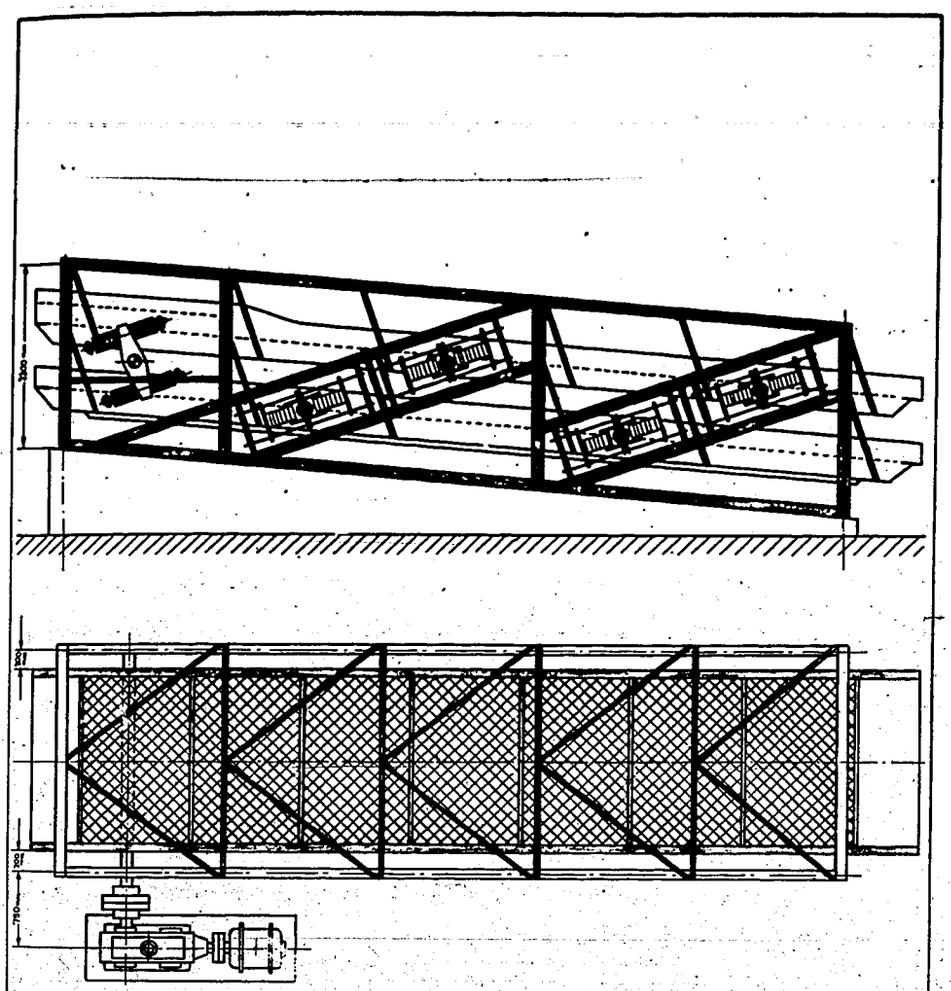


FIGURE 15 - THE SCHIEFERSTEIN RESONANCE SCREEN

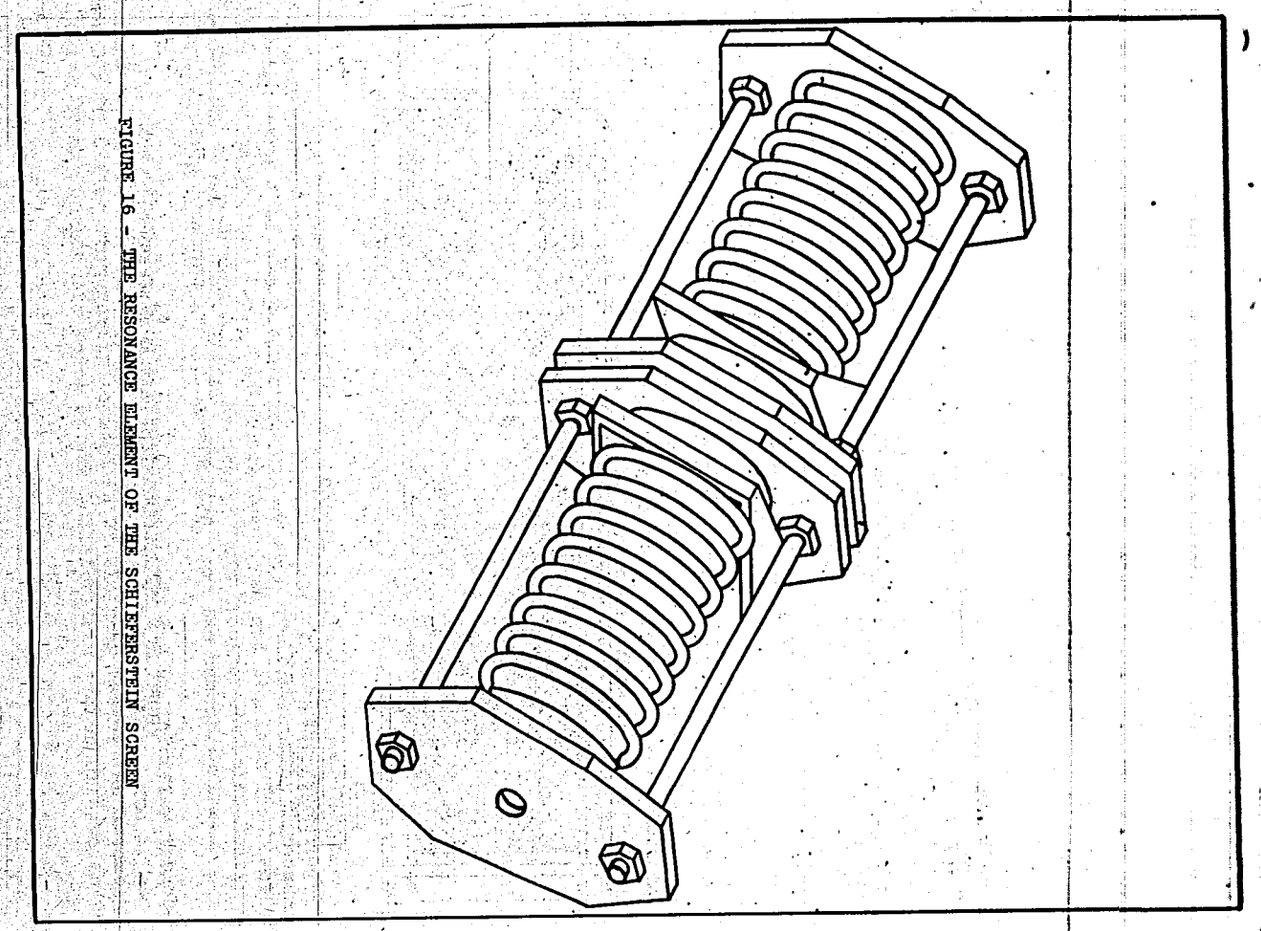


FIGURE 16 - THE RESONANCE ELEMENT OF THE SCHLEFERSTEIN SCREEN

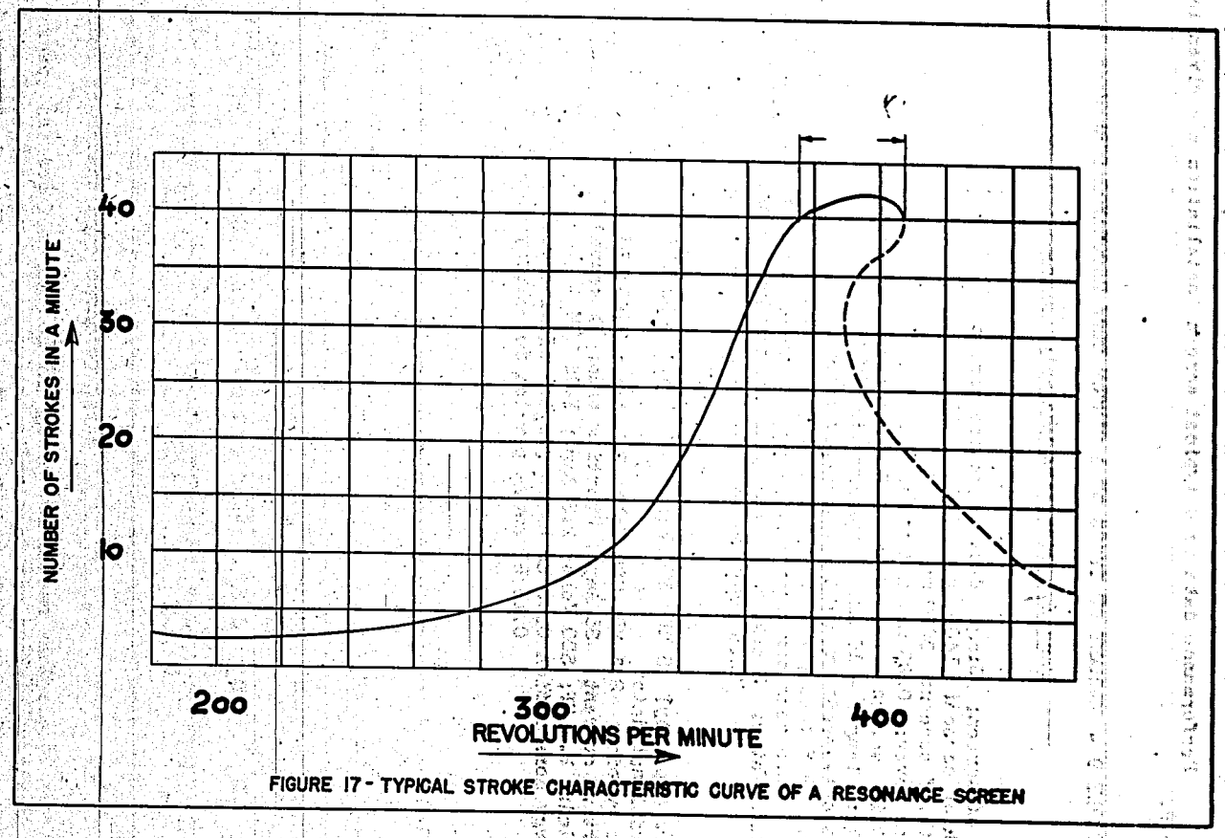


FIGURE 17 - TYPICAL STROKE CHARACTERISTIC CURVE OF A RESONANCE SCREEN

Performance data on a typical screen installation are given in Table 9.

TABLE 9 - SUMMARY OF TESTS OF A SINGLE DECK RESONANCE SCREEN

Part I - Operating Characteristics

Type of screen: Single deck Resonance screen
Width of screen: 1400 mm.
Length of screen: 5000 mm.
Screen cover: 0.25 mm. x 1.0 mm. mesh
Effective screen area: 4.2 x 1.3 = 5.5 square meters
Stroke: length - 10 mm. frequency 650 RPM
Transport-speed: v = 0.18 meters per second
Load: 29.5 tons per hour = 5.3 tons per square meter per hour of fine coal
16.8 tons per hour = 3.0 tons per square meter per hour of slurry
Rinsing Water: 3 sprays 7.5 cubic meters per hour each, totalling 22.5 cubic meters per hour

Motor capacity: 5 HP; 500 Volt: 5.7 Amp.; 1435 RPM
Operational data:
Idle running: 2.3 HP; 500 Volt; 2.3 Amp.; 1465 RPM
Starting current: 35 Amp., Starting time: 1 second
Loaded: 2.6 HP; 500 Volt; 2.6 Amp.; 1466 RPM
Energy consumption 0.09 HP hours per ton of fine coal
0.15 HP hours per ton for slurry

Part II

Screen

a) Fine Coal - 6 mm. x 0

Date of Test	Sample	No. of Sprays	T/H	Over 6 mm. Wt. %	Over 6 mm. Ash %	6 mm. x 3 mm. Wt. %	6 mm. x 3 mm. Ash %	3 mm. x 1 mm. Wt. %	3 mm. x 1 mm. Ash %
7.6.43	A			2.1	8.1	26.0	4.5	40.7	4.9
10 - 12h	B	1	a25	1.2	9.5	23.6	6.3	46.2	6.1
	C			-	-	-	-	-	-
7.6.43	A			1.2	13.3	24.4	7.5	41.4	6.8
13 - 15h	B	2	a25	1.4	8.9	23.9	7.2	46.4	7.6
	C			-	-	-	-	-	-
x	A			1.6	11.7	25.3	7.1	42.6	7.4
8.6.43	B	3	29.5	1.2	14.7	24.2	7.9	47.9	8.0
10 - 14 30h	C			-	-	-	-	-	-

b) Slurry 1 mm. x 0

x	A			0.8	9.0	0.8	7.9	2.1	8.2
9.6.43	B	3	16.8	0.7	13.4	1.5	13.6	4.5	6.6
10 - 13h	C			-	-	-	-	-	-

x - Items so marked were capacity tests

In end test, the top line marked "A" gives the screen analysis of the feed coal: the second line "B" gives the screen analysis of the oversize product; and the third line "C" gives the screen analysis of the undersize product.

Performance Data

Analyses

1 mm x 0.5 mm Wt. %	1 mm x 0.5 mm Ash %	0.5 mm x 0.25 mm Wt. %	0.5 mm x 0.25 mm Ash %	Under 0.25 mm Wt. %	Under 0.25 mm Ash %	Average Ash %	Solids and Water: Solids Grams Per Liter	Solids and Water: Water Per Cent
15.7	9.8	9.3	23.3	6.6	37.6	10.7		69.0
18.8	10.5	8.6	20.6	1.6	33.2	7.9		23.2
-	-	18.2	52.2	81.8	48.6	47.6	60	-
17.3	12.9	8.8	26.6	6.9	37.9	11.3		65.1
18.1	14.6	8.5	25.3	1.7	39.2	11.3		20.7
-	-	10.4	21.9	89.6	37.1	35.6	48	-
16.3	13.6	7.7	27.0	6.5	39.2	12.7		69.0
17.5	16.5	8.0	27.9	1.2	36.8	12.1		24.6**
-	-	18.1	58.2	81.9	44.8	45.9	58	-
5.1	7.5	22.5	5.7	68.7	18.2	15.5	242	-
17.6	3.9	42.3	4.7	33.4	11.7	7.2	-	35.4
-	-	5.2	12.0	94.8	25.3	25.0	126	-

** Moisture after 24 Hours — 7.9 Per Cent

Now that two of the three syndicate members are not readily accessible to the industry of Western Germany, there is a project, sponsored by the preparation plant builders, to establish a new Schieferstein screen fabricating shop in the Ruhr area.

For deslimng fine coal at 1 mm. or finer, the Humboldt screen specialists recommend Schieferstein screens at about 480 RPM with a rating of 4 to 5 metric tons of 8 mm. x 0 feed coal per hour per square meter of effective screen area.

21. The Wedag Counter-balanced Vibrating Screen

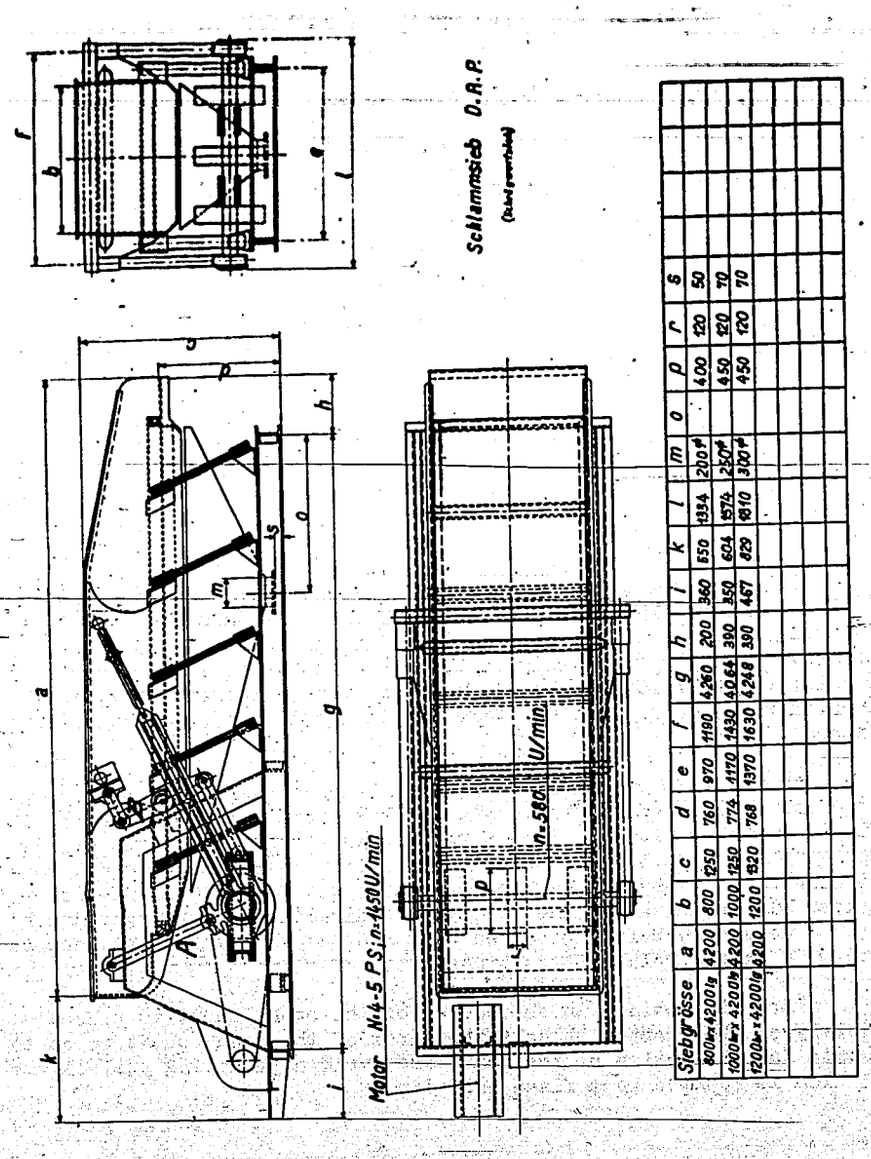
This screen devised by the staff of Westphalia-Dinnendahl-Gröppel, A.G., is shown in general assembly in Figure 18.

The unique feature of this machine is the counter-balancing scheme which apparently is very effective. The test unit operated on the floor of the works runs (without load) so smoothly that a pencil will stand up on end on the supporting frame. Several units observed in operation in the field appeared to be running very smoothly and were generally praised by the local operating officials.

Balanced operation is obtained by mounting the drive shaft in a heavy floating counter-weight member hung from the supporting structure by two swinging links "A". The machine is so designed that the combined weight of the drive assembly consisting of the crankshaft with its flywheels and drive pulley, the pillow blocks and heavy cast iron members on which they are mounted with the supporting links "A" is equal to the weight of the screen body.

The drive shaft is a single offset crank shaft with a drive arm on the crank at each end of the shaft and the shaft itself is carried in the floating pillow blocks. Thus there are in effect two driven elements in balance — the screen body connected to the drive arms and an equal counter weight connected to the pillow blocks. These two counter-balanced elements are driven with equal amplitude in opposite directions. The pantegraph Arm B is a device to hold the screen body and the floating drive support structure in proper relative positions.

The drive pulley in the center of the crank shaft is placed eccentrically on the shaft with half the throw of the crank shaft so as to compensate for the motion of the shaft and avoid a pulsating pull on the motor which is mounted in a fixed position.



Siebgrösse	a	b	c	d	e	f	g	h	i	k	l	m	o	p	r	s
800×4200 lg	4200	800	1250	760	970	1190	4260	200	360	550	1334	200		400	120	50
1000×4200 lg	4200	1000	1250	774	1170	1430	4064	390	350	604	1574	250		450	120	70
1200×4200 lg	4200	1200	1320	768	1370	1630	4248	390	467	829	1810	300		450	120	70

FIGURE 18 - WEDAG SLURRY SIEVE

22. The Wedag Vibratorsichter (Deduster)

This is an aspirating dry dedusting system developed by Westphalia-Dinnendahl-Gröppel, A.G. and used in their preparation plants for pre-dedusting of the fine coal before jigging. The dust is extracted from the coal by a high velocity air current passed upwardly through the coal while it is traversing a high speed vibrating screen.

Dimension drawings of the principal elements in a typical plant are available in the file of the subcommittee.

The dust carried up by the air stream is first settled in a coarse coal catching chamber where the granular material is deposited and thence to a cyclone in which the fine dust is settled. The dust catchers and the transferring column above the screen are operated under suction of about 15 to 20 mm. of water measured above the coal feed screen. The fan is placed on the suction side of the collector.

In some installations the air is handled in a closed circuit, in which case about 25 per cent of excess outside air is taken in by leakage at and above the screen, and an equal amount must then be diverted to a fine dust collector back of the cyclone which discharges 25 per cent of the circulating air load to the air. This may be a bag filter or a water spray dust catcher. Where wet coal is to be anticipated, the excess air must be increased.

The typical dedusting unit has a net screen area of 125 cm. by 150 cm. set at an inclination of 4° from the horizontal. The screen is a round hole punched plate with 1.5 mm. openings. The pattern is 460 holes per square decimeter to separate the coal at 0.3 mm. size and 570 holes per square decimeter to separate the coal at 0.5 mm. size. The air circulation is at the rate of 400 cubic meters per minute and the pressure at the fan discharge is 60 to 100 mm. of water.

The rated capacity of such a unit is 50 tons per hour of 10 mm. x 0 coal.

In some installations, heated air has been used to advantage for handling wet coal. It increases the effectiveness of dedusting and partially drying the dedusted coal, but performance data were not available.

23. Humboldt Rapidsichter (Deduster)

In the Humboldt deduster, the fine coal is introduced into the air stream in a thin curtain that falls through the rising air current and then discharges to the storage hopper via an inclined fixed screen. This screen serves mainly as a chute for the dedusted product, although the circulating air current passes upward through the screen before coming in contract with the feed coal.

The coal is fed evenly into the air stream by a rotating drum distributor that delivers the coal in a very thin stream across the entire width of the drum. In handling the dustladen air, the Humboldt deduster is similar to the Wedag system described above except that a Raymond type classifier is used to catch the granular coal ahead of the final air clarifiers which usually are cyclone collectors. The classifiers and cyclones are sometimes lined with porcelain tiles to eliminate replacement delays.

A typical drawing of a double unit Humboldt deduster is shown in Figure 19. The curves of Figure 20 show typical performance data, and Figure 21 gives some typical data on the effects of moisture and overloading on the efficiency of operation.

At a large washery installation handling Westphalia coal, two of these Humboldt dedusting units handled 220 tons per hour of 10 mm. x 0 coal. Each unit consisted of 1 double deduster, 2 classifiers, 1 exhaust fan and motor, 2 collectors, 1 feed hopper with feeders, and 2 gear boxes with motors. Data on performance of this plant are given in Table 10.

TABLE 10 - PERFORMANCE (MONTHLY AVERAGE) OF HUMBOLDT DEDUSTER PLANT

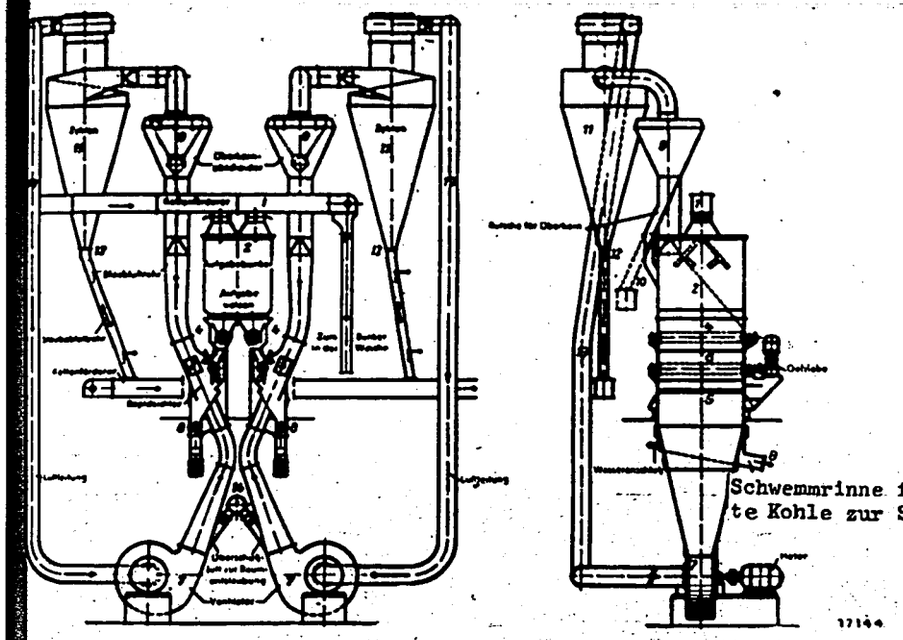
a) Dedusting set at 0.5 mm. size
   Dust in feed: 22.3 per cent - 0.5 mm. x 0
   Dust in dedusted coal 2 - 5 per cent - 0.5 mm. x 0
   Oversize in dust: 13 per cent plus 0.5 mm.
   Moisture content of feed: 2.1 per cent

b) Deduster set at 0.3 mm. size
   Dust in feed: 14 per cent - 0.3 mm. x 0
   Dust in dedusted coal: 2 per cent - 0.3 mm. x 0
   Oversize in dust: 11 per cent plus 0.3 mm.

24. The S.K.B. Froth Breaker

This is a device used to break down the froth from the flotation machines to facilitate handling and filtering of the product. It is similar in effect to the Elmore Vacuum flotation machine in that the froth is dispersed in vacuum.

A schematic drawing of the device is shown in Figure 22. The froth from the flotation machines is discharged at rather high velocity into the vertical cylindrical vacuum tank where it impinges upon a central baffle plate. Details of the vacuum tank are shown at the left side of the illustration and the sequence of operations is shown in the upper right hand sketch. The air is exhausted from the tank by the water ring vacuum pump. The defrothed coal slurry discharges through the conical tank hopper and then goes to the vacuum filters. The sponsors of this



Schwemmrinne fuer entstaubte Kohle zur Setzmaschine

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Schema einer Humboldt - Sichtanlage nach dem Umluftverfahren

FIGURE 19 - THE HUMBOLDT DEDUSTER

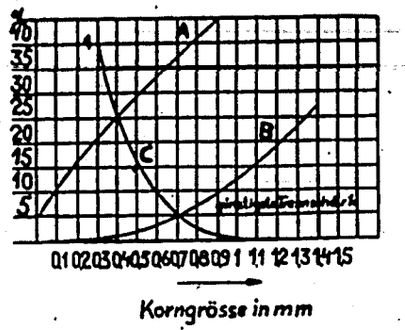


FIGURE 20. - HUMBOLDT DEDUSTER PERFORMANCE SEPARATING AT 0.7. MM WITH RAW COAL OF 2.8% MOISTURE.

Curve A - Screen Analysis of 3 mm. x 0 Raw Coal
Curve B - Screen Analysis of Dedusted Coal
Curve C - Screen Analysis of the Dust.

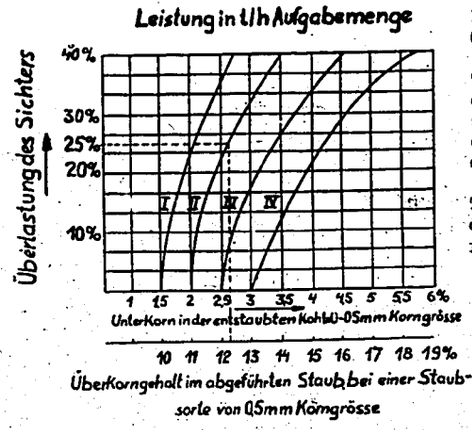


FIGURE 21 - THE HUMBOLDT DEDUSTER - EFFECT OF MOISTUPE AND OVERLOADING ON PERFORMANCE.

The vertical scale shows percentage overload. The horizontal scale shows per cent undersize in dedusted coal; and lower scale, per cent of oversize in the dust.

The different curves refer to different moisture contents of the feed coal;.
Curve 1 - 2%
Curve 2 - 3%
Curve 3 - 4%
Curve 4 - 5%

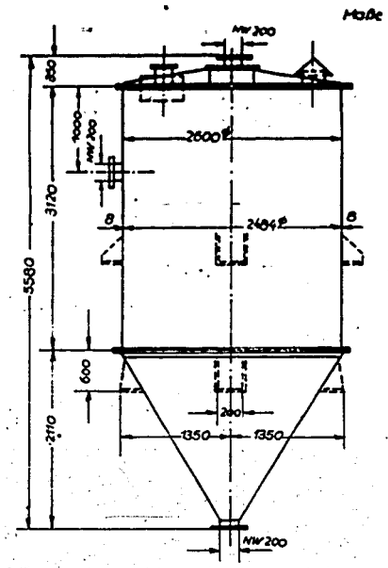
The example for curve No. 2: A 25 per cent overload of 3% moisture feed makes 2.6 % undersize in the dedusted coal and 12.3 % oversize in the dust.

Vakuum-Schaumzerstörer

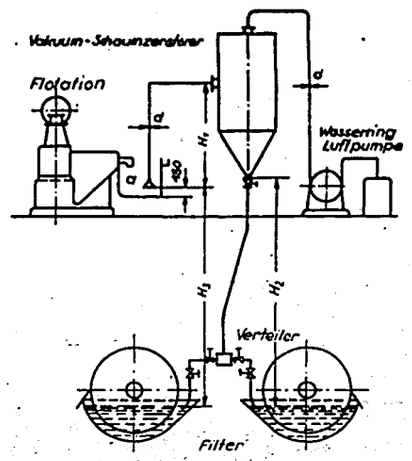
Bergbau

DIN

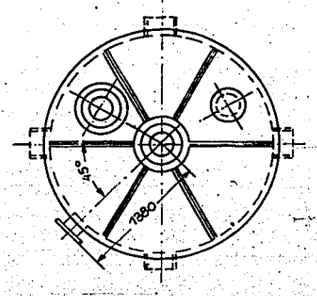
Maße in mm



Einbau eines Vakuum-Schaumzerstörers



Bezeichnung eines Vakuum-Schaumzerstörers 2500
Vakuum-Schaumzerstörer 2500 DIN 23130



Flotations-Konzentrat l/h	Wasserringluftpumpe Saugstutzen d mm	Angesaugte Luftmenge m³/min
< 10	150	20
10 – 20	150	26
20 – 30	200	32

Höhen in m					
H_1	2	4	6	8	9
H_2	5	6	7	8	8
H_3	7	6	5	4	3

Höhenlage und Umfangsstellung der Tragpratzen können den jeweiligen Einbauverhältnissen angepaßt werden. Bei Fehlen einer besonderen Vorschrift werden die Tragpratzen nach den eingetragenen Maßen ausgeführt.

Für die Werkstattausführungen sind die Einheitszeichnungen der Arbeitsgemeinschaft Aufbereitungsmaschinen maßgebend.

Hauptausschuß Maschinen beim Reichsminister für Munition und Kriegsproduktion
Arbeitsgemeinschaft Aufbereitungsmaschinen
Fachnormenausschuß für Bergbau beim Deutschen Normenausschuß.

FIGUPE 22 - THE S.K.B. VACUUM TANK FROTH BREAKER

device report that it doubles the rate of filtering as compared to the method of filtering the frothy product direct from flotation machines.

The table in the illustration gives the principal design data and load rates. These data in English translation are given in Table 11.

TABLE 11 - DATA OF THE S.K.B. VACUUM FROTH DESTROYER

Flotation Concentrate Tons Per Hour	Water Ring Air Pump	
	Suction Pipe Diameter mm.	Amount of Air Aspirated Cubic Meters Per Minute
10	150	20
10 - 20	150	26
20 - 30	200	32

HEIGHTS IN METERS
Possible Combinations

H_1	2	4	6	8	9
H_2	5	6	7	8	8
H_3	7	6	5	4	3

25. Discharge of Fine Coal From Bunkers

In the S.K.B. plants, froth flotation filter cake is stored in narrow conical hoppers fitted with rotating plate discharge gates that are reported to be effective for handling extremely sticky wet fines that ordinarily give much trouble in chutes and bins.

A rough sketch of this device is shown in Figure 23. These hoppers are always limited to one meter in diameter at the bottom discharge end and the sides are almost vertical 80° to 85° from the horizontal. The entire bottom of the hopper is open and the contents are retained by a rotary plate gate a little below the bottom of the bin.

To discharge material, this plate is rotated at a per second peripheral speed of about 50 centimeters per second. The coal in contact with the disc is moved out toward the periphery by centrifugal force and is plowed off into the conveyor by a steel blade set at an angle on the rim of the disc.

In an alternate design for the most stubborn materials, shown in the right hand view, a conical member is substituted for the plane discharge disc.

26. Washery Control Devices

Automatic control devices for wash boxes are similar to those in common use in American and British fields. A float riding on the slate bed communicates its motion to an oil operated piston that opens and closes the slate gates.

In a modification of this system found in a few of the S.K.B. washeries, the motion of the float is communicated also to the air inlet valves so that an excessive accumulation of slate in the wash boxes brings about an increase in the air introduced into the pulsion chamber.

Fine coal jigs, even those operating with feldspar, use these floats to regulate the discharge of refuse.

In the heavy media washers, two methods of control were observed. (1) Measured samples of the medium were weighed at intervals to determine its specific gravity. In some plants mechanical devices were used to automatically weigh a measured quantity of medium recovered from the rinse water circuit and to recirculate the pulp back to the thickening device when the specific gravity is too low. (2) A specific gravity indicating device consits of two static tubes inserted into the bath at a measured difference in level. Air is introduced through both tubes so that it bubbles at a uniform rate into the bath and a sensitive pressure guage in a U tube connection linking the two measuring points registers the difference in pressure between the two levels in the bath.

Figure 24 shows a scheme advanced by one of the plant building firms for maintaining a constant rate of delivery to the washery. This consists essentially of an automatic diverting gate to by-pass peak loads and store the excess of raw coal in a hopper from which it can later be returned to the main circuit during a slack period.

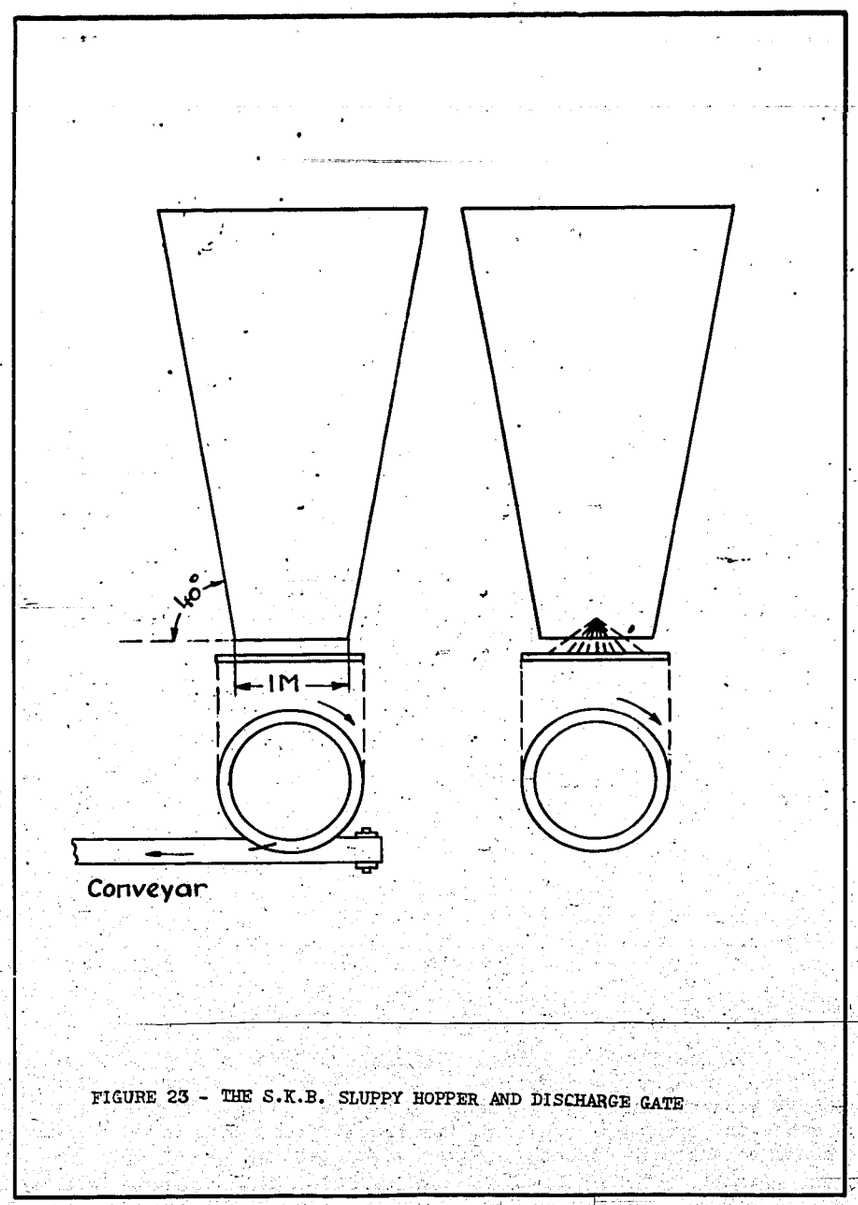
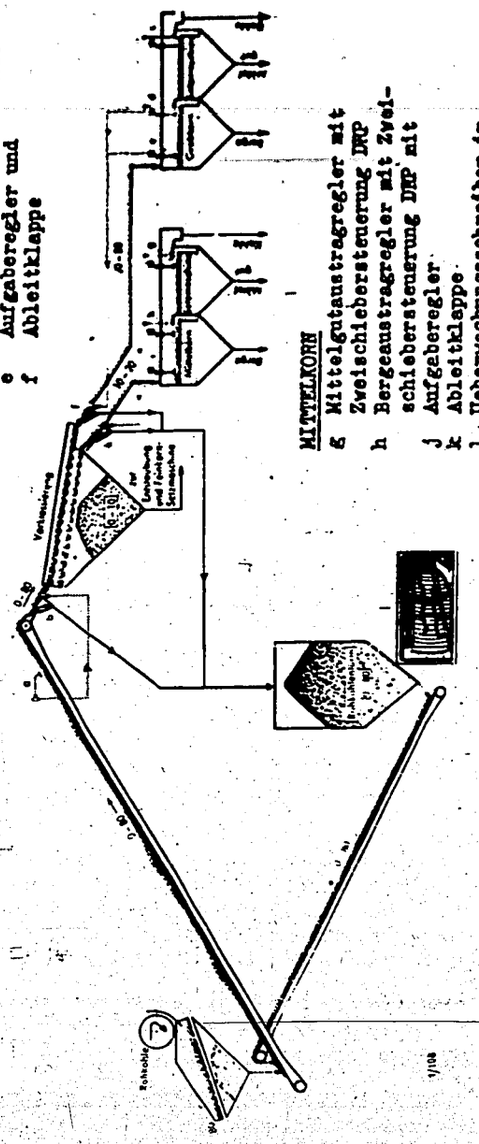


FIGURE 23 - THE S.K.B. SLUPPY HOPPER AND DISCHARGE GATE

a. Taster oder Bandwage mit mit Zeitrelais fuer Rohkohlenaufgabe und
b. Rohkohlen Ableitklappe

GROBKORN

c Mittelgutaustragregler mit Zweischiebersteuerung DRP
d Bergeaustragregler mit Zweischiebersteuerung DRP mit
e Aufgaberegler und
f Ableitklappe



MITTELKORN

g Mittelgutaustragregler mit Zweischiebersteuerung DRP
h Bergeaustragregler mit Zweischiebersteuerung DRP mit
j Aufgaberegler
k Ableitklappe
l Ueberwachungsschreiber im Buero fuer Aufgabe - und Austragregler Steuerleitungen.

FIGURE 24 - SCHEME FOR REGULATING DELIVERY OF RAW COAL TO WASHERY BY DIVERTING AND RECIRCULATING PEAK LOADS

27. The Electrostatic Separator

At Koenigin Elizabeth Colliery the Reinstkohle plant was being equipped in one section with Electrostatic Separators furnished by Lurgi Apparatenbaum A.G., of Frankfurt.

Research of the application of the electrostatic process to the ultra refining of fine coal for special uses was undertaken by this firm as a part of the wartime development program already referred to above. It appears that these researchers followed the principles embodied in early electrostatic separaters exploited in America by the Huff Electrostatic Separator Company. The experimental work for the Koenigin Elizabeth plant was done at the research laboratory of Lurgi Apparatenbaum in Mousonstrasse, Seckbach, Frankfurt. This plant was visited November 21, 1945. There is now a small laboratory apparatus in condition to operate sufficiently to demonstrate the process; Dr. Weindel and Dr. Zopf are available at the laboratory or at the offices of the company in temporary quarters in Böhmerstrasse 10, Frankfurt.

The separating element consists of a horizontal polished rotating drum and parallel to it a filament housed in a recess in a fixed cylinder. This filament is said to produce the electrostatic field in the area between these two parallel elements by a spray of ions. The tension may be regulated in a range of 15,000 to 45,000 volts. The finely divided and closely sized coal is fed over the moving roller which turns over towards the filament. This roller acts as a feed distributor as well as taking part in the separation. The feed is evened out on this roller by an adjustable blade-shaped control gate.

The feed particles receive an electrostatic charge upon entering the charged area. Those which have a high conductivity give up their charges immediately to the feed drum and drop vertically from it, while the particles of lower conductivity retain their charges longer and are carried farther around on the drum so that they are discharged into a separate hopper.

The Lurgi specialists are of the opinion that fusain can be separated from the coal electrostatically because it has a higher conductivity than clarain and durain. Closely sized feed is essential to effective operations and the size range was reported to be $1\frac{1}{2}$ mm. to $\frac{1}{2}$ mm.

28. Loading Coal into Ships

Leading builders of cranes, bridges, and tippling appliances for handling coal at tidewater piers are J. Pohlig A.G., Cologne and Demag, A. G., Duisburg.

The general arrangement drawings of two outstanding installations by Pohlig -- one at Dresden and the other at Born, Holland -- are shown in Figures 25 and 26. The mechanical equipment comprises a traveling bridge spanning the railway tracks and/or storage piles, with a cantilever extension over the water way carrying a shuttle conveyor carriage and boom section to deliver into the ship's hold alongside. A crane operating on the bridge hoists the loaded car to the bridge level where it is placed upon a tippler that pours the contents out into a small feeder hopper then delivers it to a belt conveyor in the bridge structure. This belt in turn delivers its load to the shuttle conveyor for delivery to the hold.

In the Pohlig system, this loading conveyor is a steel bucket conveyor line that traverses the horizontal and inclined portion of the boom like a deep pan bucket line and in the adjustable vertical part, it functions like a bucket elevator running backwards, taking its load at the top. Upon rounding the tail sprocket, the buckets dump their contents into the hold of the ship through the casing of the conveyor which is open at the bottom. Figure 27 shows this anti-breakage device hoisted to its upper position to clear the ship. When operating, it is lowered through the hatch.

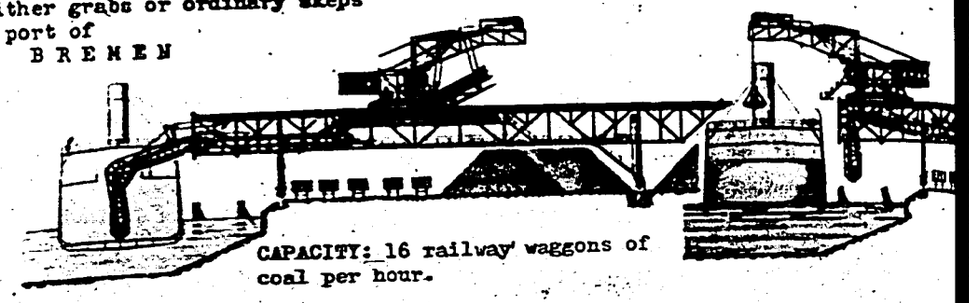
For loading canal barges, as at the Born piers on the Juliana Canal shown in Figure 26, the vertical lowering section is not required. This device is reported to be effective for preventing breakage when operated carefully. It is designed particularly to handle coke, briquettes and sized coal. The capacity of these bridges is reported to be as high as 1000 tons of coal per hour.

29. The Büttner Rotary Kiln Dryer

Büttner Werke supplies an interesting innovation in the inside equipment of conventional rotary kiln dryers which is said to increase the efficiency. The interior of the shell is traversed longitudinally by cross-shaped (+) steel plate shelves so arranged that the material cascades gently from shelf to shelf as the shell turns. After one complete turn from the feed end, the load is uniformly distributed among all the shelves which are, in turn, distributed over the cross-section of the shell. By this means the load is effectively exposed to the drying effect of the hot gases traversing the shell. The accompanying sketch, Figure 28, shows approximately the arrangement of shelves in section. Longitudinally the shelves are broken into four or more separate banks (depending upon the length of the dryer), each set of shelves being generally 1.80 meters long.

At the discharge end of the dryer, there is a series of spiral guide vanes, similar to the spiral feed spout of a tube mill, that delivers the dried material from the shelves to the periphery of the shell where it is discharged.

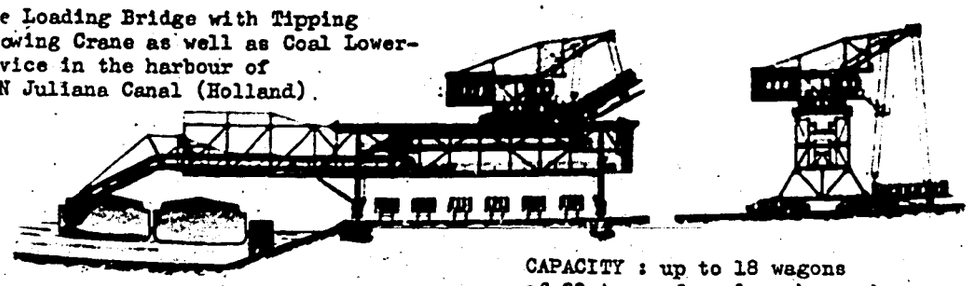
Movable Loading Bridge with Tipping and Stewing Crane and Coal Lowering Device, tipping as well as working with either grabs or ordinary skeps in the port of
B R E M E N



CAPACITY: 16 railway waggons of coal per hour.

FIGURE 25 - COAL HANDLING EQUIPMENT AT THE PORT OF BREMEN

ovable Loading Bridge with Tipping nd Stowing Crane as well as Coal Lower- ng Device in the harbour of BORN Juliana Canal (Holland).



CAPACITY : up to 18 wagons of 20 tons of coal each per hour

FIGURE 26 - COAL HANDLING EQUIPMENT AT THE PORT OF BORN, HOLLAND FOR LOADING BARGES ON THE JULIANA CANAL

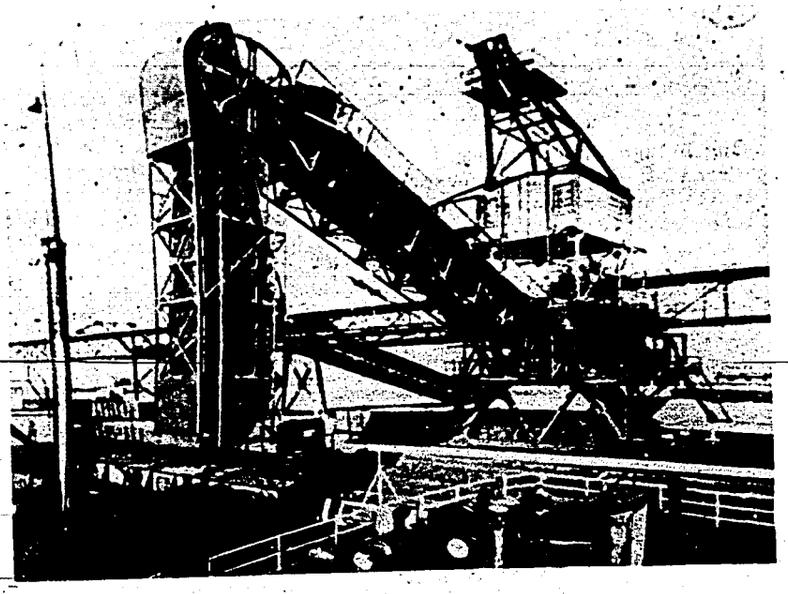


FIGURE 27 - THE POHLIG ANTI-BREAKAGE SHIPLOADING DEVICE

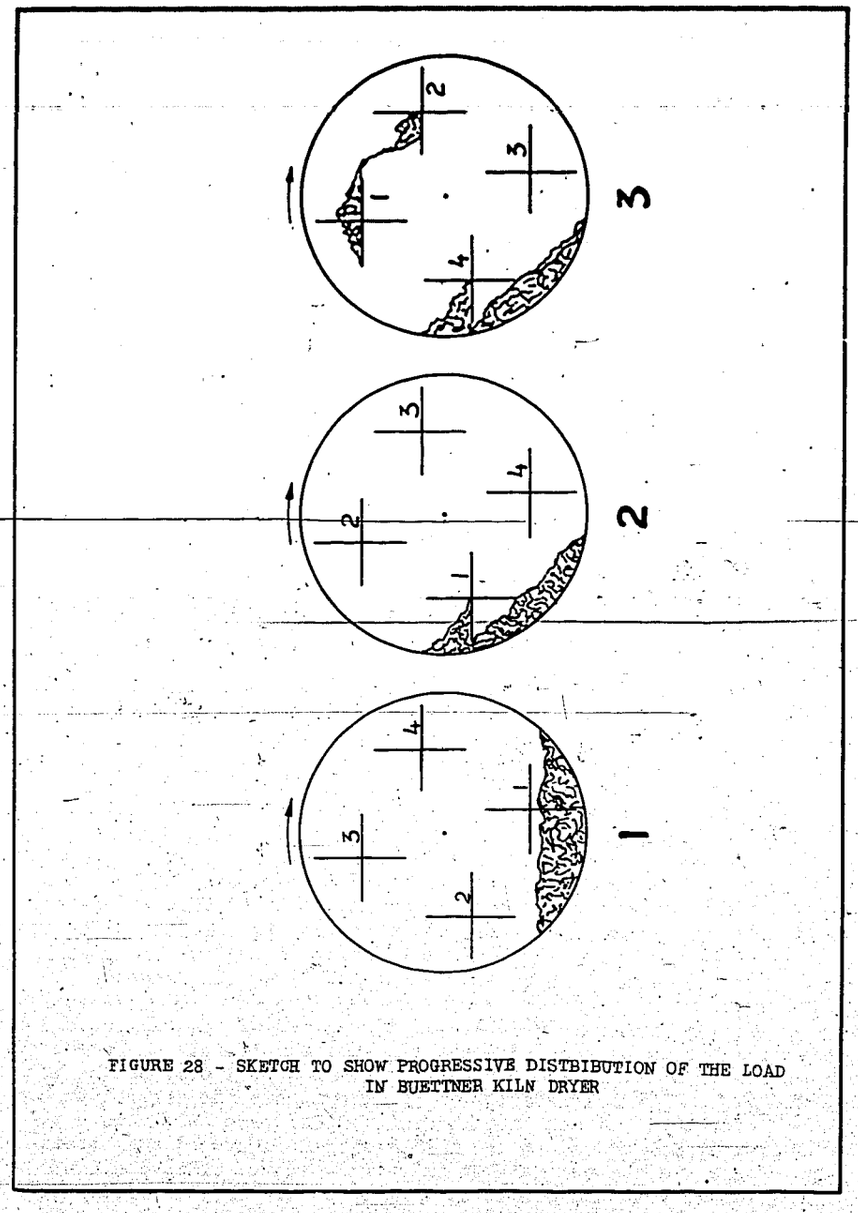


FIGURE 28 - SKETCH TO SHOW PROGRESSIVE DISTBIBUTION OF THE LOAD IN BUETTNER KILN DRYER

The temperature graph, Figure 29, shows the rate of change of temperature of the dryer gases and of the load material in the dryer with the circulatory gases traversing the kiln in the same direction as the load. In this graph, "l" is the length of the dryer and "t" is the temperature. The "a" curve shows the temperature of the gases and "b" shows the temperature of the load material. The manufacturer reports that the rapid drop in temperature in the first part of the dryer is characteristic of the Büttner design and is facilitated by the distributing vane arrangement.

30. The Turbo Dryer

The Turbo dryer is extensively used for agricultural and chemical products but is also adaptable to the drying of coal where it is important to handle the load gently to avoid breakage.

The dryer shell is a vertical cylindrical drum carrying a series of ring shelves arranged one above the other and supported on a central frame work around a series of turbine fans in the center that maintain a definite ventilating system. The shelf assembly rotates very slowly (10 - 15 minutes for one complete revolution). Figure 30 shows the general arrangement of the Turbo dryer.

The feed material to be dried is spread out uniformly on the uppermost shelf by a feeder above and it progresses downwards from shelf to shelf until it is finally discharged from the lowermost shelf.

This transfer from shelf to shelf is effected by means of discharge gaps placed axially in the shelves and dividing each shelf into a number of equal segment-shaped sections separated by discharge slots staggered with respect to those above and those below.

For each shelf there is a stationary flexible discharge blade that pushes the load off the shelf segment into the discharge slot following it when the segment passes under the blade. The first blade (for the top shelf) is located just behind the feeder so that the wet coal makes one complete revolution on the top shelf; it is then scraped off into the next shelf and the empty segment passes immediately under the feeder to receive a fresh load. There is also a spreading blade that levels off the conical pile on each shelf following the feeder.

The central fans maintain a circulation of the air current in opposite directions between adjacent segments and the air has a generally spiral motion. Thus, if the air enters from the periphery of the drum in the lowermost inter-shelf section, it is drawn into the central turbine and discharged into the next annular intershelf space above where it moves spirally outward and at the periphery passes upward and returns to the turbine via the next higher intershelf space. This continues until the air discharges at the center at the top at 98 per cent saturation.

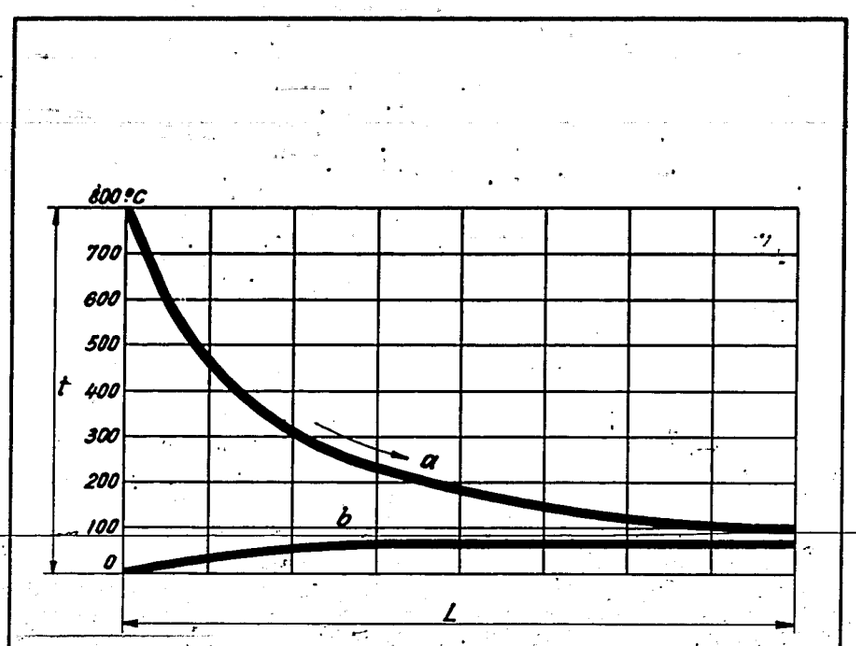
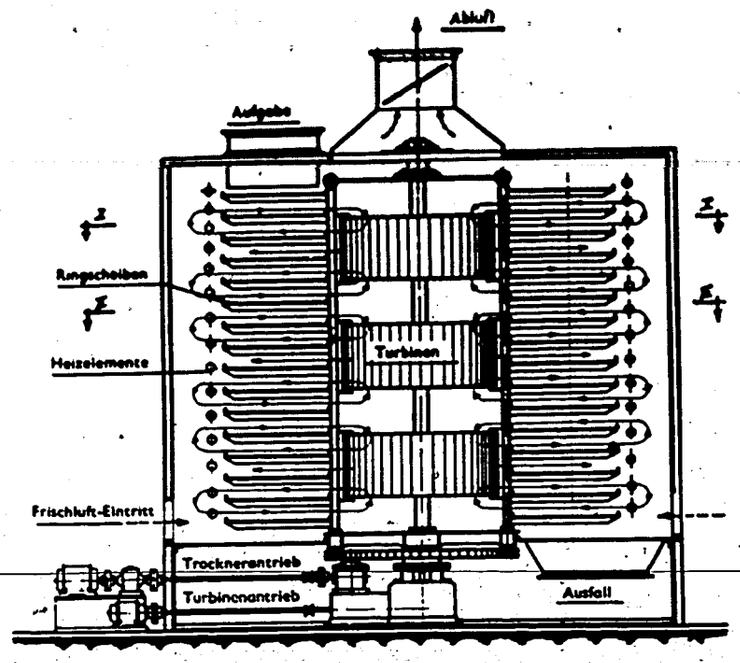
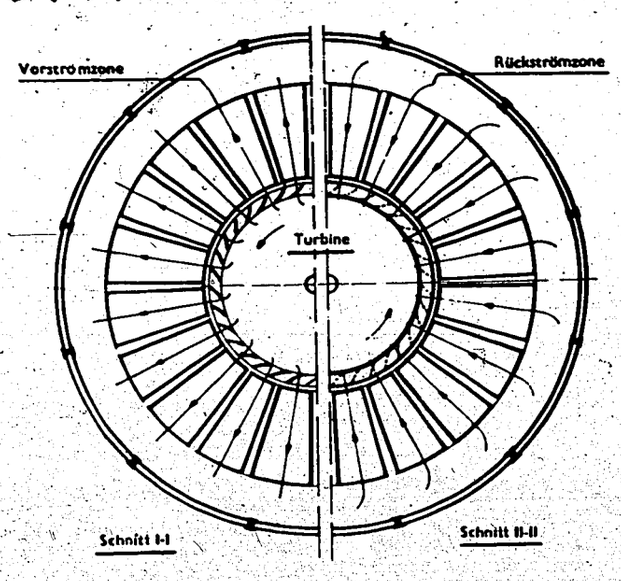


FIGURE 29 - RATE OF TEMPERATURE CHANGE OF GASES AND COAL TRAVERSING THE KILN DRYER





Schema-Zeichnung des Turbinentrockners mit Ringscheiben

FIGURE 30 - THE BÜTTNER TURBO DRYER

Where it reverses at the periphery, the drying air is reheated. In air dryers used for chemicals, foodstuffs and the like, the air passes over heating elements there. In coal dryers, the circulating gases are heated by furnace gases or waste heat as may be available introduced through ports in the shell and distributed vertically as may be desired. Figure 31 shows the rate of temperature change of the drying gases in passing through the dryer when drying bituminous slack.

The works manager gave an estimate of 35 tons per hour capacity for drying bituminous slack from 8 per cent moisture to 1 per cent moisture in a dryer 10 meters in diameter by 12 meters high. Expressed another way, the rate of evaporation was estimated at 1.5 to 2 kilos of water per square meter of drying surface per hour; the 10 meter x 12 meter dryer has 1200 square meters of drying surface.

This dryer is reported to handle the drying of friable brown coal with very little degradation. Figure 32, reproduced from data furnished by the manufacturer, shows the screen analysis of four types of German brown coals of 6 mm. top size dried in Turbo dryers. In each set of curves the solid line shows the cumulative screen analysis of the wet feed coal and the accompanying dotted line shows the screen analysis of the dried product.

Each pair of curves represents a different coal. Number 1 is designated from west of the Elbe, Number 2 from near the Rhine, Number 3 from west of the Elbe L, and Number 4 from east of the Elbe.

A modification of the Turbo dryer, developed for handling fragile materials without transferring the load from shelf to shelf, is shown in Figure 33. In this design the drum is stationary and the load is carried entirely through the dryer on a spiral conveyor. The conveyor consists essentially of a series of pans functioning exactly like the segments of the shelves of the normal Turbo dryer, but the individual pans are carried on a single strand of side pull chain. Within the dryer, this chain follows a spiral path downward around the inner shaft that houses the turbines. The outer sides of the pans are supported on a fixed track on the dryer frame. The entire shelf assembly is driven by the inner drum which supports the chain track and, hence, there is no movement of the chain and pans relative to the supporting frame.

At the bottom of the dryer, where the pan assembly passes out of the shell, the shelf segments released from the outer track support dump themselves automatically, and then return to the top of the dryer to be reloaded.

Figure 34 shows the variations in moisture content of the various size increments of fine sizes of brown coal dried in Turbo dryers. Data on two such samples are shown. The solid lines show the percentage of each size -- size in mm. is indicated on the horizontal scale at the top and screen percentages on the vertical scale. The broken line shows the moisture

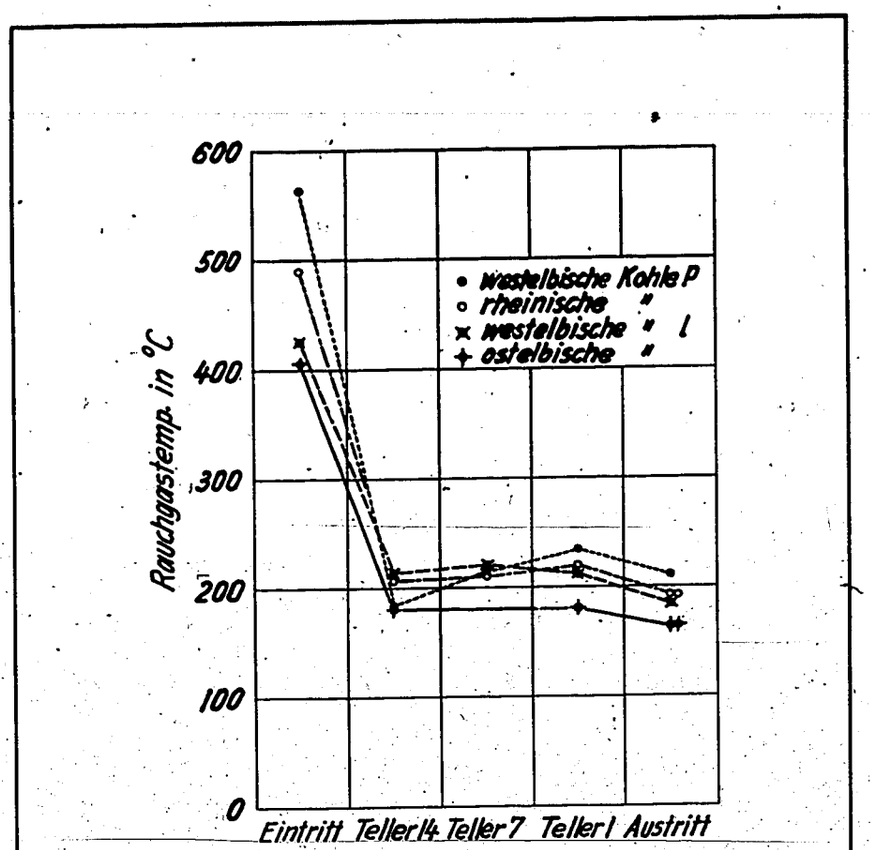


FIGURE 31 - RATE OF CHANGE OF TEMPERATURE OF DRYING GASES CIRCULATING IN THE TURBO DRYER OPERATING ON BITUMINOUS SLACK

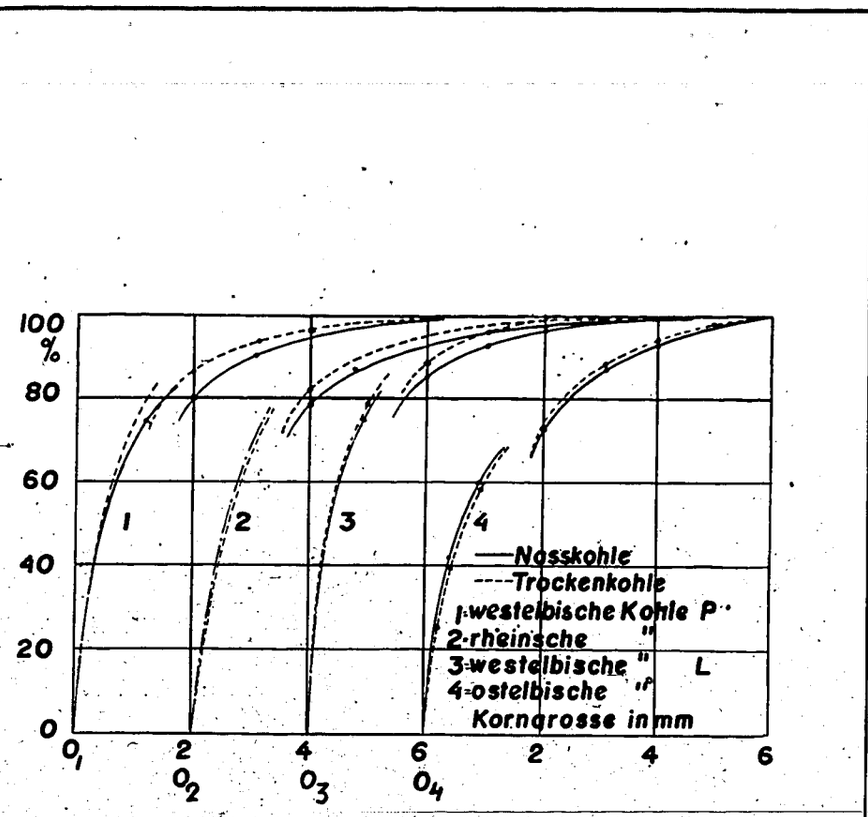


Bild 13. Duchgangskornungskennlinie von Nass- und Trockenkohle bei Verarbeitung im Turbinen Ringscheiben Trockner.

FIGURE 32 - DEGRADATION IN THE TURBO DRYER HANDLING GERMAN BROWN COALS

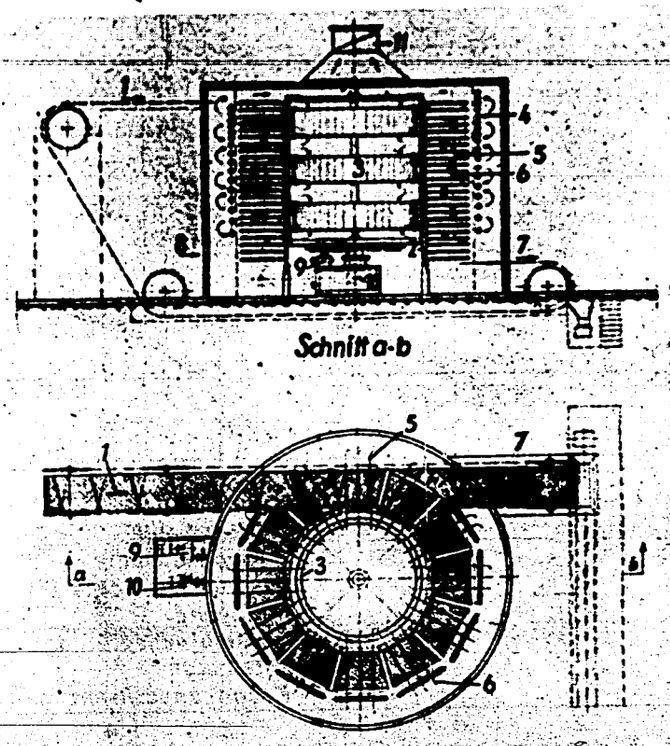


Bild 6.

Schema eines dampfbeheizten Turbinen-Band-Trockners mit selbsttätiger Entleerung
1 Materialaufgabe, 2 Drehgerüst, 3 Turbinen, 4 Heizelemente, 5 Rückströmzone, 6 Vorströmzone, 7 Trockengutauslaß, 8 Frischlufteintritt, 9 Bandantrieb, 10 Turbinenantrieb, 11 Abluftschlot.

FIGURE 33 - THE BÜTTNER TURBO - CONVEYOR DRYER

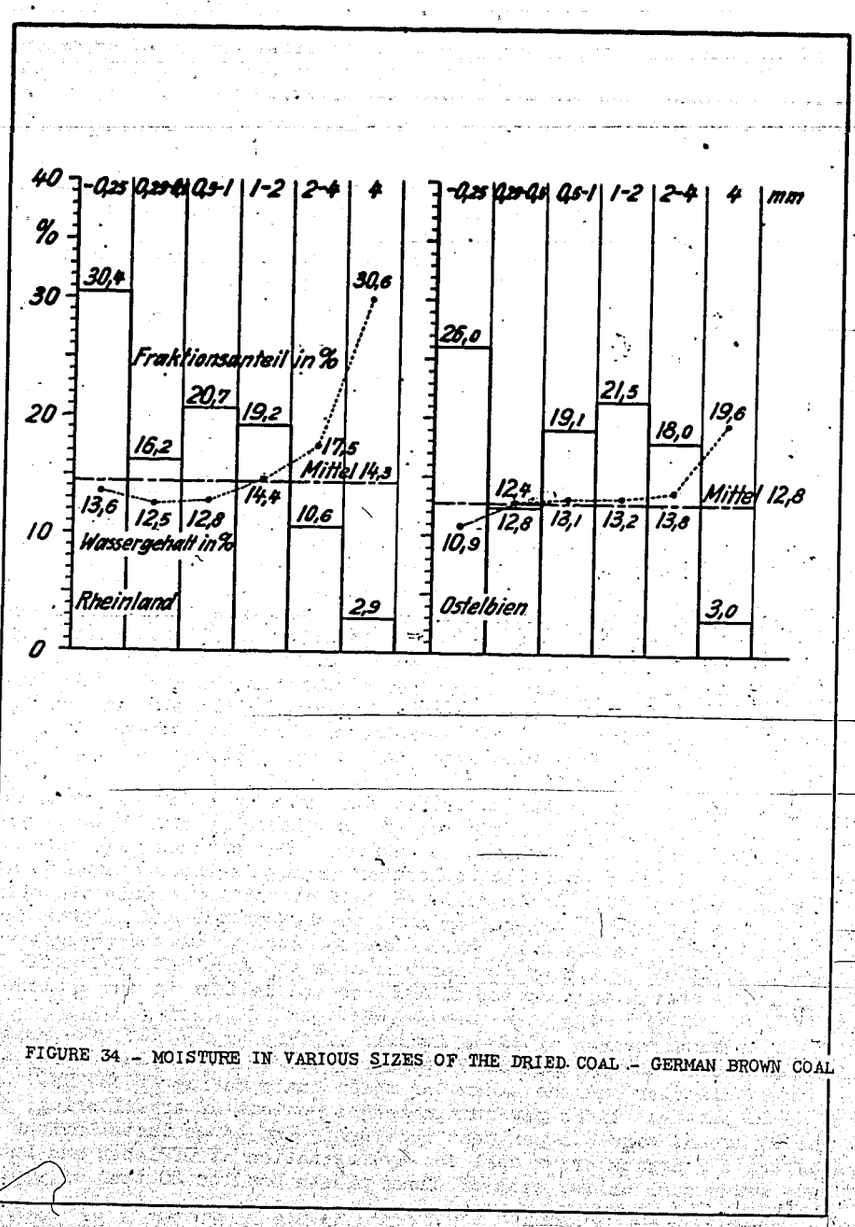


FIGURE 34 - MOISTURE IN VARIOUS SIZES OF THE DRIED COAL - GERMAN BROWN COAL

content of the same size fractions. Thus in the first sample after drying, the minus 0.25 mm. fraction is 30.4 per cent of the sample and its moisture content 13.6 per cent, the 0.5 mm. x 0.25 mm. fraction is 16.2 per cent of the sample and the moisture content is 12.5 per cent. The average moisture of this entire sample was 14.3 per cent.

Figure 35 shows the progressive drying of the coal as it passes through the dryer from shelf to shelf (brown coal). The numbers on the bottom horizontal scale are shelf numbers from top feed shelf to bottom discharge shelf, and the vertical scale shows average moisture content. The four curves show the data on four different types of German brown coal of the same series as shown in Figure 30.

31. The Aspirator Dryer

The manufacturer calls this the "Rapid Circulation Dryer", Rema-Rosin system. It is similar to the "Flash" dryers developed in America.

In this system the coal is dried and conveyed in suspension in a high velocity current of hot gases. In the Büttner system one exhauster is used and the entire system operates under suction. An assembly scheme is shown in Figure 36.

Hot gases from the furnace or other source are drawn into a vertical drying column, and the wet material to be dried is fed continually into a constricted section of this column (generally by a screw conveyor). The air current in the drying column dries and classifies the coal. The fine dry coal that is light enough to be carried upward by the air current is transported over the top to a cyclone collector which is operated under suction by the exhauster on the discharge side of the cyclone.

The coarser or wetter particles that cannot be carried by the current drop downwards against the current and gravitate to a mill which crushes the coal and exposes fresh surfaces for drying. The crushed coal returns to the primary drying and classifying column or in an alternate scheme to a second drying column which again delivers to a classifier. This classifier likewise delivers finished dried fine coal to the cyclone and returns the coarse wet particles to the mill which thus operates in closed circuit with the drier and automatically the system recirculates the feed material until it is dry and fine enough to pass the classifier and deliver to the cyclone.

The manufacturer cited an example of this type of drier operating on bituminous coal at the rate of 60 tons per hour. The drying column is one meter in diameter and the exhauster motor has a rating of 150 KW. Coal slurry of 20 per cent to 35 per cent moisture content, after filtering, can be dried to around 2 to 2.5 per cent moisture. Two large installations of flash dryers for drying brown coal for hydrogenation at Offleben and Lutzhendorf have seven such units, each of these plants handled 20 tons of wet coal

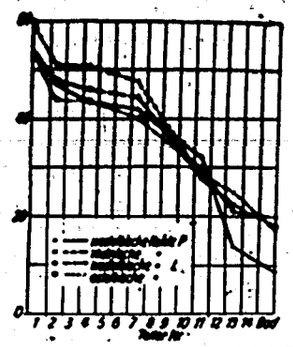


FIGURE 35 - PROGRESSIVE DRYING FROM SHELF TO SHELF OF TURBO DRYER HANDLING BROWN COALS

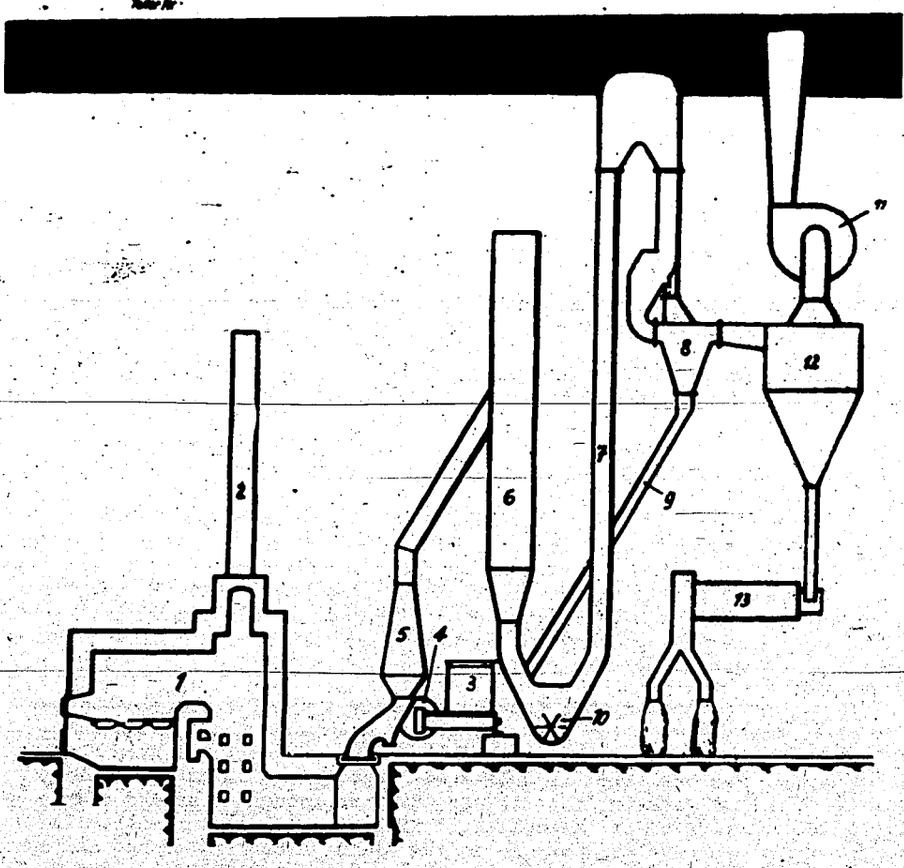


FIGURE 36 - TYPICAL ARRANGEMENT OF BUTTNER FLASH DRYER

per hour and delivered 13 tons of dry coal. Each dryer tube evaporates 1 ton of water per hour.

Figure 37 shows the rate of change of temperature of the circulating gases in the Flash dryer. In this graph, "l" is the length of total travel of the drying gases in meters, "t" is the temperature in degrees Centigrade. The "A" curve shows the temperature of the circulating gases and the "B" curve shows the temperature of the load material being dried. The break point at "C" is where the recrushed coarse material returns to the dryer stream. This initiates a second phase of rapid evaporation and correspondingly rapid drop in temperature of the circulating gases.

32. Dust Collecting

In addition to the conventional cyclones and cloth filters, Büttner Werke manufactured multiple unit cyclones under the patents of the Dutch firm of Kennemer Machinefabriek, Beverwijk, Holland, developed by van Tongeren. This is a line of metal tube dust collecting units similar to the "multi-clone" and "Polyclone" systems of the Research Corporation.

In the beginning they installed some multi-clone plants with small tubes 200 millimeters in diameter and as many as 680 tubes in a plant, but these early installations were found to be uneconomical mainly because of high power requirements. The present practice favors the use of a small number of much larger tubes of 750 to 1100 mm. diameter similar to the Polyclone type. The Dutch firm of van Tongeren has installed these multi-cyclones up to 2200 small tubes of 12 cm diameter at the Central North Power House, Amsterdam.

33. The Buttner Pulverizing System

This firm had an extensive business in the manufacture and installation of coal pulverizing systems for powdered fuel burning.

Their standard P. F. installation consisted of a cylindrical ball mill in closed circuit with a vertical column, sorting or classifying chamber, followed by a cyclone collector and exhauster on the discharge side of the cyclone.

The characteristic feature of their system is the Flash dryer in closed circuit with the Ball mill often used when the coal is damp. In such an installation, the classifying column is replaced by a Flash dryer tube. The coal feed is delivered first to the dryer classifier column where any material that is already fine enough is sorted out, dried and transported to the collector without going to the mill. The heavy particles large and damp go to the mill. A current of hot air is drawn through the mill to carry away and dry the coal as it becomes fine enough.

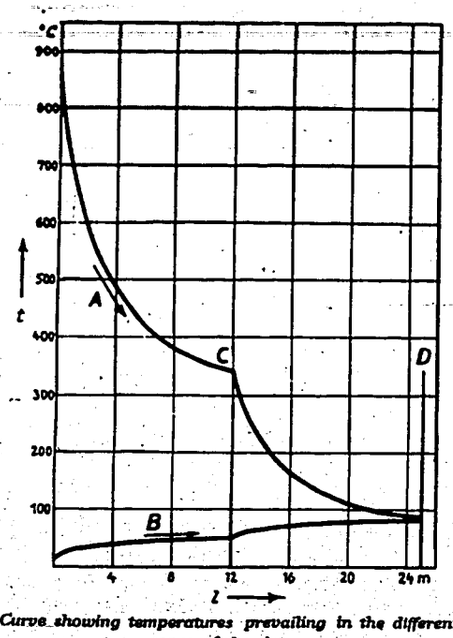


FIGURE 37 - RATE OF TEMPERATURE CHANGE IN THE FLASH DRYER.

Curve showing temperatures prevailing in the different zones of the dryer.

l = length of path given in metres.
t = temperature in centrigrades.

Mr. Flügel, the pulverizer expert who has had some experience in installation of Ball mill plants for pulverizing Russian anthracites, says these coals in the Charkov area are even harder than our Pennsylvania anthracties. He reports a steel consumption (including balls and lining of semi-manganese cast steel) at 400 to 500 grams per ton of dry coal pulverized - higher than the steel consumption in grinding cement clinker. Steel balls of 100 to 110 kg. per square millimeter tensile strength are used

He reports they have used pulverized anthracite for cement burning only in 50 per cent mix with bituminous coals.

Büttner's large tube mills are 2.3 to 2.6 meters in diameter (inside) by 4.0 to 5.0 meters long.

APPENDIX #1

GUIDES FOR ACCEPTANCE AND SUPERVISION OF COAL-PREPARATION PLANTS
Edition 1943

Technical Standardizing Committee for Mining, Part of the
German Standardizing Committee

General

These guides have been edited by the "German Committee for Coal Preparation" at the society for mining interests, Essen. They have been elaborated by this committee with the assistance of the research office for coal-preparation of this society and of the equipment firms. The purpose of these guides is to facilitate and to unify the guarantees on new plants as well as the supervising of existent coal preparation plants. As coal preparation plants in this case we are to understand such plants with mechanical handling, sieving and washing equipment.

The guarantees are based on acceptance tests which, at the same time, will be useful for effective working supervision. A uniform procedure for acceptance and supervision will make comparable the results of different tests at different plants.

The subsequently cited numerical examples apply particularly to conditions in the Ruhr district, with the usual limits of separation. They are not binding, however, and are only tentative. To support them the guaranteed quantities have to be fixed in each single case.

The guides are to apply to installations in existing preparation plants according to their sense.

(1) The purpose of these guides is to facilitate agreement on the guarantees of acceptance and performance of new coal preparation plants, and to facilitate supervision of existing plants.

(2) It is understood that by coal preparation, we mean such mechanical operations as washing, screening, flotation, etc.

Guarantees

A. Throughput

Normal throughput capacity is defined as that input per hour of raw coal with run-of-mine moisture, to which the full and successful performance of all parts and auxiliary devices of the plant are to be determined. To provid

for the fluctuations in the ratio of coarse grain to fine grain and to avoid too high or too low measurements of single machines and devices it is necessary to fix the maximum and the minimum charge of the coarse-grain fraction, the fine-grain fraction, and the finest-grain fraction.

In fixing the normal throughput capacity, the possibility of a sudden overload caused by unavoidable fluctuations in the hauling of coal from the mine to the plant has to be allowed for by providing an additional 10 percent plant capacity.

The mechanical devices of a preparation plant must be able to stand an overcharge up to 20 percent beyond the normal throughput capacity within the compass of the maximum charges fixed above. In this case, however, the quality and the purity of the sales product must not undercut the commercial limits 1/ where the middlings is regarded as a sales product.

1/ These limits are fixed for the western German coal mining industry in the "Ruhr coal handbook".

Example

In the planning of a new washing plant the throughput per hour of material to be washed at 80 mm KO size had been set up from the mining operation at 182 tons per hour. To compensate the possibility of a severe overcharge 10 percent is added from the side of the works managers. This results in a normal throughput capacity of the washery of 200 tons per hour. At the acceptance test the agreed guarantees have fully to be kept within a range of fluctuation of - 10 percent — 180 to 220 tons per hour. Beyond that the whole plant must not suffer any stop in case of a throughput capacity up to 240 tons per hour (possibility of overcharging the machines up to 20 percent).

In case the working circumstances indicate especially great fluctuations of charges in the preparation plant it is well to provide a still greater possibility of overcharging the hauling devices and driving motors.

B. Quality and purity of the products

1. Bases of quality guarantee. - The basis of guarantees are; the nature of the raw coal, the interlacing curves, the washing curves, and the granulation of the material to be washed all determined by the test coal (at least 20 tons) which is furnished by the customer in a composition that should as far as possible correspond to the character of the raw coal to be washed. Another basis of contract is a flow sheet of methods to be used.

The guarantee for the individual products should not be based on the quantitative output or on the degree of efficiency of the plant, but on the actual quality and purity of the products. As compared to the direct measurement of the quantities of feed and products throughput, the determination of quality and purity of the products can be performed easier, faster, and with sufficient exactness just by examining properly collected and treated samples. These samples are tested with regard to appearance, suitability of grain, contents of ash and water, and amount of refuse material. The individual product samples, furnish the fastest and most comprehending method of valuing the success of the washing.

To ascertain purity of products that can be obtained it is necessary to fix on the washing curve certain separating lines between pure coal, medium coal, and refuse with the proportions for these limits, the so-called separating weights. 2/ To appraise the effectiveness of any washing process the results must be compared to the weights which correspond to these separating lines on the washability chart.

2/ In case of the analysis by float-and-sink tests in heavy fluids, these are prepared by mixing bromoform (s.g. 2.89), carbon tetrachloride (s.g. 1.59), and xylene (s.g. 0)86). In case of coarse grain up to s.g. 1.85 also zinc chloride solutions can be used.

In case the raw coal is essentially changed during the time between purchase and acceptance of a plant or in case the customer changes his requirements as to the purity of the products, the separating proportions have newly to be set up. Since cases may occur in which the plant cannot be started at the preliminarily fixed separating weights it would be useful to provide in the contract a plan by which a new set of separation standards should be set up.

In such a case, the tolerances for refuse material in the product should be raised only if the new curve of intermediate material shows 1.5 times as much material in the range of 0.05 specific gravity on either side of the selected washing gravity as compared to the former curve on which the contract was originally based.

To the extent that the not-to-be-used parts are undersize grain this has to be taken into account in the valuation.

2. Preparation of coarse grain and medium grain.-

a. Classification.

(1) Dry screening:- At a surface moisture of the raw fine coal, size 10 mm x 0 mm, up to 4 percent and without complicating contents of clay 3/, the size consist has to meet certain requirements.

3/ A coal is considered strongly clayey for example, if the sieve openings up to 6 mm of round punching become clogged at a surface moisture of less than 5 percent and if the sieve bottoms become incrusted on the surfaces. This happens with coals containing water disintegrating clays.

Example

Grade or Size	Tolerances: Percentage Undersize	Tolerances: Percentage Oversize	Tolerances: Percentage in designated size
Lump	2	0	98
Overschlägig	2	10	88
Nut I	2	6	92
Nut II	3	6	91
Nut III	4	8	88
Nut IV	5	10	85
Nut V	6	12	82
Grindings	0	14	86

3. Preliminary classification before washing. - In the preliminary sizing the allowable maximum amounts of false size grain have to be fixed in relation to the surface moisture of the raw fine coal and to the clay content of the raw coal since the false grain interferes with the sharp separation of subsequent washing processes. In case the raw coal contains much clay the results of screening are bad. In using jigs with feldspar bed, the raw fine coal must in no case contain oversize grain which is larger than the perforations of the jig-sieves.

Size mm.	Surface moisture: Up to 2%	Surface moisture: Up to 4%
80 x 30	Not more than 3% undersize	Not more than 6% undersize
30 x 6	Not more than 5% false size	Not more than 8% false size
6 x 0	Not more than 6% oversize	Not more than 6% oversize

This example is true for test sievings of the undersize on round perforations with a diameter that is about 10% smaller than the lower limit size of grain of the respective granulation. The test of the oversize is made on sieves with round punching of normal diameter.

4. Subsequent classification (after washing).- At the subsequent classification the maximum amounts of false grain have to be fixed for each group of grain separated into undersize and oversize.

Example A.

Nut I	2% undersize	0 oversize	98% correct size
" II	3% "	6% "	91% " "
" III	4% "	8% "	88% " "
" IV	5% "	10% "	85% " "
" V	6% "	12% "	82% " "
Grindings	0.0% "	14% "	86% " "

Example B.

Nut I	2% undersize	0 oversize	98% correct size
" II	3% "	2% "	95% " "
" III	4% "	2% "	94% " "
" IV	5% "	3% "	92% " "
" V	6% "	4% "	90% " "
Grindings	—	5% "	95% " "

Example B is valid in test sieving of undersize on round punchings with a diameter about 10% smaller than the lower limit size of grain of the respective granulation. The test sieving of the oversize is made on round punching of normal diameter.

5. Loading.- The nuts to be loaded (samples drawn behind the loading sieves) are reviewed according to their appearance (visibly free from slates, interlaced pieces and foreign substances) 4/ and according to the false grain

4/ For example wood and paper insofar as special devices for removing foreign substances are provided in the contract.

and the amount of small coal. The samples of the single grain groups must contain not more than a specified maximum amount of false grain. It is particularly important for the sized coal to be free from slack. Slack is defined as a coal of a size of 6 mm x 0. In case of Nut V the small coal guarantee has to be omitted.

Examples of nuts loaded according to the size of grain.

Example A.

Nut I to III, 80 mm to 18 mm not more than 10% of undersize, limited to 5% slack.

At Nut IV and V, 18 mm to 6 mm not more than 15% of undersize, limited to 5% slack (in case of Nut IV).

Example B.

Nut I to III, 80 mm to 18 mm not more than 5% undersize, limited to 5% slack.

At Nut IV and V, 18 mm to 6 mm, not more than 8% undersize, limited to 5% slack (in case of Nut IV).

Example B is true for test sieving the undersize on round punchings with a diameter about 10% smaller than the lower limit size of grain of the respective granulation. The oversize is tested on a roundly punched sieve with normal diameter of the perforation.

b. Washing (concentration)

1. Wet Washing

(a) Clean coal

In the clean coal behind the washers the allowable maximum amounts of pure slates (Reinberg) and interlaced material (not usable coal, false outputs) referred to the agreed separating gravity have to be fixed and guaranteed. Samples of the washed coarse grain and medium grain shall be drawn directly behind the respective washers.

In case of heavy liquid methods the allowable weight fluctuation of the separating liquid has to be fixed.

Examples of purity with a proportion of interlaced material of less than 12% in the input.

In case of coarse grain 80 mm x 18 mm

	at jig and trough washeries			at heavy liquid washeries	
Pure coal	95	97	98.2%	98	99.4%
Interlaced material	4	2.5	1.6%	2	0.6%
Pure slates	1	0.5	0.2%	free from slates	

In case of granulation 18 mm x 6 mm

	at jig and trough washeries			at heavy liquid washeries	
Pure coal	94	95	37.2%	97	98%
Interlaced material	4.5	4	2.5%	3	2%
Pure slates	1.5	1	0.3%	practically free from slates.	

(b) Intermediate coal and medium coal 5/

5/ In planning and outlining new plants the possibilities of the development of colliery power plant have to be regarded insofar as they concern the production of the medium coal or the further treatment of intermediate coal.

At jig washeries and trough washeries the content of true medium coal in the middlings product often amounts to 50 to 60% when the proportion of interlaced material in the input is 4 to 12%. If the input contains more than 12% of interlaced material heavy liquid washing has to be taken into consideration.

In case of heavy liquid washing, the minimum content of true medium coal in the middlings product should amount to not less than 90% in case of coarse grain and not less than 85% in case of medium grain, with the raw coal containing at least 3% of interlaced material. The lower limit size of the medium grain then must be higher than 10 mm. If the lower limit of the medium grain is about 6 mm the content of medium coal should amount to not less than 80%.

Besides it is useful to restrict also the proportion of pure slate in the middlings. The share of slate should not be higher than the share of pure coal.

The slate of the washers shall contain no more than X% of raw coal and Y% of interlaced material referred to the agreed separating gravity.

Example of guarantee where the amount of interlaced material is less than 12% in the input.

	at jigs and trough washeries					at heavy liquid washerics	
	Coarse grain			Medium grain		Coarse and Medium grain	
Pure slate	96	94	95.5%	96	94%	96	98%
Interlaced material	3	5	4.0%	3.5	5.3%	4	2%
Pure Coal	1	1	0.5%	0.5	0.7%	practically free	

2. Dry Cleaning

No equally high demands, particularly with regard to the interlaced aterial in the medium coal, can be made to coarse grain dry cleaning if sing air jigs or tables. So it is sufficient to fix only a general figure or float in the dry slate, and sinks in the dry coal. For the intermediate roduct in general the slate content is specified. It is necessary to specify he coal content only when a middling product is to be returned continually to he feed.

xample

Air jig or table plant for 50 mm x 10 mm coal

Clean coal	94 to 96% pure coal	4 to 6% slate & boney
Intermediate coal	max. 60% pure coal, min. 20 boney	max. 20% slate
Refuse	90 to 92% slate	8 to 10% coal & boney

III Washing of fine grain

a. Sizing

1. Sorting

On separating the finest grain from the raw fine coal by sorting r sieving, the allowable maximum amounts of coarse grain in the dust and of ine grain in the dedusted coal have to be fixed for the agreed grain separa- ion, which generally is between 0.2 and 0.5 mm. This guarantee has to be eferred to certain content of dust in the input and to a limiting surface oisture in the 6 mm x 0 grain. It may be necessary also that the clay con- ent of the finest grain should be taken into consideration.

xamples of sifting of 6 mm x 0 coal

oisture in feed %	Undersize in dedusted product			Oversize in dust			
ust in feed	Under 2	2 to 3	3 to 5	Under 2	2 to 3	3 to 5	6/
nder 15%	2 to 3%	3 to 4%	7 to 8 %	15 to 17%	18 to 20%	23 to 25%	
5 to 20%	3 to 4%	4 to 5%	9 to 11%	12 to 16%	15 to 19%	21 to 24%	
ver 20%	4 to 5%	5 to 6%	11 to 13%	10 to 15%	12 to 18%	19 to 23%	

/ Examples true of coal from Upper Silesia.

2. Pre-dedusting

If pre-clearing from dust is provided as an addition to or as a substi- te of dry finest grain sifting then, on the pre-clearing, there has to be

fixed and guaranteed the content of finest grain remaining in the cleared coal and the oversize in the dust.

Examples of pre-clearing from dust at 0.5 mm grain separation

FE (fine grain in the clearod coal)	4%	6%
OS (coarse grain in the dust)	20%	18%

b. Enrichment (washing)

1. Wet Washing

(a) Washed Coal

It should be guaranteed that the washed fine coal, greater than 0.3 mm should not contain more than X% of interlaced material and Y% of pure slates, referred to the agreed separating gravity.

To obtain an economically advantageous addition of finest grain to the washed fine coal, the fine grain washing devices must be able, with respect to grain greater than 0.3 mm, to deliver products of different ash contents to suit varying conditions and these have to be fixed according to the requirements. For these sizes it may be necessary to agree on several alternate separation gravities and several sets of tolerances. (Compare part VII, page 15).

Examples of washed coal specifications

	Jigs				
	Main washing			Rewashing	Launders
Pure coal	95	96	97.4%	90%	96%
Interlaced Material	4	3.5	2.3%	8%	3.5%
Pure slate	1	0.5	0.3%	2%	0.5%

(b) Intermediate coal and medium coal. The fine grain intermediate product of the main jig is given the name "medium coal" only when it will not be subsequently rewashed. Otherwise a finished medium coal is obtained only at the rewash jigs. Besides washed coal from the rewash, rewash refuse; and, if necessary, feedback or return material must be specified. The medium coal and the intermediate coal have to be guaranteed on the basis of minimum percent of true medium coal as determined by the definition of interlaced material in the raw fine coal or in the input feed to the rewashers. With more than 4% true middlings in the raw fine coal, the content of coal in the medium product of the subsequent washing should be 50 to 60%.

When there is a subsequent rewashing, a guarantee of the intermediate coal of the main washing can be waived.

If there is no subsequent rewashing, the medium product should contain at least 25% of interlaced material, if 4 to 12% of it is in the input.

Examples for the composition of the middle product of the main fine grain jig.

Interlaced material in feed	6.0	6.3%
Pure coal	28.4	31.3%
Interlaced	40.6	35.0%
Pure slate	31.0	33.7%

Slates:

The guarantee is that the fine slates greater than 0.3 mm of each machine separately are not allowed to contain more than X% of pure coal and Y% of interlaced material with relation to the agreed separating gravity.

To control the loss of coal sludge going away with the slates it is recommended that at new plants or at new installations for cleaning washery water, the ash contents of the fine slates is to be lowered not more than 1% and in old plants not more than 2% by the 0.3 mm x 0 fines carried away with the slate.

Examples

	Jigs						
	Main washing			Rewashing			Launders
Pure slates	94	96.6	97.6%	90	92.8	94.8%	95.0%
Interlaced	5	3.0)	2.4%	8	6.8)	5.2%	3.5%
Pure coal	1	0.4)		2	0.4)		1.5%

2. Dry Cleaning

No equally high requirements can be made for the dry cleaning of fine grains namely with respect to the composition of the middleproduct. In general, it is satisfactory to specify the delivery of pure dry slate and recycled coal and cleaned dry coal. So for dry cleaning it is sufficient to guarantee fixed tolerances for false particles in the clean coal and the refuse. For the intermediate product however, only the proportion of slate can be guaranteed.

Examples

(a) For air jigs and tables on 10 mm x 3 mm grains

Clean coal	3 to 5% slate and bone	95 to 97% pure coal
Middlings	15% slate	85% bone & coal
Slate	92 to 95% slate	5 to 8% bone & coal

(b) For air jigs and tables on 3 mm x 0.5 mm grains

Clean coal	5 to 7% slate and bone	93 to 95% pure coal
Middlings	15% slate	85% bone & coal
Slate	96% pure slate	4% bone & coal

(c) Fine grain dewatering

1. The allowable average water content 7/ of the washed fine coal

7/ According to DIN 21934 older coal (anthracite to fat coal) contains less than about 1% moisture in air dry state, gas coal contains 1.6 to 3.0%, gas flame coal 2.8 to 6% and flame coal more than 6%)

can be guaranteed for dewatering devices only by relation also to the draining time. Moisture guarantees thereby can be made only for surface moisture because this can be mechanically removed.

Examples:

(a) where fine coal has been precleared of dust
8% after 18 hours time of standing

(b) at dripping towers
9% after 24 hours of standing

For the fine grain dewatering in centrifuges it is useful to fix the following guarantees:

1. The quantity per hour of centrifuged coal indicated on the dry weight basis.
2. The average water content of the centrifuged coal.
3. The quantity per hour of centrifuged sludge, indicated on the dry weight basis and in grains per liter.
4. The energy in kwh/t converted into the dryweight of the centrifuged coal.

These guarantees then have to be related to certain characteristics of the input coal with regard to:

(1) Water content
(2) Grain composition of the centrifuge input
(3) Ash dispersion - particularly clay content
(4) Method of preliminary dewatering

For example, with an input coal of 20 to 30% moisture, 12 to 15% of finest grain under 0.5 mm size and without aggravating clay content 8/ the following guarantees would be appropriate:

8/ An aggravating clay content would suppose the granulation under 0.075 mm size to contain more than 25% of ash and amount to more than 10% of the solid substance of the feed.

1. Throughput 50 tons per hour of centrifuged coal (dry weight)
2. Surface moisture average 8%
3. Throughput loss up to 5% referred to dry input
4. Consumption of 0.4 kwh/t of dry input

2. The Middlings

For the dewatered middling a guarantee of maximum average water content can be undertaken after fixing the draining time.

Example:

11% of average surface moisture in the dripping tower after 24 hours of standing.

IV Handling of finest grain

(a) Slurry sieving

In handling the slurry by sieving it is customary to guarantee the undersize grain in the sieve overflow (coarse sludge) and, if necessary, also the contont of oversize grain of the sieve run through.

Example for slurry screening at a separating grain size of 0.3 mm

Gs (coarse in the fine sludge, sieve run through)	15 to 18%
Fe (fine in the coarse slurry product)	20 to 25%

(b) Froth flotation

In cleaning sludges by flotation the throughput (dry coal in tons/hour) and the consumption of reagents (in grams/ton solid material in the raw sludge) can be guaranteed. It is usual to fix in the contract also a given ash content of the input coal, the maximum ash content of the cleaned coal and the minimum ash content of the slate, depending on whether or not a middle product is to be made. Because of the disadvantageous influence of the oversize grain, it is necessary to fix the upper grain limit of the input coal. It is usual to fix the amount of the grain greater than 0.5 mm as well as the ash contents of this grain. The results are very different depending on the nature of the raw sludge and the reagents used. Guarantees for flotation therefore can be agreed only after special researches are made.

Example:

For 0.75 mm x 0 no grain greater than 1.0 mm, ash content 25 to 30%, the clean coal should contain not more than 6 to 7% of ash, the slate should contain not less than 60% of ash when a middle product is not made. For consumption of reagents refer to the "Merkblatt über die Einsparung von Flotationsölen ber der Schaumschwimmaufbercitung der steinkohle" edited by the Bergbau-Verein (mining society) Essen.

Example of the effect of size consist of the feed coal

Share of grain greater than 0.5 mm in the slates	22.2%	2.8%
Ash in the grain greater than 0.5 mm	57.3%	25.9%
Ash in the grain smaller than 0.5 mm	66.3%	75.7%
Average ash of the slates	64.3%	74.3%
Deviation of the ash content of the grain greater than 0.5 mm from the average ash content	7.0%	48.4%
Decrease of the ash content of the grain smaller than 0.5 mm by the grain greater than 0.5 mm	2.0%	1.4%

(c) Filter operation

In case of filter operations it is usual to guarantee the filtering rate in dry weight of filtered sludge in tons per square meter per hour, the water content of the filter cake and the allowable solid matter in the filtrate. Their specifications must be related to the finest grain content of the input, the pulp density (grams/liter) and, if necessary, the ash dispersion.

Example (for unfloated sludge)

Suppositions	Guarantees
Not more than 20% under 0.075 mm	power 0.5 t /m²h
Density of the pulp about 350 grams/liter	surface moisture less than 22%
Without aggravating clay content 9/	solid material in the filtrate less than 20 g/l

9/ A more difficult condition is to suppose the granulation under 0.075 mm shows more than 25% ash and amounts to more than 10% of the solids.

V Breaking and grinding

For the disintegration of lump coal; for the grinding of nut coal; for the production of finer nut sorts from washed coarser nuts; for the breaking of intermediate sizes; or for the mixing grinding of coking coals; it is usual to fix the throughput rate and the grinding fineness or the degree of breaking respectively by fixing the minimum proportion of the desired grain and the allowable quantities of additional oversize grain and of undersize grain.

Examples:

(a) for breaking lump coal not more than 5% over 80 mm and not more than 15% under 10 mm.

(b) for breaking nut coal

(1) Production of small nut sorts out of washed coarse nuts not more than 15% over 18 mm and not more than 25% under 10 mm.

(2) Production of coking or briquetting coal respectively out of washed nut sorts; not more than 10% over 6 mm and not more than 20% over 3 mm.

(c) for crushing middlings

(1) coarse middlings 80 mm x 30 mm not more than 10% over 30 mm and not more than 7% under 0.5 mm.

(2) medium grain middlings 30 mm x 10 mm; not more than 40% over 10 mm and not more than additionally 11% under 0.5 mm.

(d) for mixing grinding

The finished coking coal mixture out of the rinsed fine coal and the ground nuts is to contain:

For fat coal - at least 80% under 3 mm granulation.
For gas coal - at least 95% under 3 mm granulation.

VII Finished fine coal

A guarantee for the average ash content and surface moisture content of the final fine coal and for the quantity of added finest grain can be fixed only when the responsibility for the handling and the distribution of the constituent products and of the process of washing is vested in the contractor. Special guarantees must be agreed upon concerning the grain fineness and the uniformity of the total moisture content if, at the coking coal washeries, there are mixing and grinding plants also included in the contract.

Examples:

(a) Grain fineness for the coking coal mixture without addition of ground nut coal at least 80% under 2 mm

(b) Allowable fluctuations of the total moisture content of the mixture up to — 1.0%

VIII Wash water clarification

In regard to the clearing of wash water guarantees can be fixed for the various circuits - ordinarily for main washing water, the rewash water and the waste water clearing, separately. The guarantees should cover the solids allowable in the cleared wash water. No sludges containing useful coal or middlings should leave the plant. Further, there should be no loss of any wash water (except together with the final products or by vaporization), except where an unusually high content of sodium chloride or surplus water from the nut sprays forces such a loss.

Examples of allowable solids in the clarified water in grams per liter

	With Clay-rich coal	With Clay-poor co
In the main washing	Not more than 40 to 60	30 to 40
In subsequent washing	Not more than 50 to 70	40 to 60
In the wash water (after 1-1/2 hrs. of standing)	Not more than 0.5 cm^3/l	0.5 cm^3/l

IX Room dusting

The room dusting is to prevent dust losses and to keep the plant and plant atmosphere clean. The size of the room dusting equipment has to be fixed according to the surface moisture of the raw coal.

Within 24 hours the deposit of dust on places, which have to be agreed upon, must not be higher than 5 grams per square meter of horisontal plane. The vented air should be visibly free from dust.

C. Other Guarantees

1. Working expense

The working expense has to be guaranteed per ton of mine-moist input material. It is to be subdivided into:

(a) Energy need

The need of current for washing plants should amount to not more than 4 kwh/t without filtration, grinding, centrifuging, froth flotation or room dusting when working at 20% overcharge in excess of the guaranteed throughput. At plants handling only fine grain, the need of energy is allowed to be higher.

(b) Heavy suspension plants

Heavy liquid plants guarantee the expense for heavy substance used to make the suspension.

(c) Fresh water need

Particular care has to be taken to save fresh water consumption. Fresh water should be used, if possible, only at the following places: nut spraying, packings at pumps, laboratory cleaning, cooling of the water-ring pumps at filtration and flotation plants.

II Specifications of quality for machines and auxiliary apparatus

Where no standard conditions exist, the specifications of the purchaser shall be taken as the basis of negotiation. The same is true for the building materials to be used and for the construction of the buildings for the preparation plant.

III Protection against patent infringement

It is recommended that provision be made in the guarantee conditions for protecting the purchaser against unauthorized use of patents valid or applied for or of registered designs.

IV Tolerances

The guarantees shall be considered without tolerance, i.e., they shall be unconditional maximum or minimum values. If a tolerance is reserved it must be positively stated in the guarantee agreement.

V. The Acceptance test

In the guarantee agreement there must be a specification of the time, kind, number and duration of the particular tests for the guarantee, and provision also for settlement in case the guarantees are not fulfilled.

The formal acceptance test may be waived if the operating results of 14 days correspond on an average with the required guarantees. But the overload test must be carried out separately.

It is necessary to provide, in the construction plans, for equipment for satisfactory sampling. The contractor must demonstrate that the agreed quality promises for the prepared products are really attainable when operating the plant. He must provide sampling places that are accessible and it must be possible to take authentic (especially not disintegrated) and satisfactory samples by appropriate construction of sampling utensils and sampling places.

The contractor must be allowed adequate time for adjustment and adaptation of all particular equipment between the time of starting up the plant and the performance of the acceptance test of the preparation plant or of particular equipment.

Acceptance Tests

A. Preparation during the practicing period.

During the several weeks of practicing preceding the acceptance tests the purchaser must be currently informed of the preparation results. The successful operation of the most important working processes during this period shall be seen therefrom. The supervising and attending personnel shall be trained during this time.

Which working processes shall be currently examined and supervised everyday during the practicing period follows from the specific guarantees fixed by agreement. Besides, there is recommended an examination of intermediate processes of screening, crushing, concentration, dewatering clarification, etc., so far as its results have essential influences on the final results; or a separate test of the operations shall be provided for at a later date. In this case it is necessary to provide also here for the necessary accessibility and sampling equipment.

B. Performance of Acceptance Tests.

I. Acceptance Plan and Load. The acceptance test is usually carried out jointly by the purchaser and the contractor persons according to a previously agreed plan, as soon as the technical conditions therefor are exactly examined in all details. The purchaser decides how the plant shall be operated for the acceptance test within the agreed acceptance plan, how long the test shall last and whether all samples shall be taken simultaneously when a signal is given; or group-wise, successively when going round, how the samples shall be processed and evaluated, whether the samples shall be tested at once, or in what way the particular samples shall be stored.

When proving the guarantees, the throughput must be adjusted to the rated capacity as exactly as possible; inevitable deviations up to ±10 percent are admissible and, beyond that, short overloading and underloading peaks. If the load deviations are greater and if there is no possibility of compensation, the acceptance test must be interrupted until the normal throughput is reached again and the under-or overloading effect has had sufficient time to slow down.

II. Duration of the acceptance test. Frequency and validity Sampling.

If there are no accidental results, no strong deviations of operating conditions due to insufficient possibility of mixing, bunkering, or compensating as to variations of quantity, granulation, and ash of the material to be processed and if sampling is not too extended, acceptance tests can be carried out on one test day during the main output time uninterruptedly for at least 4 hours. Otherwise it is necessary to carry out the acceptance tests during several days in the same way and, if necessary, to separate the sampling according to separable groups.

The collected samples of each day shall be evaluated daily, if possible, when the acceptance test is continued for several days in order to prevent failing of the acceptance tests because the quantity of the particular samples cannot be satisfactorily controlled or because the individual packing and safe storage of the samples is too difficult.

All receptacles for collecting samples must be provided with a sample card; they must be well marked outside and still be portable. The sample card is left with the sample after emptying the container. The sample containers shall be set up as near as possible to the sampling place, and as far as possible from other collecting receptacles so that mistakes about sampling will not occur.

Missed or rejected samples cannot be made up by a more rapid sampling because the material conformity with the other samples is not maintained. If there are disturbances or too high a surface moisture,

sampling is discontinued as long as the interference with the method of working of the preparation machine in question lasts.

Sampling places must be clearly marked by the sample number; and the particular quantity and frequency for the sampling in question must be noted.

III Sample quantities.

With a sampling sequence of 10 minutes there are obtained 24 samples within a test time of 4 hours. The collected samples in this case have, therefore, finally reached 24 times the quantity of the single samples. If smaller gross samples are sufficient, it must be decided in every case whether the single sample shall be taken in a smaller quantity or less frequently.

The minimum amounts of sample for oversize or undersize in screened products or for determining floats in the refuse and sinks in the coal should amount to .025 to 0.5 percent of the feed. The smaller number relates to great quantities of material or to a uniform quality and the greater one to small quantities or non-uniform quality.

The minimum quantities in kilograms for float-and-sink tests shall amount to:

Sizes in mm.	Raw coal	Prepared coal	Middlings	Refuse
80 x 10 (6)	250	—	—	—
80 x 50	150	30	35	40
50 x 18	50	12	15	20
18 x 10 (6)	12	3	5	10
10 x 1	5	2	3	5
below 1	0.5	0.3	0.3	0.5

For intermediate grain ranges mean values are to be taken. Apparently pure refuse may be weighed without testing, but not pure coal and intergrown material (Verwachsenes) because the appearance may be deceptive in these cases.

With fine-grain material, washing curves and intergrowth curves (Verwachsungskurven) as well as float-and sink tests are made with material screened over with a 0.3 mm screen.

The minimum quantity 10/ of the collected samples for test screening and incinerations 11/ shall amount for both raw coal and prepared grain to:

Grade	Size mm.	For screening	For incineration
Raw coal	80 x 0	500 kg	150 kg
" "	80 x 10 (6)	350 "	150 "
Grain	80 x 50	50 "	40 "
"	50 x 18	30 "	40 "
"	18 x 10	10 "	40 "
"	10 x 6	7 "	40 "
Intermediate material	80 x 10 (6)	65 "	300 "
Tailings	80 x 10 (6)	80 "	200 "
Fine grain	10 x 0	8 "	40 "
" "	6 x 1	5 "	40 "
Finest grain	1 x 0.5	1 "	10 "
	—0.5	0.3 "	10 "

10/ The indicated quantities correspond with those usually in the operating practice but they are partly considerably different from the theoretically necessary quantities.

11/ The prescriptions of DIN 53711 and DIN DVM 3712 are to be applied accordingly.

The utensils for carrying out float-and-sink tests and screen tests shall be, if possible, the same as are used later on for plant control. The crew shall be practiced in the handling of the utensils and become acquainted with the test methods. Therefore, it is best to complete the equipment of the laboratory for plant control before starting the preliminary experiments.

C. Examination and Evaluation of Samples. Direction for Test Screening.

1. General - It shall be proved by screen tests how far the screening and sifting equipment has separated the material correctly into the different grain classes. Every screen test can, especially in the case of soft coal, produce additional breakage which obscures the result by a higher yield of undersize than is found in reality. When defining the admissible portion of undersize it is, therefore, recommended to consider that fact. An objection because of the abrasion which cannot be determined practically in a reliable way shall then be expressly avoided. It is also advisable in the case of soft coal to screen out first the grains greater than 1 mm so that they may not be exposed to additional abrasion during the whole time of test screening.

II. Taking and preparing samples - The samples for the test screening shall be taken as good average samples during a sampling time of several hours when fully operating in previously fixed times and quantities. Sampling is made immediately at the overflow of the screen before the next bunkering from the full screen breadth. Greatest care should be taken during sampling, transport for further processing, quartering and test screening that the formation of smaller pieces is avoided.

Quartering of samples for test screening is only recommended with grains below 18 mm. If the granulation is coarser, test screening of the whole, i.e., not quartered, sample quantity is specified.

Samples below 18 mm are to be quartered in a suitable manner to the test screening quantities named above. The prescriptions of DIN 53711 must be considered. Before quartering, the material is carefully separated, if necessary, in coarse and fine (below 10 mm) particles. For quartering the fine particles the use of a quartering utensil is recommended. (Rzezacz: "Sampling and Sampling Utensil," Glückauf 71 (1935) Page 702. Plessow: "Sampling in Coal Washeries," Bergbau 50 (1937) Page 411).

Samples from screening or sifting processes of dry material are examined in the state in which they are taken. Especially humid samples from nominally dry processes are treated in the same way as wet samples. Samples from wet screening processes are carefully and tenderly dried in the air or at temperatures of not more than 40° C, until the surface moisture has disappeared and no grains adhere to coarser grains. Before carrying out a screen analysis, coal sludge must be screened in a wet state or sprayed on a 0.12 mm screen.

III. Surface moisture and its determination - In all cases, where guarantees are given for a definite surface moisture or are made dependent on it, take special moisture samples of 100 to 200 grams each are to be used for test. They are closed tight to air at once.

The determination of the surface moisture is usually carried out by 3 hours' drying at 40° C in a drier. The height of bed of the samples of fine and finest grains shall not surpass 10 or 3 mm, respectively. Wet samples should not be examined simultaneously in the same drier.

IV. Carrying out Test Screening. - Test screening is carried out in a different way according to the grain size of the sample.

It is restricted to the determination of the exactness of the grain separation, and so does not refer to a checking of the dispersion of the grain within these grain limits.

Above 1 mm round-punched screens are to be used, the opening width of which has exactly to correspond to the fixed grain limits. In washed nut coals, the width is uniformly through all the Reich 80, 50, 30, 18, 10 and 6 mm.

(a) For grains of a size equal to 18 mm or over 18 mm the test sieving is made by hand on a fixed sieve plate. To avoid grinding the test sieve is to be used only as gauge for the dubious or obvious false grain. (Stick through method).

(b) For grains of size under 18 mm the test sieving is made on a hand sieve. The test sieving of grain of a size under 1 mm is accomplished according to DIN 53705.

Round-punched sieves accordingly DIN 1170 are employed also for the medium grain of a size of 18 to 6 mm and for fine grain down to 1 mm inclusive.

In case of finest grain, however, use test screens with standard square mesh fabrics according to DIN 1171. For test sieving of fine grain under 10 mm and of finest grain it is recommended to apply uniformly, the following sieve grades:

Sieves according to DIN 1170 with round openings	10.0 mm	(5.0) mm
	(8.0) "	3.0 "
	6.0 "	(2.0) "
		1.0
Sieve fabric according to DIN 1171 with mesh widths in the clear as follows:	0.75 mm	(0.12) mm
	0.5 "	0.09 "
	0.3 "	(0.075) "
	(0.2) "	0.060 "

V. Evaluation and false grain determination

In testing grains over 6 mm a piece is to be regarded as undergrain only if all its measurements are smaller than the opening of the test sieve and as overgrain only when at least 2 measurements are greater than the opening of the test sieve.

Hereafter, a stalled grain belongs to that grain group in which is found at drawing the sample. That means it has to be counted as if belonging to the correct grain size. This determination being practically difficult in case of grain under 18 mm the sieve throughrun in this case is subsequently to be tested on a sieve about 20% smaller than the first one and the then remaining coal is to count as normal grain.

In case of grain under 6 mm the result of the test sieving is directly decisive. Stalled grain has not to be determined and to be re-counted

This manner may result in a higher content of false grain than is the true fact. The same is valid for the test sieving of fine dedusted coal. Allowance for this possibility must be made when fixing the tolerances for false grain.

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FIAT FINAL REPORT 818

USE OF SODIUM AMALGAM FOR REDUCTION OF NITROBENZENE AND OTHER ORGANIC COMPOUNDS AND PRODUCTION OF SODIUM HYDRO SULFITE

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OFFICE OF MILITARY GOVERNMENT
FOR GERMANY (US)

FIELD INFORMATION AGENCY, TECHNICAL

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FIAT FINAL REPORT NO. 818 25 JUNE 1946

USE OF SODIUM AMALGAM FOR REDUCTION OF NITROBENZENE AND OTHER ORGANIC COMPOUNDS AND PRODUCTION OF SODIUM HYDRO SULFITE

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ABSTRACT

Describes process and equipment for reducing nitro to azobenzene for benzidine manufacture. Reactor obtaining sodium amalgam from a 20,000 ampere chlorine cell reduced batches of nitro benzene to azobenzene in 8 hours, making 50% NaOH simultaneously. Hydrazobenzene produced with difficulty. Substituted anthraquinone, substituted nitrophenol, and substituted diphenylethylene also reduced. Sodium hydrosulfite produced during high price of zinc.

PERSONNEL OF MISSION

Dr. William C. Gardiner	T.I.I.B
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INTRODUCTION

Objective:

The purpose of the investigation was to learn uses of sodium amalgam from mercury chlorine cells for other than caustic soda production.

Evaluation:

This report describes a plant at Leverkusen for reducing about 3000 kg. per day of nitro-benzene to azobenzene with sodium amalgam in a batch process, using a special reactor connected to a 20,000 ampere mercury chlorine cell. The plant was not in operation. Hydrazobenzene and several dye intermediates had been produced by the same general method, but there was no demand for the products. Sodium hydrosulfite had been produced in a different reactor at the rate of 30 to 50 tons per month when zinc for the usual process was expensive.

Guide to the Reader:

This report describes the reduction of nitrobenzene with sodium amalgam at Leverkusen, plus some other reductions that have not yet been of commercial importance. Sodium amalgam is also used for Na_2S production as described in F.I.A.T. Final Report No. 790, and for metallic sodium in a pilot plant, F.I.A.T. Final Report No. 819.

PRODUCTION OF NITROBENZENE

Brief Description of Process:

Nitrobenzene is reduced in aqueous suspension with sodium amalgam at about 100°C. while cooling with water. The reaction is carried out in a nickel reactor (A) Fig 1, having a steel jacket. Sodium amalgam is produced in mercury cells (B)(see FIAT FINAL REPORT No.816 for description of mercury cells) in which a sodium chloride solution is electrolyzed. Sodium amalgam flows from the cell electrolyzer to the reactor, then to the standard amalgam decomposer (E) and back to the electrolyzer. Circulation is effected by means of a mercury pump (C) between the decomposer and the electrolyzer and by the intense stirring of the amalgam in the reactor. The reduction is carried out in batches, but the cell can operate continuously.

The reaction proceeds according to the equation

$$2\,C_6H_5NO_2 + 8\,Na + 4\,H_2O = C_6H_5N{:}NC_6H_5 + 8\,NaOH$$

Azoxybenzene, hydrazobenzene and small amounts of aniline are formed as by-products.

After the reaction is complete, the mixture is run into heated iron tanks where it separates into two layers. The upper layer is azobenzene (with by-products); the lower layer is caustic soda solution. The two layers are drawn off separately. The azobenzene layer is washed with hot water and the caustic soda solution is purified with chlorine. The latter is still rather impure and is used for the manufacture of fluorides.

This process was stated to be cheaper than when zinc is used for the reduction since chlorine and 50% caustic soda are simultaneously produced.

When the plant was closed down due to destruction of the rectifier station by a bomb, there were eight units in operation and four more were being built; each unit consisted of a 20,000 ampere mercury chlorine cell and a reactor. A diagram of the plant layout is shown in Fig. 2, with the reactors, electrolyzers and mercury pump being shown at (A), (B) and (C) respectively. The tanks for handling, washing and storing the liquids are shown at (D).

Two operators per shift operated the reactors, the cells connected to the reactors, and handled the products.

Flow Sheet for Azobenzene Plant:

A flow sheet of the azobenzene plant is shown in Fig 3. The equipment is identified in Table 1 along with the number and capacity of the units and their materials of construction.

Detailed Process Description:

Nitrobenzene is stored in tank (1) and forced up to a small measuring tank (2) where 100 lit = 130 kg. are measured. The reduction is run in batches of 130 kgs. in the reactors (3). The reactor is shown in Fig. 4. Further details of its construction may be found in M.C. Drawing No. 226. Essentially it is a nickel-lined, round bottomed, vessel, 1 m. high, 1 m. diam., with a nickel cooling coil and a nickel stirrer operating at 80 rpm, which is fitted to within 3 - 7 mm of the bottom to agitate the amalgam as well as to provide agitation at higher levels. An amalgam inlet is provided at bottom centre and an amalgam outlet at the junction of the rounded bottom and straight side at about 80 mm. higher level. A nozzle, 40 mm. inside diam., is provided on the side of the reactor, 247 mm. above the reactor bottom, to drain liquids other than mercury from the reactor. Through the top of the reactor are openings for cooling coil inlet and outlet, for the stirrer, for introducing nitrobenzene, for water and for venting. All connections to the reactor or cell, except for the amalgam piping, are electrically insulated by introducing a length of glass pipe or rubber hose.

After running the nitrobenzene into the reactor, the agitator and amalgam flow are started, and purified water is added at the rate of 28 liters per hour. Water cooling keeps the reaction temperature at 90° to 110°C.

The amalgam for each reactor is provided by the 20,000 ampere mercury chlorine cell (4). This cell is 14 meters long x 0.6 meters wide, described in F.I.A.T. Final Report No. 816. It consists of two parallel troughs sloping in opposite directions, one being the electrolyzer, where sodium chloride solution is electrolyzed, forming chlorine and sodium amalgam; and the other being the amalgam decomposer, where sodium amalgam is reacted with water to form hydrogen and caustic soda. A mercury pump elevates spent amalgam from the low end of the amalgam decomposer up to the high end of the electrolyzer. The low end of the electrolyzer is joined to the high end of the amalgam decomposer by an end-section. In the standard cell this end-section has a groove filled with amalgam with a partition dipping into it that separates the brine of the electrolyzer from the caustic soda in the amalgam decomposer, but allows the amalgam to flow through. A cell producing amalgam for reducing nitrobenzene has a special end-section fitted with two rubber valves which allow the amalgam to flow to either the reactor or the amalgam decomposer. See M.C. Drawing No. 227. The relative levels of the electrolyzer, reactor and amalgam decomposer are such that amalgam will flow through them in series, when the reactor agitator is running, at the rate of 600 - 700 liters of mercury per hour. Each cell and reactor system requires about 1300 kgs. of mercury. The electrolyzer supplies amalgam containing 0.025 to 0.50% Na. The amalgam from the reactor returns to the high end of the amalgam decomposer where any remaining sodium is decomposed with water. The water-feed to the decomposer is regulated to try and make 50% NaOH on the average.

The reduction step has been found to require 170,000 ampere hours, thus requiring 8 to 8½ hours. The reaction is slow during the azoxybenzene reduction stage and at the end, as shown by the concentration of sodium in the amalgam leaving the reactor.

At the end of the reduction the amalgam flow is changed from the reactor to the amalgam decomposer. The purified water flow into the reactor and the agitator is stopped and 20 minutes settling time is allowed. Then the contents of the reactor, above the amalgam, are drained off and a fresh charge of nitrobenzene run in. It requires 10 minutes to drain, recharge and start the next reduction. Carrying the reduction to the next step, where hydrazobenzene is formed is to be avoided because of the violent reaction between the hydrazobenzene left behind after draining the reactor and the fresh charge of nitrobenzene.

The reduced charge from the reactor is drained into a pipe (5) that runs the length of the installation and is large enough to receive the combined products of all eight reactors. This pipe is heated and insulated both thermally and electrically.

The pipe lines between the reactors and the storage pipe have lengths of glass pipe for electrical insulation, and the pipe draining the storage pipe (5) into vessel (6) also has a length of glass pipe for electrical insulation. The valve at the outlet of pipe (5) is a special steam-heated valve. See M.C. Drawing No.228.

The combined, reduced batches are drained into tank (6) which has a cone-bottom and is steam jacketed. In this vessel the three layers of mercury, azobenzene and caustic soda separate. Two of these vessels are provided, but normally only one is required. A period of 1 to 2 hours settling is used. Mercury can be drained from the bottom of the tank. The other two layers are emptied by air pressure through a pipe running nearly to the bottom of the tank. The bottom, heavy layer of caustic is run into the separating vessel (7) until the azobenzene appears in a glass section of the line, then valves are changed to send the azobenzene into vessel (8). Vessel (7) is divided into two parts by a partition running almost to the bottom. The caustic soda containing some azobenzene is run into the compartment on one side of the partition. The caustic flows under the partition and out an overflow on the opposite side while the azobenzene is retained and occasionally drained out. The caustic soda is collected in vessel (10).

The caustic soda contains considerable organic matter. Cl_2 is introduced with stirring, into vessel (10) until the solution is bleached to a pale yellow. Salt and insoluble organic matter are taken out on a sand filter. The caustic soda from the amalgam decomposers is blended with this filtered caustic soda to average 50% NaOH and stored in the 3 storage tanks (11).

The azobenzene in vessel (8) is washed with hot water. Vessel (8) has an overflow near the top which flows through a mercury trap to the sewer. The vessel is about 2/3 filled with azobenzene. Then the water is passed through continuously, while the azobenzene is agitated, until the water overflows clear. The azobenzene is then forced with compressed air, to storage tanks (9) through a pipe reaching to the bottom of vessel (8)

The product of the process is as follows:-

Azobenzene	80%
Azoxybenzene	9-10%
Hydrazobenzene	7-8%
Aniline	2-3%

This is a conservative analysis and most batches are higher in azobenzene. On storage, the amount of azobenzene increases due to a slow reaction between azoxybenzene and hydrazobenzene.

The electrolytic department was not too concerned about the analysis of the product because it was sent to another department where it was reduced further with zinc dust for benzidine production. Aniline formation is the only detrimental side reaction. It was considered that this operation would only be of interest in conjunction with a benzidine plant.

Mercury or amalgam collects in the bottom of containers all through the system, most of which can be drained out and returned to use. However, some mercury cannot be recovered so simply. One trouble is the formation of emulsions with the organic and aqueous layers. Dinitro compounds in a raw material are bad for causing these mercury emulsions. Mercury butter, which is mainly due to iron in the mercury, has to be removed daily from the end-section of the cell. Periodically the system is cleaned out to recover the mercury. Several methods of mercury recovery were used.

The method that was used most of the time, was to stir the mercury residues in a closed kettle with steam bubbling into the mercury. The condensate overflowed near the top of the kettle, and coalesced mercury was drained from an outlet at the bottom of the kettle. Some types of emulsions containing mercury were stirred with 0.1 to 0.5% sodium amalgam in which case the sodium reduced the oils and dissolved the mercury. As a final method the mercury residues were distilled.

The reactor lasts only 18 months due to caustic embrittlement and failure at welds. It may not last this long if welds are poor.

OTHER REDUCTIONS

The same equipment has been used for other reductions either experimentally or on a very small commercial scale.

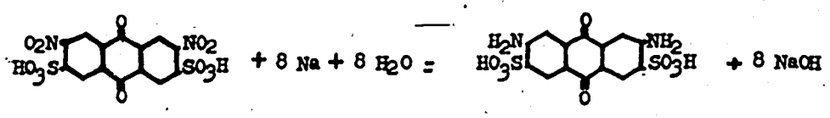
Hydrazobenzene:

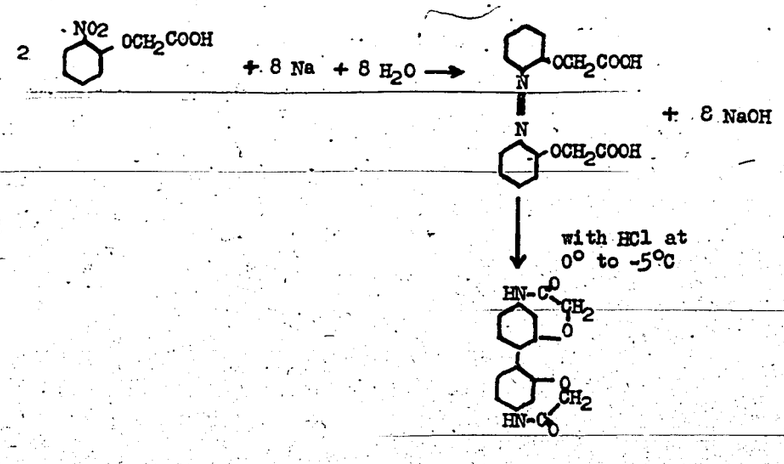
For some reason not stated, hydrazobenzene was required to be made without the use of solvents. A total of 200 tons was produced. Hydrazobenzene melts at 127° so the reduction had to be carried out above this temperature. A steam-heated pipe was installed between the cell and the reactor so that a temperature of 135°C would be obtained. The amalgam had to be 0.5% Na entering the reactor. The hot hydrazobenzene and 50% NaOH were separated hot and the molten hydrazobenzene was sprayed into water giving pea-sized particles. These were ground under water to wash out NaOH and then filtered. The yield was only 82% because of greater aniline formation.

The operation was hazardous because of the violent reaction between hydrazobenzene from a preceding batch and a fresh charge of nitrobenzene. The initial stage of the reaction with amalgam was also quite vigorous. It was thought that a reactor which could be more completely drained might help but it had not been tried.

Reduction of a Substituted Nitro Anthraquinone:

The following substituted nitro anthraquinone was reduced with sodium amalgam:-

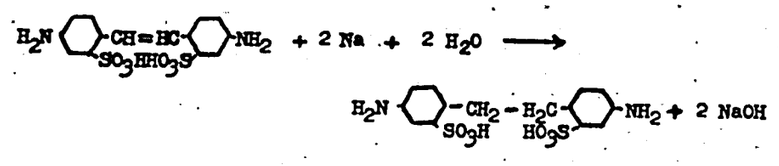




This was to be used for a dye-stuff intermediate from which one SO_3H group was to be split off in a later operation. This second reaction was not satisfactory so the intermediate was of no interest.

Reduction of a Substituted Nitro Phenol:

The following dye-stuff intermediate was prepared using sodium amalgam with 83% yield, compared to a 47% yield by other methods. There was little demand for the dye-stuff. The reactions involved are as follows:-



Reduction of 1 - 1' Diamido 3 - 3' Disulfo Diphenylethylene:

The following reaction was carried out to yield a dye-stuff intermediate with a yield of 94%. One part of the reactant with 15 parts of water were circulated from a storage vessel through the reducer. The solution had to be alkaline to start the reaction.

There is no demand for this intermediate.

Sodium Hydrosulfite:

It was stated that the first mercury cells at Leverkusen were built in order to make sodium hydrosulfite when the price of zinc was high. At one time 30 to 50 tons of sodium hydrosulfite per month were made from sodium amalgam. The process was discontinued when the price of zinc dropped.

The essential reaction is:-

$$2\ NaH\ SO_3 + Na = Na_2S_2O_4 + 2\ NaOH \text{ ---------- (1)}$$

The solution must be rapidly circulated and the NaOH neutralized to prevent the following reaction:-

$$Na_2S_2O_4 + 4\ NaOH = Na_2S + 2\ Na_2S_2O_3 + 2\ H_2O \text{ ---------- (2)}$$

The solution must also be kept cold to prevent another reaction:-

$$2\ Na_2S_2O_4 + H_2O = 2\ NaHSO_3 + 2\ Na_2S_2O_3 \text{ ---------- (3)}$$

Still another side reaction occurs:-

$$Na_2S_2O_4 + 8\ Na + 4\ H_2O = 2\ Na_2S + 8\ NaOH \text{ ---------- (4)}$$

The reactor in this case was a saucer-like shallow enamelled-iron pan, having a cooling jacket. Amalgam (0.2% Na) entered a nozzle through the bottom centre of the pan and depleted amalgam and solution left through an outlet near the top. An agitator spread the amalgam over the surface of the pan and kept the solution agitated. Refrigerated water was circulated through the jacket to keep the temperature of the solution at 25°C. The pan had a cover with an inlet for bisulfite.

The amalgam and solution were separated in a trap, the amalgam returning to the cell and the solution being pumped through a filter back to the reactor. Between the filter and reactor, SO_2 was bubbled into the solution to neutralize the NaOH. As the solution recirculated, crystals of $Na_2S_2O_4\ 2H_2O$ separated out and were caught on the filter and dried. In the drying process there is some decomposition according to equation (3). The overall yield was 52 - 53% on the current. Eventually the circulating solution had to be discarded because of high $Na_2S_2O_3$ concentration.

APPENDIX 1

LIST OF GERMAN PERSONNEL INTERVIEWED

Name	Position	Location
Dr. Bencker	Supt. Chlorine Department.	I.G. Farben, Leverkusen
Dr. Wagner	Asst. Supt. Chlorine Department.	I.G. Farben, Leverkusen
Dr. W. Fuhke	Chemist, Chlorine Department.	I.G. Farben, Leverkusen

APPENDIX 2

LIST OF TARGETS VISITED

Name	Location
I. G. Farben	Leverkusen, nr. Cologne.

APPENDIX 3

BIBLIOGRAPHY

Copies of the reports, documents and microfilm listed below were transmitted to Washington, D.C. Inquiries should be addressed to:

Office of Publication Board
U.S. Department of Commerce
Washington 25, D.C.

1. FIAT FINAL REPORT NO. 816 - Horizontal Mercury Chlorine Cell.

2. FIAT FINAL REPORT NO. 819 - Metallic Sodium from Sodium Amalgam at Gersthofen.

3. M.C. Drawing No. 225 - Azobenzene Flowsheet Leverkusen No. 121717

4. M.C. Drawing No. 225a - Azobenzene plant - Leverkusen Floor Plan.

5. M.C. " " 226 - Azobenzene Plant, Leverkusen. Details - Reactor I.G. 117383.

6. M.C. " " 227 - Azobenzene Plant, Leverkusen. Details - End Box and Separator I.G. 95708

7. M.C. " " 228 - Azobenzene Plant, Leverkusen. Details - Heated Valve I.G. 94191

APPENDIX 4

TABLE I

DESCRIPTION OF EQUIPMENT SHOWN IN FIG.3

Flow-Sheet for Azobensene Plant

No.	No.of Units	Kind of Apparatus	Description
1	1	container	iron; with capacity of about 20 tons nitrobenzene
2	1	measuring vessel	iron, capacity about 100 liters
3	8	reactors	nickel-lined steel shell nickel layer = 3 mm; diam. 1 m, height, 1 m, nickel stirrer, number of revolutions to be regulated between 50-75-100 rpm; 2 Kw motor nickel coil for cooling 13 m of 18.25 mm od. pipe of about 200 dm^2 area.
4	8	mercury cells,	maximum load 20,000 Amps; horizonted type; electrolyzer 14 m long x 0.60 m wide; round decomposer.
5	2	vessels	iron tube, diam. 400 m m , 7 m long, with electrical heating; insulated.
6	2	separators	cast iron, for separation of emulsified mercury, azobenzene and caustic soda lye; insulated; hand-operated; hand-operated stirrer capacity about 3 m^3.
7	1	separator	iron, welded; separation of caustic soda and emulsified azobenzene; capacity about 3 m^3.

APPENDIX 4 (contd)

No.	No. of Units	Kind of Apparatus	Description
8	1	washer	iron, welded; with stirrer; capacity about 15 m^3.
9	3	containers	storage vessels for azo-benzene, capacity 15 m^3 each cast iron with heating jacket to benzidine manufacture.
10	1	vessel	cast iron, capacity 15m^3, for purification of caustic soda lye with chlorine
11	3	containers	storage vessels for caustic soda lye, cast iron, capacity 15 m^3 each
12	2	pumps	cast iron, 1500 rpm, 30 m^3 hour, to manufacture of fluorides

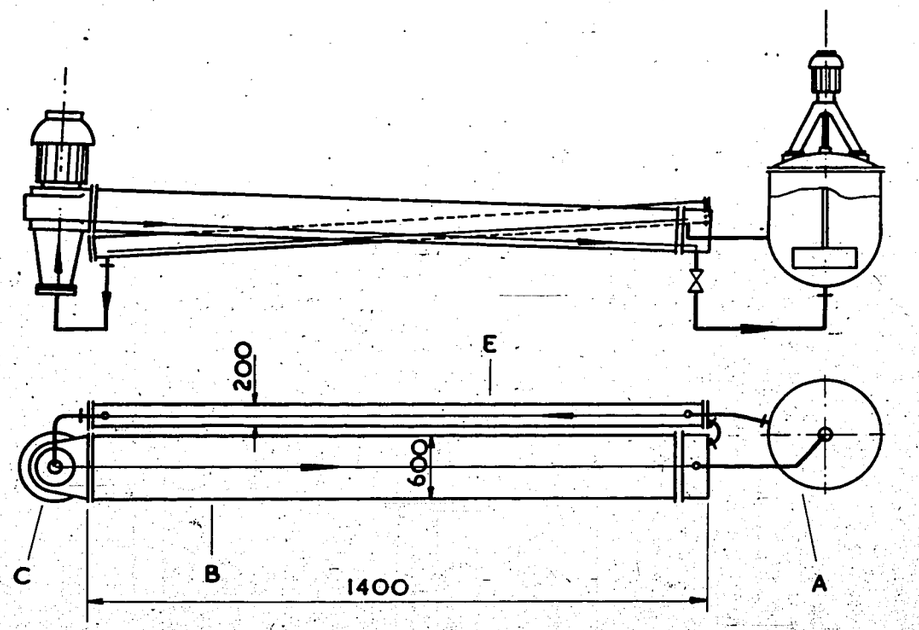


FIG. 1

DIAGRAM OF NITRO BENZENE REDUCTION EQUIPMENT

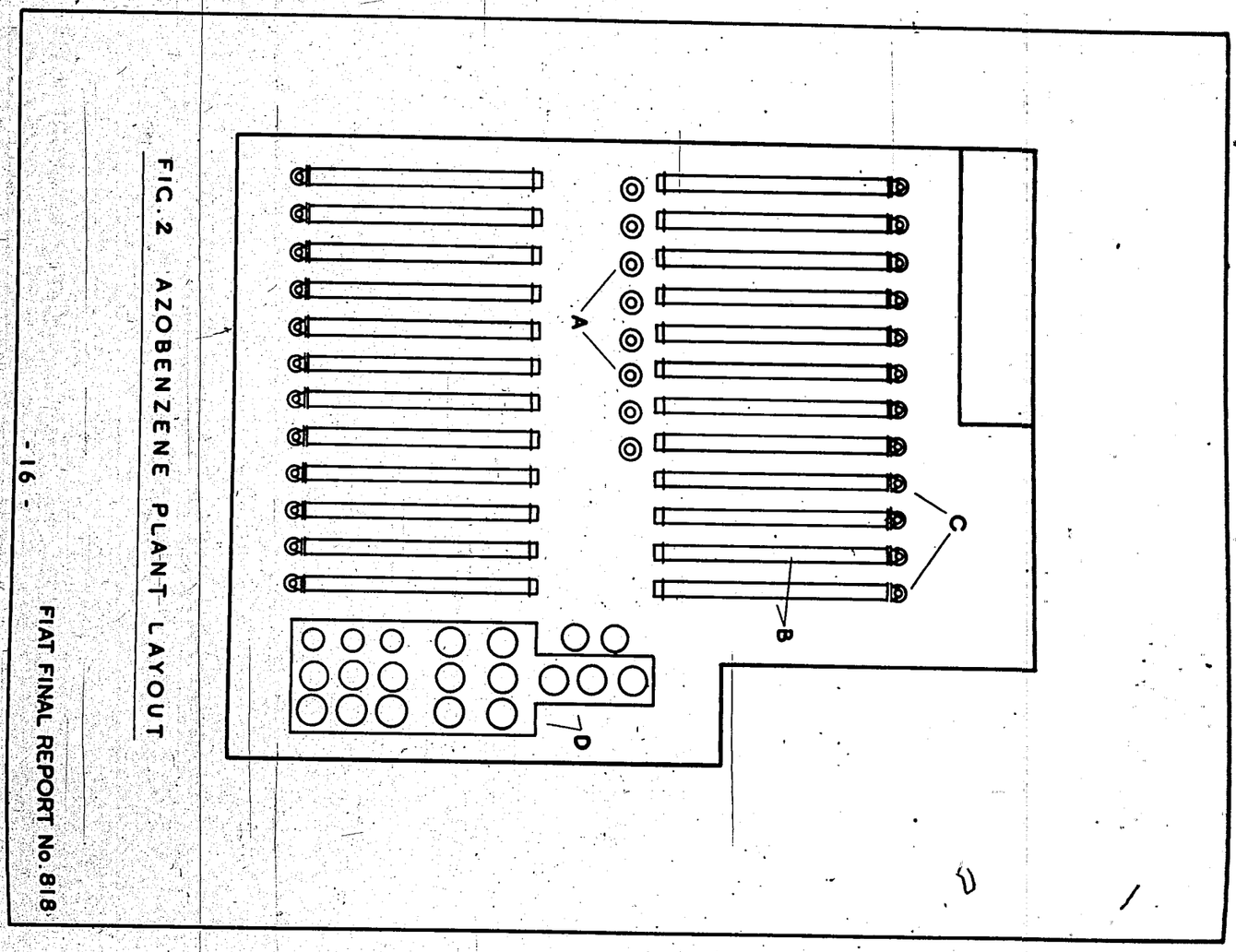
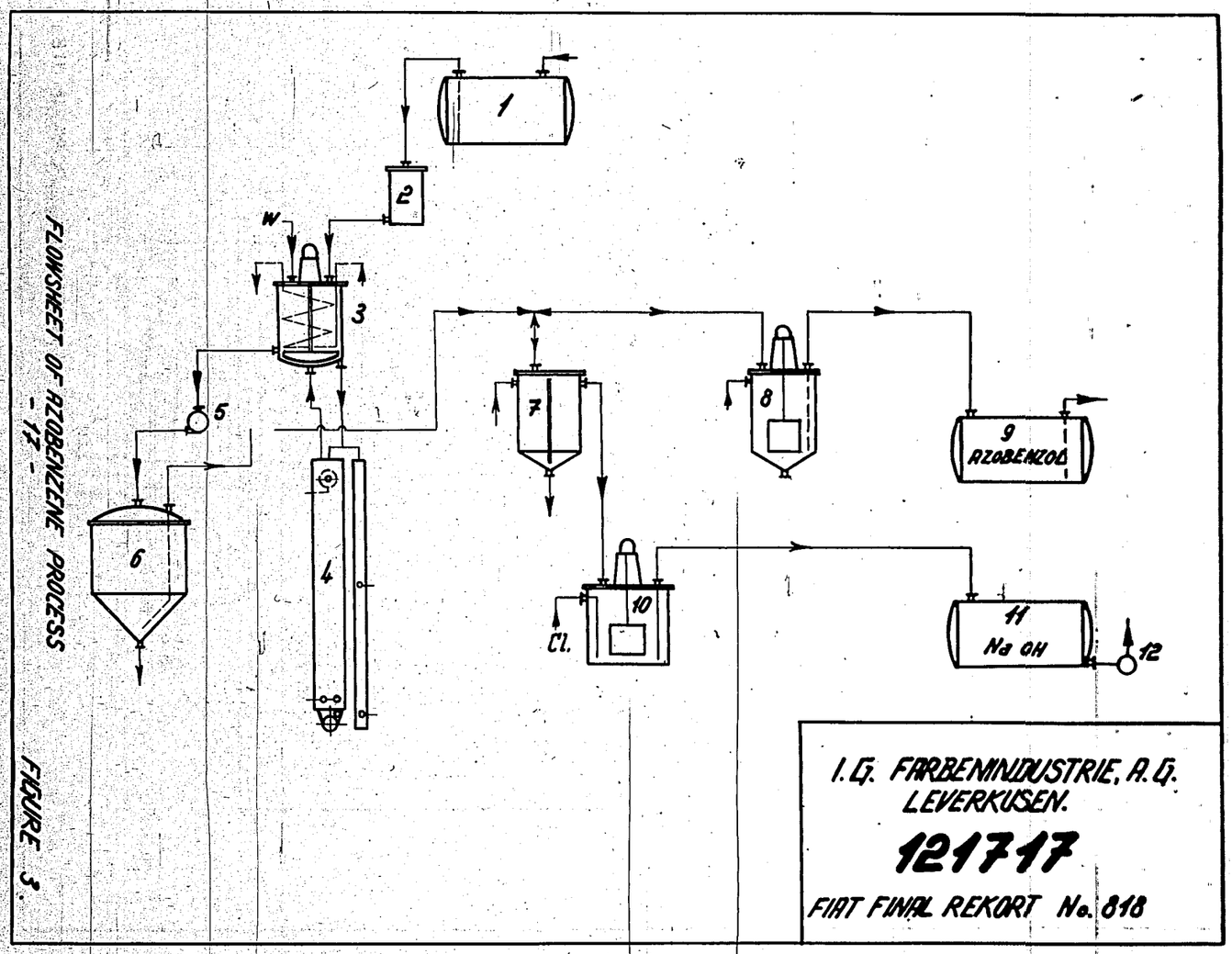


FIG. 2 AZOBENZENE PLANT LAYOUT



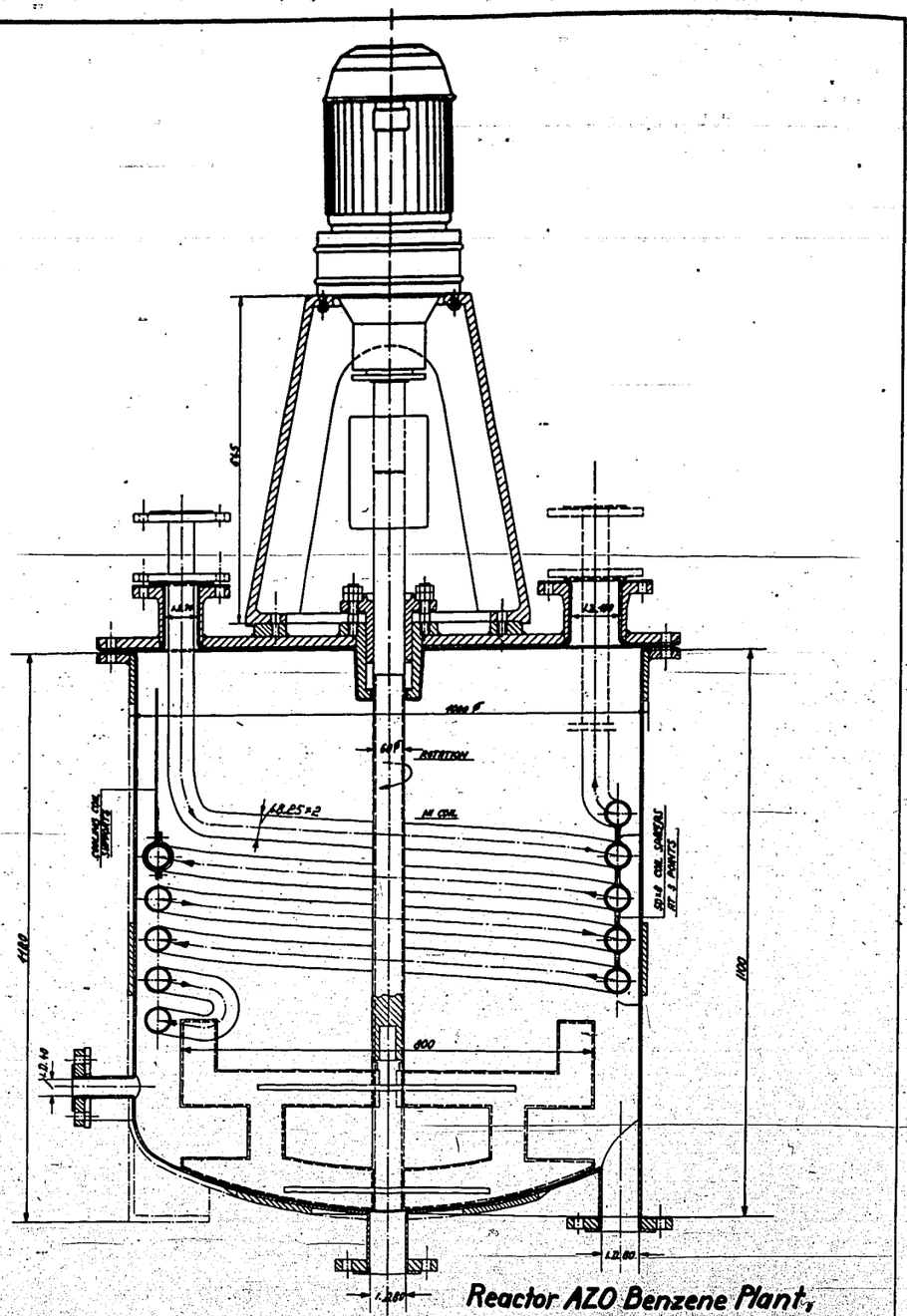
FLOWSHEET OF AZOBENZENE PROCESS

FIGURE 3.

I.G. FARBENINDUSTRIE, A.G.
LEVERKUSEN.

121717

FIAT FINAL REKORT No. 818



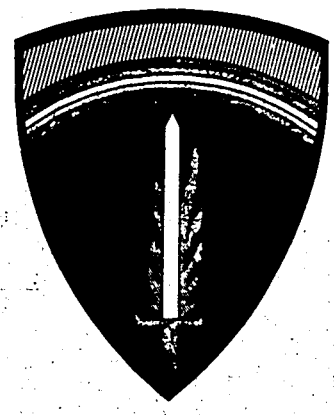
Reactor AZO Benzene Plant, Leverkusen FIGURE No. 4

Copy 1

FIAT FINAL REPORT 817

VERTICAL MERCURY CHLORINE CELLS
I. G. FARBENINDUSTRIE, A.G.

(Gardner, William C. Hoist, Roy A.; Hurst, Howard E.)



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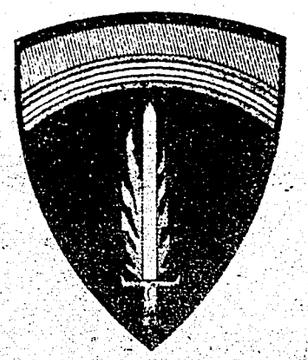
FIAT FINAL REPORT 817

VERTICAL MERCURY CHLORINE CELLS
I.G. FARBENINDUSTRIE, A.G.



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TECHNICAL INDUSTRIAL INTELLIGENCE BRANCH

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FIELD INFORMATION AGENCY, TECHNICAL

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U.S. DEPARTMENT OF COMMERCE

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A B S T R A C T

The design of the vertical mercury chlorine cell is adaptable to the building of individual cells capable of unusually high production which require a minimum of floor space. One complete cell, occupying about 60 square feet of floor area, is capable at normal load of producing 700 - 750 Kg. of chlorine daily at a current efficiency of 92 - 94 percent. The present cells were designed for a normal load of 24,000 amperes at an average of 4.5 volts. The normal current density for the two principal designs described are 1720 and 2400 amperes/m. respectively. As in the case of operating the horizontal mercury cell, the sodium chloride anolyte must be purified. Although several installations of the vertical type cells were made during the war, one of which was capable of producing 100 metric tons of chlorine daily, the design is still considered to be in the development stage.

PERSONNEL OF THE CHLORINE INDUSTRY TEAM

William C. Gardiner, TIIB
Roy A. Horst, "
Howard E. Houser, "
Errol H. Karr, "
C.E. Lyon, "
Kenneth C. Rule, "
Arthur D. Tucker, "

TABLE OF CONTENTS

INDEX TO EXHIBITS

INTRODUCTION

Objective:

The purpose of this report is to describe the design, operation and maintenance of the I.G. Farbenindustrie vertical or rotary mercury cathode, chlorine cells, to supplement a previous report covering the horizontal, mercury cathode, chlorine cells; FIAT Final Report No. 815.

Evaluation:

Although there are four commercial installations of the vertical type cells in Germany, all personnel interviewed unanimously agreed that these installations were constructed prematurely from the development point of view. The experience to date, however, has shown that this type of cell has possibilities, particularly in regard to designing cells capable of high capacities while requiring only about one-half of the floor space necessary for other types of mercury cells.

Guide to the Reader:

The processes and equipment used in conjunction with both the horizontal and vertical type cells are the same. For this reason, such processes as: recovery and purification of hydrogen; drying, compression and liquefaction of chlorine; de-chlorination, resaturation and purification of brine; analytical procedures, water purification and mercury poison hazards, etc., which have been described in the previous report are not repeated.

A list of related drawings and microfilms have been filed with J.I.O.A. in Washington, D.C. For a list of the I.G. Farbenindustrie Chlor-Fako and Chlor-Uko reports, including other pertinent information relative to the German Chlorine industry, reference is made to the Appendix No. 3 of FIAT Final Report No. 816.

SIGNIFICANT DATA ON VERTICAL CELL DEVELOPMENT.

The original development of the vertical cell was carried out at the I.G. Farbenindustrie plant at Ludwigshafen. The first experimental cell, of laboratory scale, was constructed there early in 1937. This was followed by a series of experimental cells which finally culminated in the construction of one 24,000 ampere cell, on a commercial scale, early in the Spring of 1939. After approximately three months of experimental operation the decision was made to install 120 cells of this type in an I.G. Farbenindustrie plant to be built at Huels. Construction of this plant began in the summer of 1939 and operations began in October 1940. This same design, with a few minor changes, was also used in an I.G. Farbenindustrie plant at Heydebreck; construction of the 60 cell installation there began in the fall of 1941 and operations in the summer of 1943. In October 1943 the I.G. Farbenindustrie plant at Rheinfelden started to replace Billiter type diaphragm cells with the same type vertical

cells installed at Huels and had 20 cells operating by September 1944. Meanwhile, an improved model, known as the "Drum Cell", had been developed and built on plant scale at Ludwigshafen in the Spring of 1943. This cell operated experimentally until the air-bombing in September 1944 stopped all work. This "Drum Cell" design was used in an expansion program at Ludwigshafen and in a proposed installation of 126 cells, rated at 24,000 amperes, 28 of which were actually installed but not operated by September 1944. The professed advantages of the "Drum Cell" over the earlier types of vertical cells have not been proven other than on an experimental scale.

The need of additional chlorine capacity which could not be produced in cells of existing types due to limited available space at Ludwigshafen, prompted the development of the vertical cells. Detailed German reports of the vertical cell development may be found in J.I.O.A. microfilms, Reel No. C-86, Frames 245 to 289, 635 to 674 and 679B to 738.

Comparative cost data in the I.G. Farbenindustries "Chlor-Uko" report for the year 1943, see M.C. File No. 247 indicates that chlorine production costs at Huels with vertical cells were 156% of the average costs of eight other plants where horizontal mercury cells were used; being 114% of the plant with the highest costs and 189% of the plant with the lowest.

Development work on the vertical cell contemplated before the war ended, included the following:-

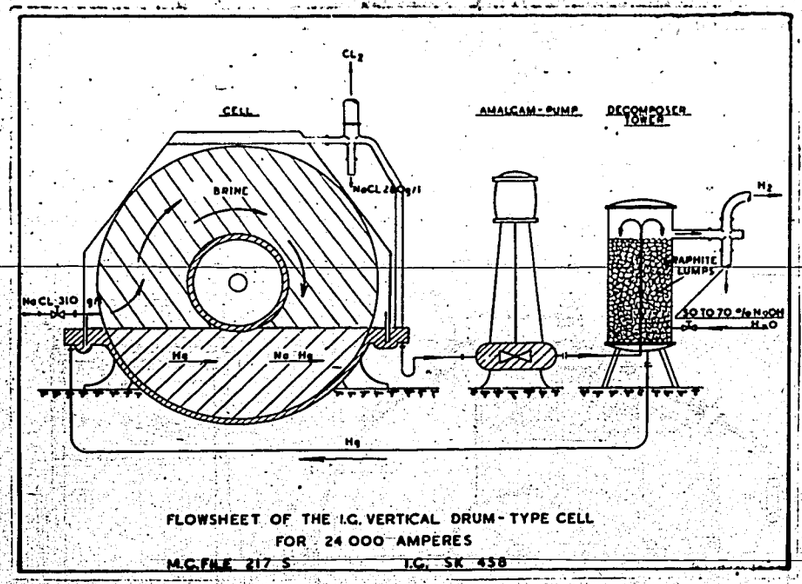
1) Means to improve the current efficiency.
2) Designs to eliminate joints and stuffing boxes in the electrolyzer body.
3) Improved methods of removing graphite particles and other foreign material from the electrolyzer during operations and thus decrease hydrogen evolution.
4) Simplification of electrolyzer design to eliminate the precision work now required in cell maintenance.
5) Improved means of adjusting anode-cathode gap.
6) Cells of larger capacities to further reduce building areas and operating labor costs.

The Huels plant was the only vertical cell plant visited that was in operation. Approximately one third of the rated capacity of 3000 metric tons of chlorine per month was being produced. This earlier type vertical cell, referred to as the "Huels Cell", is the principal subject of this report and, unless otherwise indicated, is the type described.

CELL DESIGN AND ASSEMBLY

There are three major component parts of the vertical mercury cathode cell: the electrolyzer, the amalgam pump and the amalgam decomposer. In the electrolyzer, sodium chloride brine is decomposed to metallic sodium and chlorine gas by the passage of an electrolyzing current from graphite anodes to a rotating mercury cathode. The chlorine gas is removed from the electrolyzer through a pipe connected near the top and above the electrolyte. The metallic

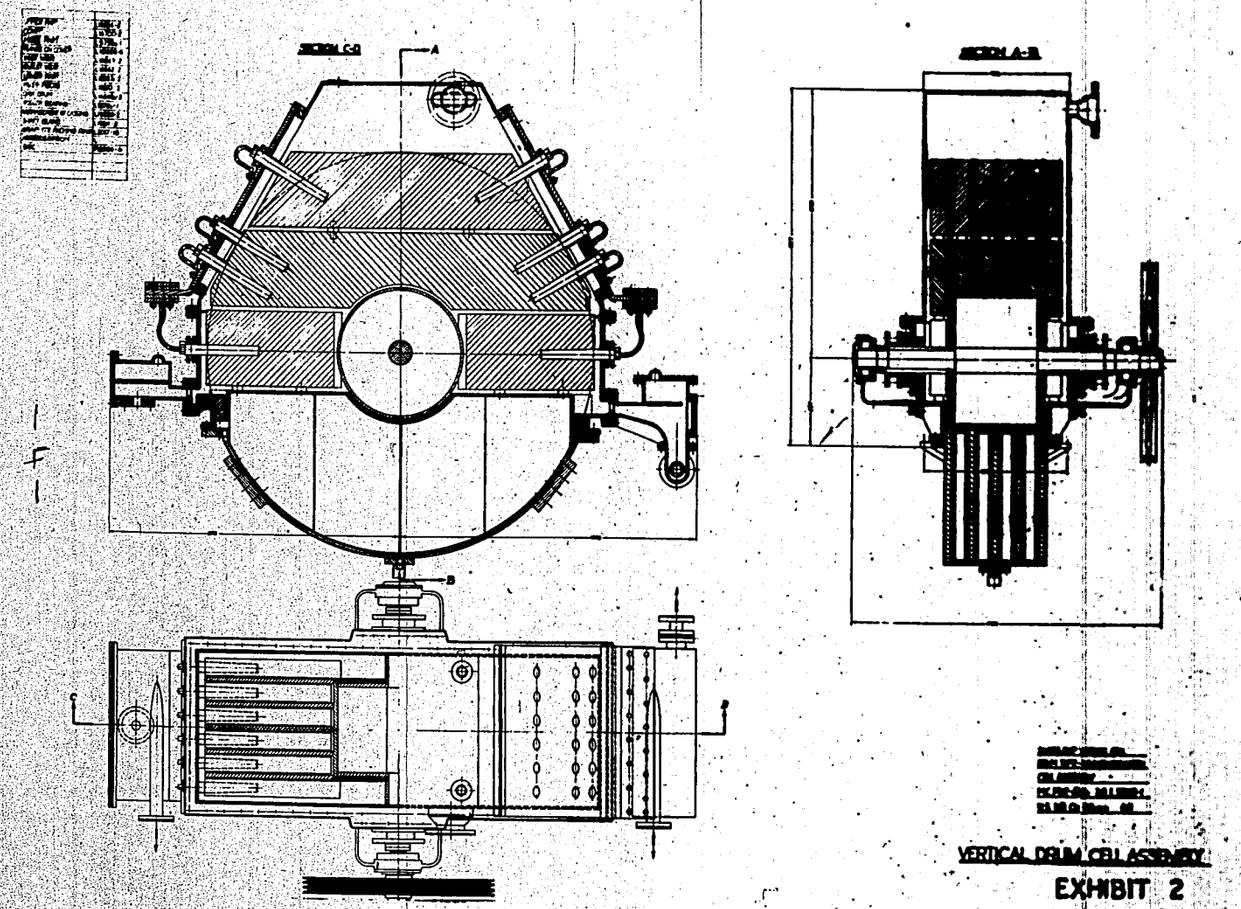
sodium thus formed unites with the mercury cathode to form sodium-amalgam which flows from the electrolyzer by gravity. The amalgam pump then elevates this amalgam to the top of the amalgam decomposer. In the decomposer the sodium in the amalgam is brought into intimate contact with purified water with which it combines chemically to form a sodium hydroxide solution and hydrogen gas. The sodium-free amalgam then flows by gravity back into the electrolyzer. This cycle is continuous and is shown diagramatically in Exhibit I.



FLOWSHEET OF THE I.G. VERTICAL DRUM-TYPE CELL
FOR 24 000 AMPERES
M.C. FILE 217 S I.G. SK 438

EXHIBIT I

Cell assemblies are shown in M.C. Drawing No. 267 for the Huels cell and in M.C. Drawing No. 217 for the "Drum Cell". Assembly cross-sections of these cells are shown in M.C. Drawings No's. 217 and 280, also Exhibits No's. 2 and 3. The component parts of the cells are described in the following paragraphs.



VERTICAL DRUM CELL ASSEMBLY

EXHIBIT 2

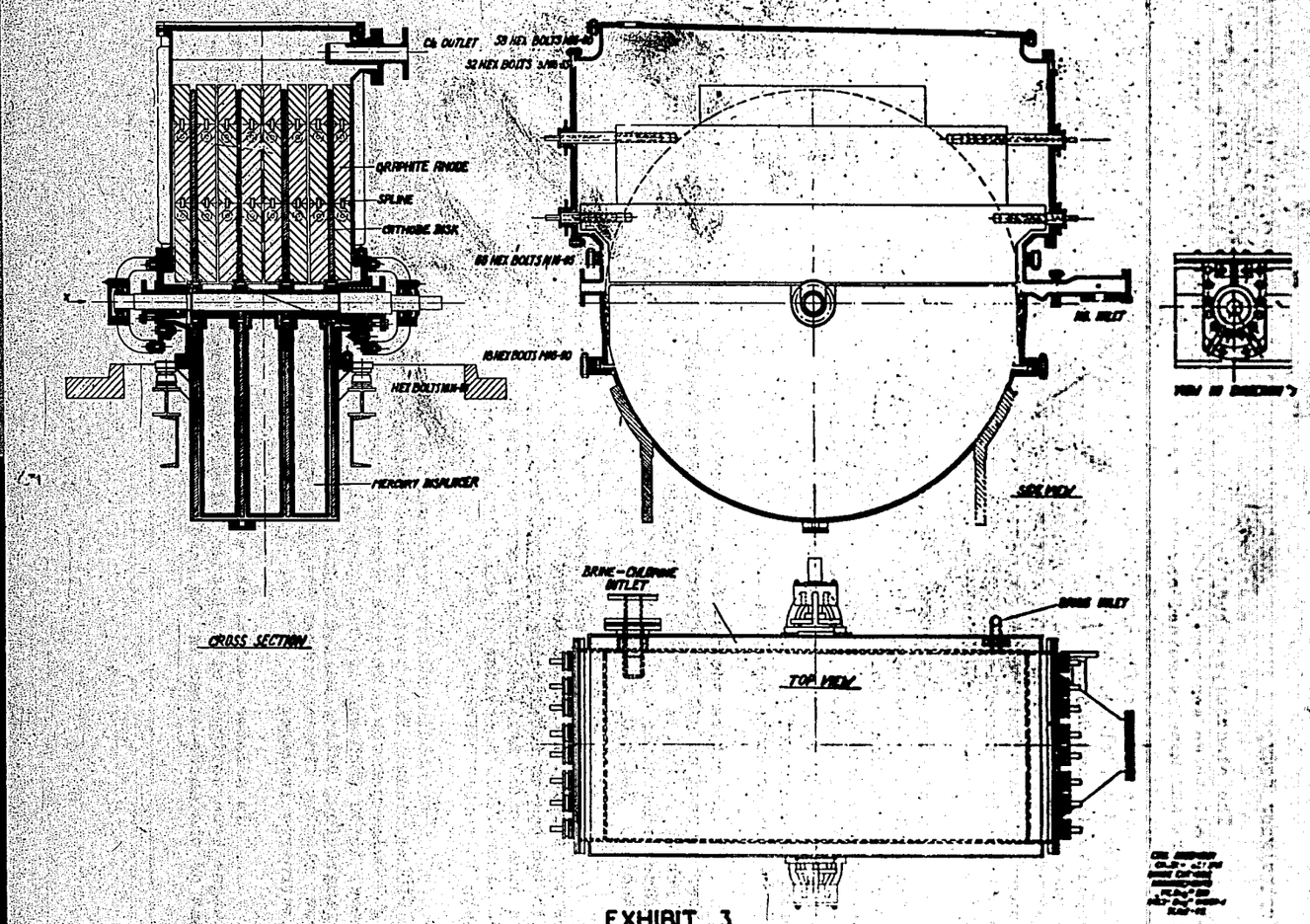


EXHIBIT 3

Electrolyzer Body.

The electrolyzer body is built in three sections; top, middle and bottom. All three sections are fabricated from mild steel plate with flanges, stiffeners and nozzles welded on.

The top section of the Huels cell is box-like in appearance and is made from 5 mm. plate. The inside length and width are 2080 mm. and 925 mm. respectively, and 965 mm. high. Stiffening bars 60 mm. x 10 mm. are welded on edge both vertically and horizontally to the outer sides of the section. Flat bars 20 mm. x 65 mm. are welded to the upper and lower edges to make flanges by which the section is bolted to both the cover plate and to the center section respectively. The ends of this section are open and are equipped with flanges to which the anodic end plates are bolted.

A steel nozzle 114 mm. in diameter is welded to one side of the top section, close to one end; the center of the nozzle is 115 mm. down from the top of the section. This nozzle forms the chlorine gas outlet of the electrolyzer and also acts as an overflow pipe for the electrolyte. The chlorine gas space in the electrolyzer is thus established. On the same side of the section, but on the opposite end, a boss is welded. This boss, with a 35 mm. hole through the side of the section, provides an opening to which is connected the inlet brine pressure equalizer which will be discussed later.

The entire section is lined with 6 mm. of rubber. This thickness of rubber is used on all the electrolyzer parts except the mercury displacers. The rubber lining is carried around all flanges and openings so that all steel surfaces that might come in contact with the electrolyte or chlorine gas are protected. See M.C. Drawing No. 274.

A flat 10 mm. steel plate cover with the same length and width as the top section is bolted to the top section flanges. This cover is equipped with two bosses for lifting eyes by which it can be lifted by a crane. There are also two 60 mm. I.D. holes, one in each opposite end corner for sampling and manometer connections to the chlorine space. The under surface of this plate is rubber covered.

The anodic end plates are made of 10 mm. steel and are 850 mm. high by 915 mm. long. Each plate has two horizontal rows of 56 mm. diameter holes, eight holes per row. Through these openings pass the graphite leads or anode stems, 16 on each end of the top section. Around each of the above holes are arranged four bolts, welded to the plate, which are used with a flange to compress tightly fitting rubber ring gaskets around each anode stem to prevent electrolyte leakage.

In a later design, the above holes were made oval in shape and the flanges were equipped with slotted holes, thus permitting some lateral movement of the anode-stems in the anodic plates. See M.C. Drawing No. 279

Exhibit 4. The above plates are covered with 6 mm. of rubber on the inside face, the rubber being extended through and around the anode-stem holes.

These plates are the only steel surfaces on the electrolyzer that are anodic, electrically. The steel flange around the anode stems may make contact with them, and are fastened to the plates by means of stud bolts. Therefore, when the plates are bolted to the top electrolyzer section, it is necessary to use insulating sleeves on the bolts to prevent flow of current.

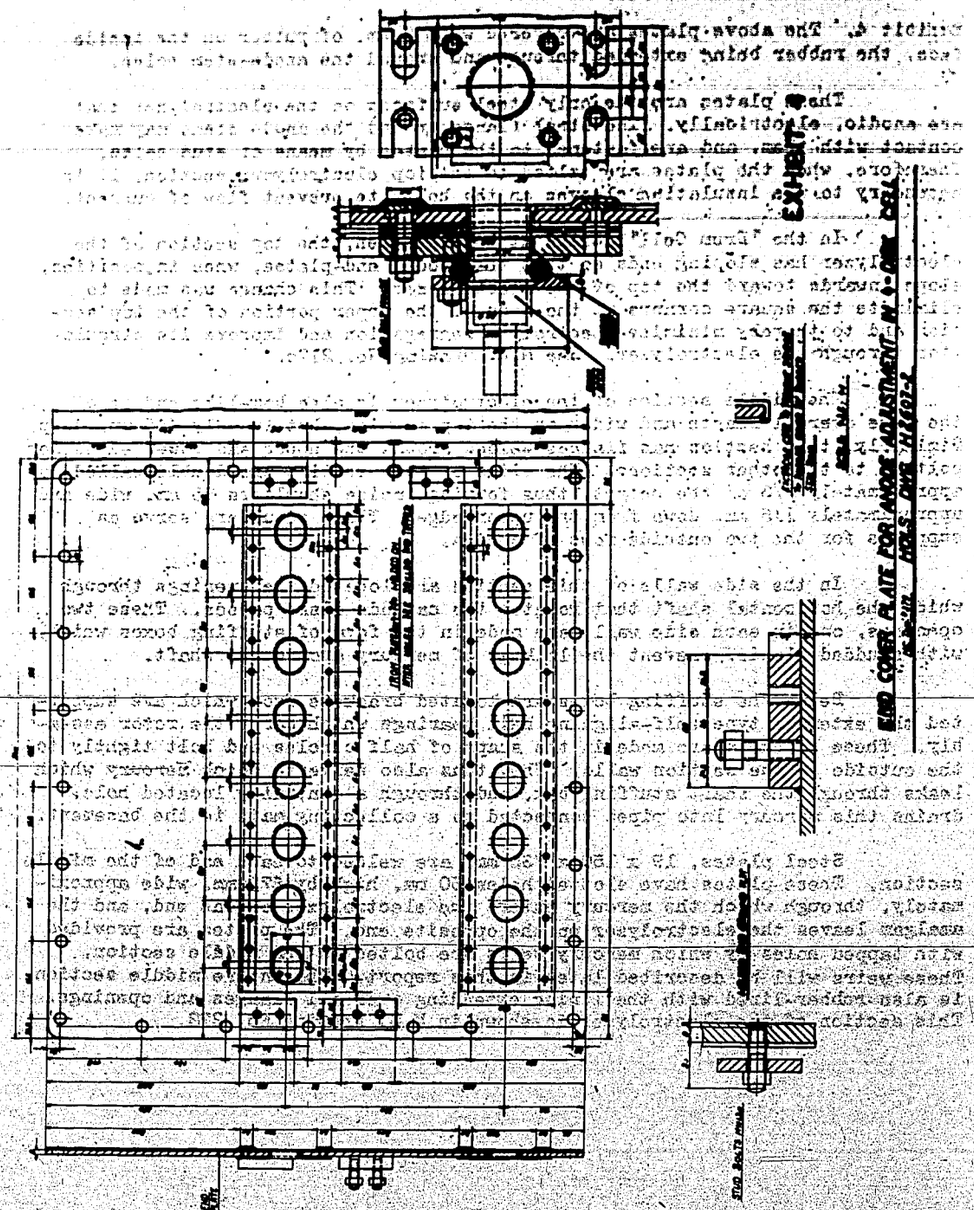
In the "Drum Cell" design at Ludwigshafen, the top section of the electrolyzer has sloping ends so that the anodic end-plates, when in position, slope inwards toward the top of the electrolyzer. This change was made to eliminate the square corners at the ends of the upper portion of the top section and to thereby minimize electrolyte segregation and improve its circulation through the electrolyzer. See M.C. Drawing No. 217c.

The middle section of the electrolyzer is also box-like and is of the same overall length and width as the top section, but is only 445 mm. deep. Similarly, this section has flanges welded around the upper and lower edges for bolting to the other sections. The sides of this section are double-walled for approximately 2/3 of the height, thus forming inside shoulders 95 mm. wide and approximately 115 mm. down from the upper edge. These shoulders serve as supports for the two outside rows of anodes.

In the side walls of this section are located the openings through which the horizontal shaft that rotates the cathode disks passes. These two openings, one in each side wall, are made in the form of stuffing boxes which, with studded glands, prevent the leakage of mercury around the shaft.

Below the stuffing boxes are located brackets from which are supported the external type self-aligning ball bearings which carry the rotor assembly. These brackets are made in the shape of half circles and bolt tightly to the outside of the section walls. They thus also serve to catch mercury which leaks through the shaft stuffing box, and through a centrally located hole, drains this mercury into pipes connected to a collecting main in the basement.

Steel plates, 19 x 150 x 735 mm. are welded to each end of the middle section. These plates have slotted holes 60 mm. high by 675 mm. wide approximately, through which the mercury enters the electrolyzer on one end, and the amalgam leaves the electrolyzer on the opposite end. The plates are provided with tapped holes by which mercury weirs are bolted to the middle section. These weirs will be described later in this report. The entire middle section is also rubber-lined with the lining extending over all flanges and openings. This section of the electrolyzer is shown in M.C. Drawing No. 272.



The middle section of the "Drum Cell" electrolyzer body is of a similar shape and construction, but is equipped with a horizontal row of 6 anode-stem holes, 58 mm. in diameter, on each end. This permits additional electrical leads to the anodes which will be discussed later. This section is shown in M.C. Drawing No. 217c.

The bottom section of the Huels electrolyzer is fabricated from 8 mm. steel plate and has a 160 mm. stiffened flange, 25 mm. thick, welded to the upper edge, along both sides. The flanges on the two ends are 56 mm. wide but of the same thickness. The outside dimensions of this flange are the same as on the middle and top sections. The inside dimensions of the upper part of the bottom section are the same as the inside dimensions of the lower part of the middle section. This bottom section has a semi-circular cross-section when viewed from the side and is 674 mm. deep at the center. This cross-section provides minimum clearance between the section and the circular cathode disks and thus minimizes the volume of mercury required to fill the spaces.

Inside the upper end flanges of the bottom section, are located recesses or shoulders to which the mercury displacers, to be described later, are bolted.

Below the end flanges, near the upper part of the circular bottom, are located the cathodic bus bar connections of the electrolyzer. These portions of the section consist of heavy plates welded to the section and machined to give a smooth surface to which the cathode bus bars can be fastened.

This section has a drain connection complete with valve located at the lowest point in the section through which mercury can be drained from the electrolyzer.

The heavy flanges on the upper part of the section are utilized to support the entire weight of the electrolyzer. The weight is carried from the flanges through three electrical insulators on each side to 228 mm. steel channels which are framed into the building structure. When erecting the electrolyzer, the openings in the middle section for the mercury inlet and amalgam outlet must have definite relative elevations. A surveyor's level is employed to make the outlet 16 mm. lower than the inlet. Shims above the supporting insulators are utilized to set this gradient by tilting the entire electrolyzer. This section is not rubber-lined. Details may be seen in M.C.Drawing No. 270.

The bottom section of the "Drum Cell" electrolyzer is similar in design. The principal difference is in the more rigid construction of the flanges. See M.C. Drawing No. 217v.

The electrolyzer sections are bolted to each other, through the flanges with bolts that are not insulated. Thus all three sections are cathodic, electrically. Several types of gaskets have been used in these joints between the sections. The most successful has been a round rubber-covered asbestos gasket 18 mm. in diameter. Leakage of either electrolyte or mercury

through these joints still present a serious problem.

Electrolyzer Auxiliaries.

Mercury displacers or filler pieces are located between the cathode disks in the lower part of the electrolyzer to minimize mercury requirements. These occupy the space corresponding to that occupied by the middle four graphite anode rows in the upper portion of the electrolyzer. There are three displacers, one between each pair of cathode disks, which clear the disks by 5 mm. and closely follow the lower contour of the bottom electrolyzer section. They are of semi-circular cross section with a radius of approximately one meter, and are approximately 165 mm. thick. The upper surface is flat and horizontal when in position in the electrolyzer. This surface is about 25 mm. above the normal mercury level in the electrolyzer. These surfaces are also utilized to support the weight of anodes between the cathodic disks.

The displacers have steel lugs on each end, about 350 mm. down from the upper surface which bolt to the lower section of the electrolyzer body to hold them in position. Displacers are shown in M.C. Drawing No. 273. They are fabricated from welded steel plate and are covered with 10 mm. of rubber. Formerly the displacers were built in two sections and only the upper section, a portion of which was exposed to the electrolyte was rubber covered. This design still exists in the cells at the Rheinfelden plant. At Huels it was found that this arrangement caused deflections of the cathode disks due to magnetic attraction, and also that these sections became filled with mercury and hydrogen, apparently by diffusion through the welds. Experimental lower mercury displacer sections made of concrete and later of porcelain were tried, but these materials absorbed mercury and soon failed. The present displacers in one piece and entirely rubber covered, have overcome to a large extent the previous difficulties. The rubber covering is corroded at the elevation of the mercury surface, due it is thought, to hypochlorite formation.

The mercury displacers in the "Drum Cell" electrolyzer are four in number and are completely covered with 5 mm. of rubber. They are built in one piece and differ only from the Huels type in having a smaller cross-section and a larger depression in the upper surface to accommodate the rotor drum. See M.C. Drawing No. 217m.

The mercury inlet weir to the electrolyzer is a welded steelplate, rubber-lined device which bolts to one end of the bottom electrolyzer section as described previously. The purposes of this device are first to distribute the stripped mercury from the amalgam decomposer evenly across the full width of the end of the electrolyzer and secondly to introduce concentrated brine into the electrolyzer. The mercury enters the bottom of the inlet weir through a rubber-lined pipe approximately 38 mm. I.D. from the bottom of the amalgam decomposer and which is studded to the weir. This pipe is looped to form a mercury seal so that brine cannot flow from the weir back into the decomposer. After entering the weir, the mercury flows into a trough-like depression adjacent to and parallel with the rectangular slot in the face of the end of the middle electrolyzer section. When flowing over the lip of this depression,

the mercury is evenly distributed into the electrolyzer.

The brine feed to the electrolyzer rises vertically along the side of the electrolyzer, from a rubber-lined pipe main in the basement through a rubber-lined riser pipe 45 mm. I.D. Immediately above the operating floor, a section of rubber hose equipped with a pinch-clamp for flow regulation as well as for providing electrical insulation, is inserted in the riser. Just above this section, the feed brine passes through a rotameter with a calibrated range of 600 - 1200 liters per hour. Above the rotameter, a second section of rubber hose conducts the brine to a rubber-lined pipe loop which turns the direction of flow through a 180° angle and thus down into the side of the mercury inlet weir. The highest point in this brine feed pipe loop is vented into the chlorine space in the top section of the electrolyzer through the opening previously described. The loop is necessary to prevent the brine from emptying out of the electrolyzer in case a rubber hose or glass meter tube should break. The vent is necessary to prevent syphon action in such a case.

The brine is brought into the side of the mercury inlet weir above the mercury level. This point of entry was believed necessary for good brine distribution throughout the electrolyzer, but sampling now indicates that there is sufficient turbulence in the electrolyzer to ensure uniform distribution wherever the brine might be admitted. At Ludwigshafen it was claimed that results indicate that to obtain good brine distribution in the electrolyzer it must be admitted through the mercury inlet weir. Some scaling occurs at the mouth of the mercury inlet to the weir due to traces of sodium in the mercury and resultant formation of sodium hydroxide crystals. For this reason, a 12 mm. pipe welded to a small cover plate, is bolted over an opening in the top of the weir. This pipe extends downward through the weir and into the feed pipe for a distance of about 50 mm. The other end of the pipe extends out of the weir cover about 150 mm. A water hose is slipped over this to flush out the mouth of the mercury feed pipe. Mercury samples to check the efficiency of the amalgam decomposer are also extracted through this pipe by means of a glass sampling tube, after forcing the stagnate mercury in the seal back with water to procure fresh quantity for test. The mercury inlet weir for the Huels cell is shown on M.C. Drawing No. 269. The inlet weir for the "Drum Cell" is slightly different in design and is shown in M.C. Drawing No. 217h.

The amalgam outlet weir is also a rubber-lined welded steel plate device which bolts to the opposite end of the middle electrolyzer section from which the mercury inlet weir is attached. The face or boss on the middle electrolyzer section to which this outlet weir is bolted has been previously described. This weir serves three purposes:-

1) Collects the amalgam as it leaves the electrolyzer for conductance back to the pump section,
2) Conducts depleted brine out of the electrolyzer, and
3) By means of a trap, prevents depleted brine from flowing into the amalgam outlet pipe.

The amalgam flows out of the electrolyzer over the bottom of the weir to a pipe connected to the bottom, through which it is conducted to the bottom of a vessel in the amalgam pump suction line which will be discussed later. In plan, the weir is triangular in shape; one side is bolted to the electrolyzer and the discharge opening is located in the angle opposite. The depleted brine from the electrolyzer flows over the amalgam surface and leaves the weir through a rubber-lined pipe attached to the weir cover. The flow of depleted brine tends to carry away particles of anode graphite and other foreign materials which leave the electrolyzer with the amalgam. For this reason, the velocity of the brine is maintained as high as possible by minimizing the space between the amalgam surface and the weir cover. This weir is shown in M.C. Drawing No. 275. A similar weir for the "Drum Cell" is shown on M.C. Drawing No. 217g. This weir is equipped with a sight glass to indicate mercury levels, see M.C. Drawing No. 217t.

Accumulated graphite particles or other foreign materials can be flushed out of the depleted brine discharge pipe by applying water pressure to the stand-pipe of the vessel in the pump suction line to be described later. This operation requires the amalgam pump to be stopped for a few minutes and is accomplished without interrupting the electrolyzer operation.

The weak brine and the chlorine gas leave the electrolyzer through a device termed the "brine overflow pipe", which bolts to the side of the top electrolyzer section via the opening in that section previously described. It is located near the same end of the electrolyzer from which the amalgam discharges. It is fabricated from welded steel-pipe sections and all surfaces that come in contact with brine or chlorine are rubber covered. The brine overflow is made from 100 mm. pipe and resembles a side outlet "T" fitting; the longer arm of the two has an overall dimension of 750 mm. and the shorter arm, located at the mid-point of the longer arm, is about 100 mm. long. The short arm, via an overflow piece to be described later, is attached to the opening in the electrolyzer top section, the longer arm being in a horizontal plane, and its length parallel to the electrolyzer. Both ends of the longer arm are closed with heavy plate glass disks to enable an operator to observe what takes place inside. In the bottom of this longer arm are located three openings to which piping connections are made by means of sections of rubber hose. The first opening is the brine inlet to the overflow which is 45 mm. I.D. It is attached by rubber hose to the brine discharge pipe from the top of the sodium amalgam discharge weir previously described. The second opening is the chlorine gas and weak brine discharge, and is 95 mm. I.D. This opening conducts the weak brine and chlorine gas into a vertical pipe to the strong chlorine main in the cell room basement. The rubber hose connecting section, approximately 500 mm. long, is equipped with a pinch-clamp for isolating the cell from the main when required. The third opening is 45 mm. I.D. and is used for the same purpose as the second opening, except that it connects to the waste chlorine main in the basement. This connection is used only when the cell is first started in operation or when the chlorine is otherwise too dilute for plant usage. The rubber hose connecting section is also equipped with a pinch-clamp for isolating purposes.

The overflow piece which connects the "brine overflow pipe" to the electrolyzer is equipped with two flanges, one of which bolts to the electrolyzer opening and the other to the "brine overflow pipe". It is 355 mm. overall length and is 50 mm. I.D. The flange that bolts to the electrolyzer is 100mm. from the flange at the end which bolts to the "brine overflow pipe". This leaves a 234 mm. length which extends inside the electrolyzer when the piece is in position. This length inside the electrolyzer has a blind end, but has an opening in its upper surface approximating 330 square millimeters in area. Normally chlorine, only, leaves the cell through this opening as it is approximately 75 mm. higher in elevation than the brine inlet to the "brine overflow pipe". If brine does flow through this chlorine outlet, it can be seen by the operator through the sight glasses described above and is an indication of a brine flow stoppage. The brine level in the electrolyzer thus established leaves a chlorine space above of about 100 mm., which is slightly wedged shaped due to the slight tilting of the entire electrolyzer assembly as previously described. The "brine overflow pipe" on the "Drum Cell" differs only in details with the Huels type described above.

Rotor.

The rotor assembly consists of four mild steel chrome-free disks, each 20mm. thick and 1.8 meters in diameter, mounted on a steel drive shaft approximately 1450 mm. long and 75 mm. in diameter. The disks are spaced 200 mm. center to center. This distance is maintained by steel spacer sleeves between the disks, which are also mounted on the shaft. The disks are keyed to the shaft, see M.C. Drawing No. 271.

When the rotor is assembled, the disks with the sleeve spacers between them are held vertically in a jig on the floor. The center section of the electrolyzer body is then lowered around the vertical disks with an overhead crane. When the shaft openings in the section are aligned with the openings through the disks, the drive shaft is then threaded through. After the stuffing boxes are packed and the outboard bearings adjusted, the entire assembly is ready to be lowered into position on the bottom electrolyzer section. Bearing and stuffing boxes are shown in M.C. Drawing No. 276, Exhibit No.

The mercury level in the electrolyzer is normally 25 mm. above the top of the rotor drive shaft. The shaft is thereby protected from the corrosive action of the electrolyte and no special materials of construction are required. The drive shaft stuffing boxes must be mercury-tight. With this arrangement, the disks are immersed in mercury to a depth of approximately 1 meter, which leaves a little less than half of each disk above the mercury level. On the four disks, the total area above the mercury level, comprising the active cathode area of the electrolyzer, is ten square meters.

When in position in the electrolyzer, the center of the drive shaft is 356 mm. above the level of the operating floor. To one end of the drive shaft is attached a 810 mm., 7 "V" belt sheave. Directly above this pulley, 1895 mm. from the floor, is the drive motor which is supported from the floor by a frame fabricated from steel pipe. The drive motor is of the totally

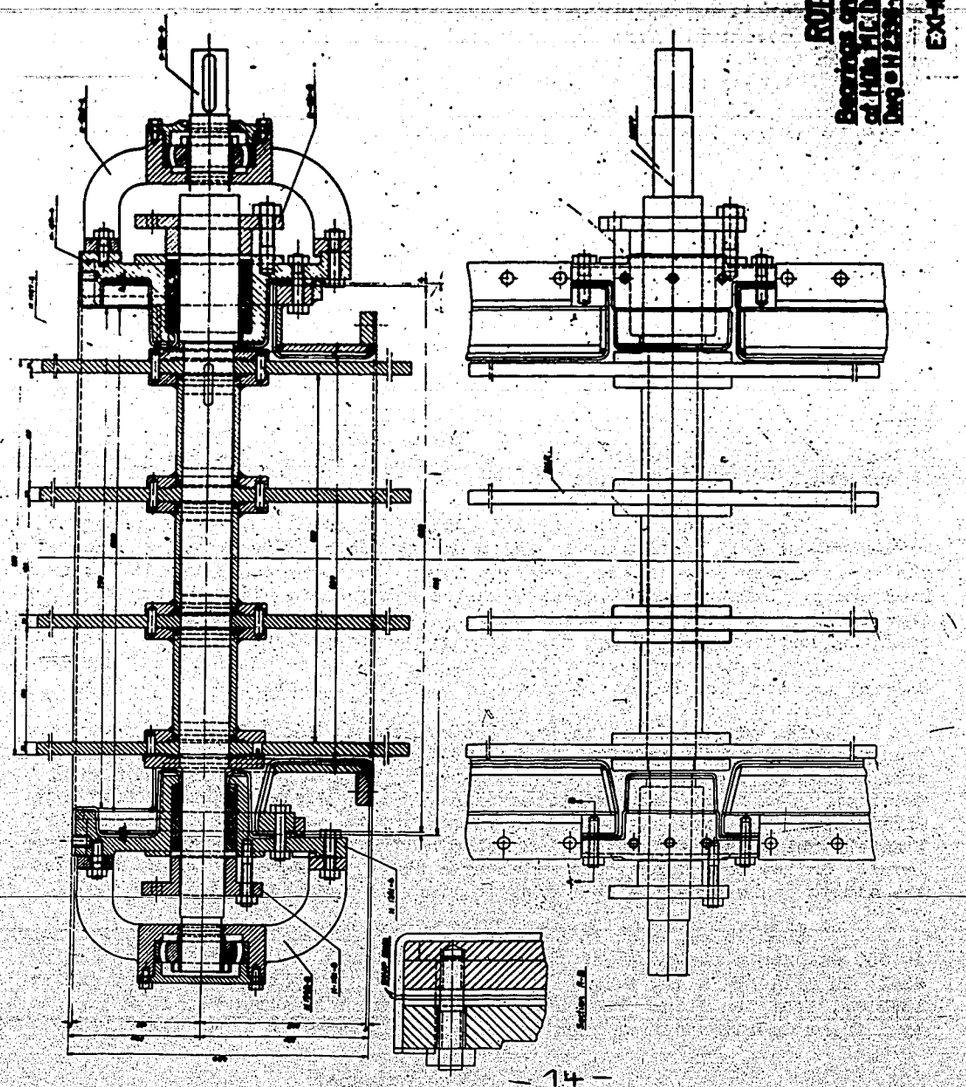


EXHIBIT 5

— 14 —

endloed type, rated at 1400 R.P.M., 500 V., and 0.55 KW. This speed is reduced to 60 R.P.M. by a built-in speed reducer. A 7 "V" belt, 114 mm. sheave is attached to the speed reducer shaft and this drives the rotor at 7½ R.P.M. in a clock-wise direction, when viewed from the drive side. The motor base plate is adjustable in a vertical plane to compensate for belt stretching. The motor normally draws 0.2 to 0.5 K.W.

The rotor assembly on the "Drum Cell" consists of five mild steel disks, 20 mm. thick and 1.845 meters in diameter, which are attached to a steel drum 617 mm. in diameter and 443 mm. long. The drum is welded to the centrally located drive shaft which is 115 mm. in diameter at the mid-point. The disks are spaced 110 mm. center to center. The three inside disks are welded to the drum and the two on the outside are attached by cap-screws. This arrangement is shown on M.C. Drawing No. 217j.

With this arrangement the level of the mercury surface in the electrolyzer is 273 mm. below the center-line of the rotor shaft. The shaft and drum ends are therefore exposed to the corrosive action of the electrolyte and are protected with rubber. The drum ends are rubber-covered and the shaft is fitted with a hard rubber sleeve which, due to wear in the stuffing boxes, is replaceable. The drum is normally immersed in the mercury bath to a depth of 35 mm. and when the electrolyzer is in operation the steel wall of the drum is a part of the active cathode area. The total active cathode area is 13.91m^2. On experimental cells it was stated that there was no serious leakage of electrolyte through the stuffing boxes which were packed with graphitized asbestos. See M.C. Drawing No. 217f and No. 217o.

The additional cathode disk in the "Drum Cell" was for the purpose of reducing the current density and thus extending the anode life. The principal reasons for the drum were to bring the elevation of the mercury level in the electrolyzer below the shaft to eliminate mercury leakage from the stuffing boxes; to decrease the mercury requirements for the cell, and to give a more rigid construction to the rotor assembly.

The rotor on the "Drum Cell" is driven by a "V" belt drive similar to that used for the Huels cell. The "Drum Cell" rotor drives on the incompleted commercial installation at Ludwigshafen had the motors suspended from the basement ceiling. This location is now considered to be possible leakages from the operating floor and to the relative inaccessibility for maintenance. The pulley arrangement rotates the rotor at 7.0 R.P.M. This rate was stated to be the optimum for minimum hydrogen evolution in the "Drum Cell". This speed was also used on the Huels type cells at Rheinfelden.

At Huels the rotor drive motor as well as the mercury pump motor, later discussed, were once equipped with ammeters and an alarm system which sounded a horn in the cell building and lighted a lamp near the motor if the motor stopped running. These features are not in operating order at present due to the shortage of labor and the scarcity of electric bulbs.

The installations at Rheinfelden and Ludwigshafen were similarly

equipped with alarm systems on the drive motors. Chemiefaden had also installed an auxilliary alarm which was sounded if the rotor stopped turning. This system was actuated by a device driven by the rim of the drive pulley attached to the rotor shaft and worked on the centrifugal force principle. This was deemed necessary as it was possible for the rotor assembly to be stopped and still have the drive motor running, such as when the "V" belts broke or became loose.

Anodes.

At Huels the anodes are of graphite and are arranged in eight vertical rows in the electrolyzer, one row on either side of each of the four cathode disks. Each vertical anode row is made up of five plates that are supported by small rubber blocks which rest on the top surface of the mercury displacers. The plates are fastened to each other with graphite splines. The anode arrangement is shown in Exhibit 3 and in M.C. Drawing No. 280.

The anodes are made from slabs which are received at the plant in two sizes, each of 80 mm. x 340 mm. cross section. The respective lengths are 1850 mm., and 1050 mm. The short lengths are also sawed into two pieces, lengthwise, for the smaller top row of anode plates. The apparent density was determined on one slab of each size as 1.59 and 1.63 respectively, and is reported to average 1.60 with a corresponding porosity of 24%. No physical tests are made on graphite at this plant.

Each of the five plates in an anode row, although differing in size and shape, is prepared by the following machining steps in the graphite shop:-

1) Each slab as received is planed on one face and one edge. This provides two flat surfaces at right angles to each other from which ensuing machining operations are guided. Usually it is necessary to remove from 1 to 2 mm. of graphite in this operation to obtain flat surfaces. The machine used is similar to a lumber plane having a stationary horizontal bed with rotating, horizontal, planing knives in the center.

2) The slabs are next moved on small wagons to the grooving machine where the grooves, 10 mm. wide x 23 mm. deep are cut for the graphite splines. This operation is performed on a machine similar to a lumber shaper which has a horizontal, stationary bed with a vertical shaft in the center, equipped with a routing tool.

3) The ends of the shaft are now trimmed with a lumber type band saw. The operator scribes lines on the slabs and then roughly saws along them. The same procedure is followed whether the end of the slab is square or odd shaped.

4) The slabs are now moved to the next operation where the holes for the anode stems are drilled and tapped. Here the slabs are clamped in a jig mounted on the tool rest of a lathe and the slab is advanced mechanically to the drill. After the hole is bored,

the drill is removed from the live center of the lathe and is replaced with a tap, and the slab is again advanced mechanically to the tap, rotating at 60 R.P.M. The tap cuts a thread approximately 1½ mm. deep with 4¢ threads per centimeter. The rotation of the lathe is reversed to remove the tap from the hole. The machining of the slabs or anode plates is now complete.

The graphite splines are also cut in the graphite shop. They are 10 x 50 mm. in cross section and are made in odd lengths as it is not essential that they be in one piece in any joint. The splines are cut in the same shape as above described. They are made to fit snugly in the grooves in the plates, and are inserted by tapping with a wooden mallet.

The graphite anode requirement for one electrolyzer is 1600 Kg. as purchased and 1375 Kg. after machining.

The lower plates in the anode assembly are made in two pieces because, first, single pieces of sufficient length are not obtainable and, secondly, the wastage of material is not as great on two short pieces as it would be on one long piece.

The anode stems are made from similar graphite, received in the plant in the form of rods 61 mm. in diameter and 765 mm. long. These are sawed into two 370 mm. lengths for the long stems to be screwed into the middle anode slab, or into three 240 mm. lengths for the short stems to be screwed into the lower anode slab. After sawing to length, each piece is preferably, but not always, rough-turned to 57 mm. diameter in the lathe referred to above. Following this a long 23 mm. diameter drill is secured in the live center of the lathe and a hole is drilled into one end of the stem which is clamped in the tool rest jig. This hole is drilled 340 mm. deep in the long stem and 210 mm. deep in the short stem. The rough turning of the stem permits greater accuracy in centering this hole.

The stems are now moved to another building for insertion of solid copper rods into the drilled holes. These rods are 20 mm. in diameter and come in two lengths, 370 mm. and 240 mm. for the long and short graphite stems, respectively. The copper rods are first tinned by dipping into a bath of molten lead in a gas fired pot. Six anode stems at a time are placed in a rack with drilled end up, and are heated by means of vertical gas burners, two to each stem, until thoroughly warmed. Then a quantity of molten lead is poured into the hole and the hot tinned copper rod is quickly inserted. The rod comes to rest with about 50 mm. projecting above the top of the stem, with molten lead overflowing from the annular space between copper and graphite.

Formerly, a mixture of 40 parts tin and 60 parts lead was used both for tinning the copper and for filling the space between copper and graphite. Due to the scarcity of tin during the war, lead was tried alone and found to be fully satisfactory. It appeared to flow even better into the graphite pores, although a somewhat higher temperature is required.

Following the above operations, the copper-fitted stems are allowed to cool, and are then transferred back to the graphite shop. Here the second machining operation is performed in the same lathe as previously used. The stem is turned to 48 mm. diameter for the entire length. Although this is not strictly necessary and has not always been carried out in the past, it is desirable preceding impregnation, for two reasons; i.e., to reduce the amount of impregnant used, and to afford somewhat better penetration.

The stems are now ready for impregnation to seal the pores against passage of electrolyte from the cell during operation. The impregnant used is a mixture of two grades of coal tar pitch, to achieve sufficient fluidity for impregnation without appreciable softening at temperatures up to 100°C. For this purpose, two parts of a grade melting between 90° and 100°C. are added to one part of a grade melting between 120° and 140°C. The impregnation is carried out in a cylindrical welded steel tank, 500 mm. in diameter by 1100 mm. deep, closed at the bottom and fitted with a flange around the top. A sufficient quantity of the pitch is melted in the tank by means of two annular gas burners located around the tank, and about 300 mm. and 700 mm. above the bottom of the tank, respectively. A steel frame rack, designed to fit inside the impregnating tank, is loaded with 60 long stems and 60 short stems, in two layers. This is now lowered into the molten pitch in the impregnating tank. The cover plate is then tightly bolted in place, and a vacuum of approximately 735 mm. is applied. For this purpose a water jet suction pump is used. The vacuum and gas heaters are left on over night, for a period of approximately 16 hours. The temperature of the molten pitch is held between 200° and 220°C. The following morning, the vacuum line is closed, and air is admitted to atmospheric pressure. The stems remain the molten bath for several hours during which period the pitch flows into the evacuated voids of the graphite. The cover is then detached and the rack removed in time for the next 24 hour impregnation cycle. Heavy fumes rise from the tank when the cover is raised, and are carried off through a hood provided with a draft.

After cooling, the stems are again transferred to the graphite shop. Now the end of the stem away from the copper is turned to 42 mm. diameter for 160 mm. of length and the balance to 45 mm., again in the lathe previously used. A "V" thread is then carefully cut on the smaller diameter, using five successive settings of the tool. There are approximately 68 threads (4½ per cm.) about 1½ mm. deep.

In the case of the few experimental cells where the anodes are shifted closer to the steel disks after only 6 mm. wear, about 40 mm. of the projecting end of the stem is again turned from 45 to 33 mm. in diameter.

The total weight of the stems used on each cell as received is 45 Kg. After machining a set of 16 long - 16 short stems, excluding the weight of the copper rods, weighs approximately 18 Kg. The density of ten stems was determined as 1.58, nominally 1.60, the same as the slabs.

The stems are now screwed into the threaded holes in the slabs by hand. The fit is very close, and considerable force is required to complete

the insertion. When finished, the stems protrude slightly more than 80 mm. for the short slabs and 210 mm. for the long slabs. The assembled anodes are now ready for mounting in the cells.

Since each of the 32 anode stems must normally carry 750 amperes, it is important that the metallic core be extended as far as possible into the stem to avoid excessive voltage loss. When the plant was first started, the threaded portion of the stems was longer and the metallic core was carried further into the anodes within the zone of electrolysis between the cathode disks. In this location, an appreciable amount of lead, tin and copper found its way into the electrolyte, also resulting in contamination of the amalgam with lead and tin. This resulted in high hydrogen in the chlorine gas, sluggish amalgam flow, and coating on the surfaces of the decomposer graphite which retarded amalgam decomposition. The entire brine system had to be cleaned, much of the mercury distilled, and much of the decomposer graphite replaced. Since shortening the stems and keeping the metallic cores of the stems outside of the electrolytic field, these difficulties have been almost completely eliminated, or confined to those cases where a stem breaks inside the cell.

The anodes are installed in the electrolyzer top section before attaching the cover plate or the two anodic end plates. Four hard rubber blocks measuring 16 mm. x 75 mm. x 135 mm. are placed on each end of the top surfaces of the three mercury displacers and on the two shoulders in the side walls of the middle section of the electrolyzer. These blocks serve not only to support the weight of the rows of anode plates but also to maintain a 15 mm. space below each anode through which the electrolyte can circulate. This circulation is important as otherwise the electrolyte confined between the anodes and the steel cathode disks would tend to become depleted in sodium chloride content and result in increased hydrogen discharge. The bottom row of anode plates (16 pieces) are now slid into their approximate positions with their machined faces adjacent to the cathode disk surfaces and on top of the hard rubber blocks. The two pieces in each row are joined together by a spline which had previously been inserted in the groove of one of the pieces. The second and third horizontal sections of the anodes are similarly set in approximate position and splined to each other.

The anode assemblies are now shifted into their final position with their faces 5 mm. from the adjoining cathode disk face. Steel strips 5 mm. thick, approximately 35 mm. wide and 1½ m. long, inserted vertically, are used as spacers in making this final setting. Graphite wedges are now lightly driven between each of the rows of graphite as well as between the electrolyzer side and the outside graphite rows. The wedges are driven along the upper edges and the ends of the graphite plates. When the entire anode assembly is securely wedged, the steel spacer strips are removed. The anodic plates are now threaded over the protruding anode stems at each end of the electrolyzer and, with insulated bolts, are fastened to the top electrolyzer section. Circular ring gaskets and next, steel holding flanges or glands are slipped over each anode stem. Then, as previously described, the gaskets are compressed to make an electrolyte-tight seal between the anode stems and the

anodic cover plates. The assembling of the anode is now complete.

The cells installed at Heydebreck were said to be patterned after an experimental cell seen at Ludwigshafen. This cell was of the Huels type but had the graphite anode slabs mounted vertically so that the anode stems passed upward through openings in the flat cover-plate. This change was to eliminate electrolyte leakage around the anode stems which had been found to be of a serious nature at the Huels plant. The change had the disadvantage of requiring additional coppering to bring the anode leads up to the top of the electrolyzer which also obstructed the overhead working space.

The anodes in the "Drum Cell" differ principally from those in the Huels type in the following respects:

1) There is a total of six vertical rows of anode plate assemblies; one row between each pair of cathode disks and a row outside of each of the outside disks. This design was intended to eliminate the need of anode adjustment as the anodes were to be discarded when the voltage requirements became excessive. It has been determined experimentally that this practice is not economical and that the Huels design is preferable.

2) Cell four of the graphite slabs in each vertical row assembly is equipped with anode stems for better current distribution. A total of 48 stems are thus required per electrolyzer.

3) The horizontal anode rows are not splined together but are separated by spacers to make horizontal openings to improve electrolyte circulation.

4) The anode stems are taper-fitted to the anodes. This construction has the one advantage of being less costly than the screw type.

The "Drum Cell" anode arrangement is shown in Exhibit 2 and in M.C. Drawing No. 217c. The anode and anode stem arrangement is shown in M.C. Drawing 217b.

Amalgam Pump.

The amalgam pump delivers the sodium amalgam from the amalgam discharge weir on the electrolyzer to the top of the amalgam decomposer. The amalgam then flows through the decomposer, and back into the electrolyzer via the feed weir by gravity. The pump is of the vertical centrifugal type with the stuffing box located high enough above the intake so that it is not subjected to positive pressures. The same pump design was used on both the Huels and drum-type cells. See M.C. Drawing No. 314 and No. 217k. The pump will deliver a maximum of 60 liters of amalgam per minute against the fixed head of 1.2 m., but normally operates at 30 to 40 liters per minute. The pump is built of cast iron, not rubber lined, and is supported on insulators which rest on the operating floor near the electrolyzer. Curves on pump operations

are shown in M.C. Drawing No. 334 and Exhibit No.

The discharge piping from the pump to the decomposer is rubber-lined and has an I.D. of approximately 40 mm. This pipe was formerly equipped with a throttling valve to control flow rates, but this was found unnecessary and most of the valves have been removed. At Huels this pipe as well as a similar pipe on the pump suction, is flushed with water every twelve hours through a 15 mm. pipe attached to the pump immediately below the stuffing box. This operation is carried out without stopping the pump.

In the pump suction piping between the pump and the amalgam discharge weir on the electrolyzer, there is a cylindrical rubber-lined vessel approximately 110 mm. I.D. and 450 mm. high, equipped with a removable cover. The amalgam from the electrolyzer enters this vessel by gravity through a standpipe in the bottom which extends upwards about 100 mm. above the point of entry. The amalgam flows from the side of this vessel near the bottom, by gravity, through the suction piping to the pump. See M.C. Drawing No. 267. This vessel serves five purposes:

1) Makes a positive seal against electrolyte entering the pump suction in that the pump will draw air from the chamber rather than suck the seal loop empty of amalgam;

2) Provides a point where the piping and outlet weir on the electrolyzer can be flushed with water for cleaning purposes;

3) Is the only point in the cell at Huels where the flow of mercury can be observed. A trained operator can determine visually whether or not additional mercury is required in the cell by inspection at this point. As previously mentioned, the "Drum Cells" and the cells at Rheinfelden had a sight-glass on the face of the amalgam discharge weir for observing mercury levels;

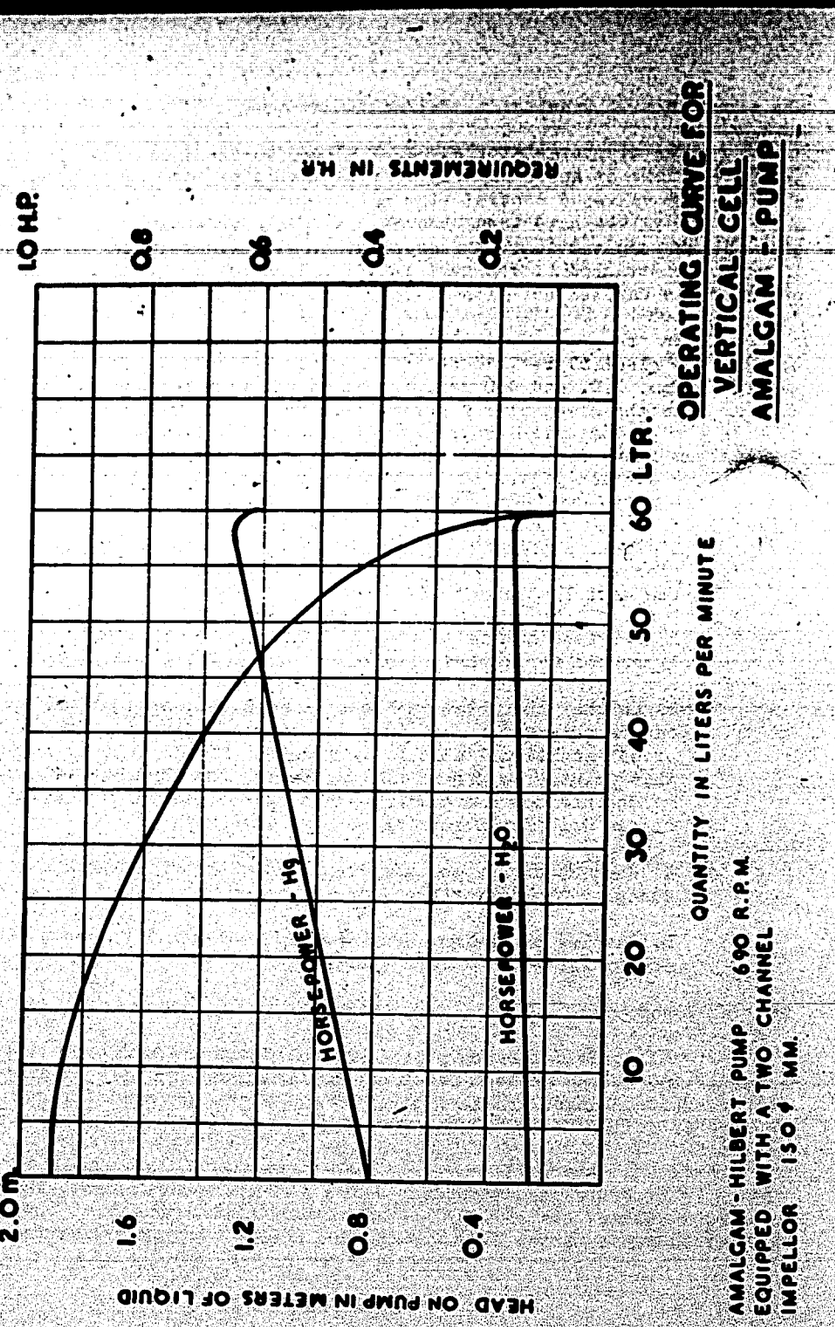
4) When required, mercury is added to the cell at this point without stopping the operations; and

5) Samples of amalgam from the electrolyzer for control analysis are extracted from this vessel.

Amalgam Decomposer.

All vertical mercury cell installations in Germany utilize the vertical or tower type amalgam decomposers. They consist of containers packed with graphite chunks, and have piping connections arranged for counter-current passage of sodium amalgam down from above, and purified water up from the bottom.

At Huels the decomposer body is of rectangular cross-section measuring 440 x 640 mm., is 980 mm. high, and is fitted with a flat cover plate and conical bottom section, M.C. Drawing No. 268. These parts are fabricated of



welded steel plate and all interior surfaces are covered with 6 mm. of rubber, which is brought over flanges and fittings so that all surfaces in contact with the caustic liquor are protected. This was believed necessary, when the plant was built, to prevent electrolysis and failure of the welds, as well as to keep the iron content of the caustic solution low. It was found that if the welds are first stress relieved, they do not fail when later submerged in caustic soda liquor, and that the iron content of the caustic liquor produced is not appreciably increased when unlined decomposers are used. For these reasons the rubber linings that have failed are not repaired nor replaced.

Both ends of the rectangular decomposer body are fitted with external flanges for attaching the top cover plate and the bottom conical section, respectively. A flange is also welded internally, 60 mm. below the top for bolting in position a perforated steel amalgam distributor plate, the function of which is described later. Four steel legs are welded to the bottom for supporting the decomposer on porcelain insulators which in turn, rest on a steel frame-work grouted in the concrete floor. An amalgam inlet weir, triangular in shape when viewed from above, is welded near the top of the side nearest the amalgam pump. It has a flanged round opening to fit the discharge pipe from the amalgam pump, and an opening into the decomposer body approximately 400 mm. long by 140 mm. high, the bottom edge of which is approximately level with the internal perforated plate flange. In the adjacent side of the decomposer body nearest the electrolyzer, and about 15 mm. below the internal flange above referred to, is welded a pipe approximately 100 mm. in diameter by 300 mm. long. This serves as an outlet for the caustic soda liquor and hydrogen gas and is connected by piping to the pipe-header in the basement. A baffle plate in the mouth of this opening maintains the caustic liquor level at an elevation slightly above the center-line.

The flat steel cover has a circular hole in the center in which a manometer is inserted during operation to measure the hydrogen gas pressure, and through which samples of outflowing caustic may be drawn. The amalgam distribution plate of perforated steel, approximately 2 mm. thick, with 1 mm. holes on 6 mm. centers, is bolted to the top side of the internal flange. In the center is welded a $\frac{1}{2}$" pipe nipple, 30 mm. high, which serves as a vent or pressure equalizer between the gas spaces above and below the plate. Between the decomposer body and lower conical section is bolted a perforated plate for supporting the graphite packing. The holes in this plate are approximately 6 mm. in diameter on 20 mm. centers.

The decomposer packing consists of somewhat less than 200 Kg. of broken graphite chunks sized preferably from 10 to 50 mm. The fill rests on the lower perforated plate and is levelled off at about 60 mm. below the upper amalgam distributor plate. Fresh material such as the anode slabscrap from the graphite shop is preferred but old graphite from discarded anodes has also been used. The large pieces are broken up in a small mill, the discharge from which is screened to remove fine particles.

Before use in the decomposer, the chunks are given a triple chemical treatment, each of which consists of the following:-

1) Overnight soaking in a solution of iron chloride made by dissolving 60 Kg. of scrap iron in 300 liters of concentrated muriatic acid.

2) Air drying.

3) Roasting to 800°C in an inclined rotating kilm through which the graphite chunks pass in about a ten minute period, counter current to hot reducing gases from gas burners.

4) Cooling in air.

This treatment deposits iron in the pores of the graphite rendering it more active galvanically. It was stated that graphite treated in this manner was ten times as active as untreated graphite. When the decomposer is newly filled, the sizing of particles is uniform from the bottom to the top. In use, the smaller eroded particles rise to the top where 100 to 150 mm. layers are removed and replated with new material when the cells are shut down for anode shifting or renewal. The main body of graphite is seldom disturbed.

The amalgam discharged from the pump enters the decomposer through the amalgam inlet weir, spreading over the perforated steel plate, through which it trickles down over the graphite bed, counter-current to the rising liquid. Stripped mercury flows out of the bottom of the lower conical section through a 2" rubber-lined pipe and into the inlet weir of the electrolyzer.

The purified water rises through a 1 inch riser pipe connected to the header in the basement and is reduced to ½ inch size above the floor. From this pipe the water passes through a rotameter about 15 mm. O.D. and 200 mm. long. The type of rotameter used has a glass float and is calibrated from 10 to 90 liters per hour. The glass tube is connected to the 15 mm. pipe above and below by soft rubber tubing. Regulation of the water flow is controlled by a pinch-clamp on the lower tube. The water then flows upward through a pipe to a point near the elevation of the decomposer cover from which it is directed downward by a 180° bend. From this pipe the water enters the decomposer via a Tee fitting and a 1" pipe which is connected to the water inlet connection near the top of the conical bottom section. To the other opening of the tee is connected a valve, normally closed, for draining the liquid from the decomposer when required. The water rises through the perforated plate supporting the graphite fill, up and around the graphite particles. As it rises it increases in caustic soda content until it overflows, together with hydrogen, through the overflow pipe previously described. To this fitting, on the outside flange, is connected the 75 mm. rubber-lined discharge pipe, through which the liquid and gas pass vertically downward into the corresponding header in the basement. A break is provided in the line, across which is connected a 450 mm. length of rubber hose which may be closed, when the cell is shut down, by means of a pinch-clamp.

The caustic liquor is very turbid and dark grey in color due to its content of graphite particles and must be filtered before use. Two filters

are installed for this purpose in an adjacent building, each equipped with twenty-four porous carbon tubes one meter long and about 100 mm. O.D.

The decomposers used on the Huels type cells at Rheinfelden and in the "Drum Cell" installation at Ludwigshafen are both circular in cross-section and are constructed of cast-iron. These designs were used for reasons of economy. The Rheinfelden decomposer is shown in M.C. Drawing No. 325 and in Exhibit No.

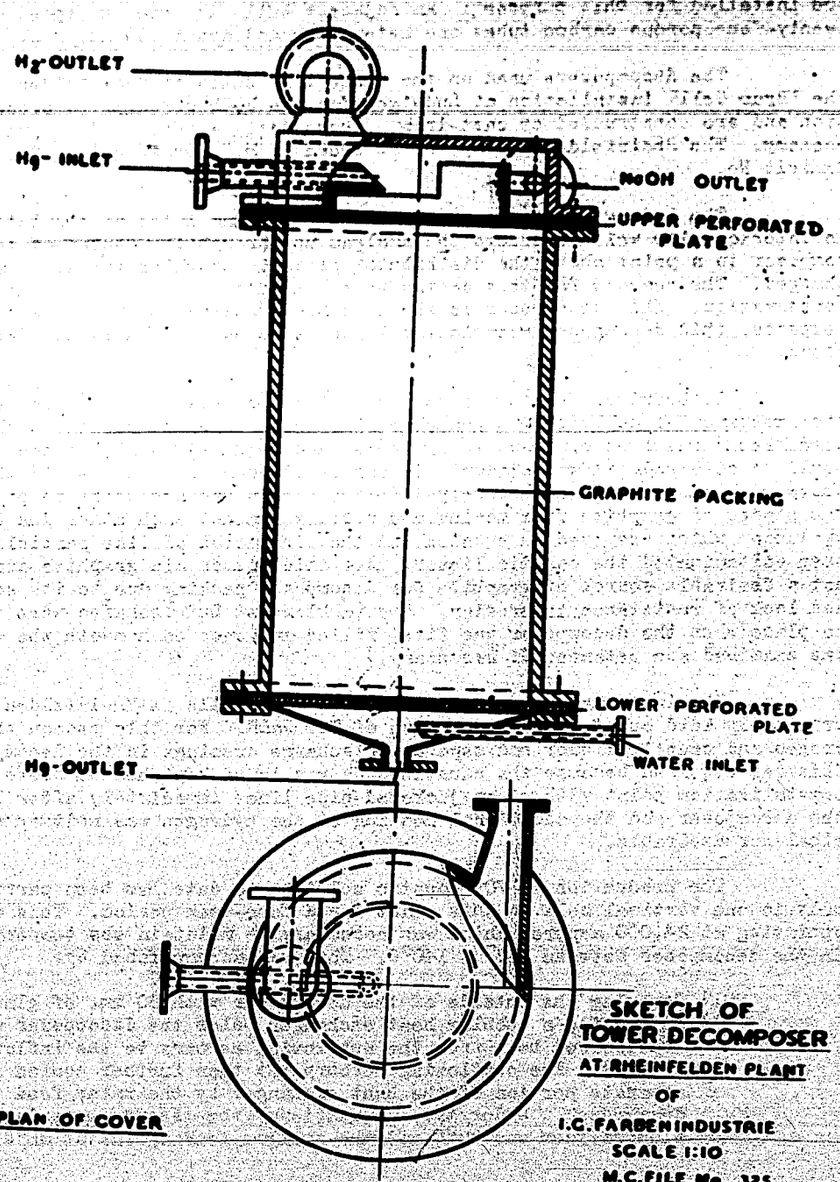
The Ludwigshafen decomposer has the amalgam inlet at the bottom with an interior pipe which conducts the amalgam up through the center of the decomposer to a point above the distributor plate on to which the amalgam is discharged. The reasons for this design were stated to be compactness and heat conservation. This decomposer is shown on M.C. Drawing No. 317L. In other respects, this decomposer was similar to the type used at Huels and described above.

At Ludwigshafen it was stated that the caustic liquor produced in the experimental cells there, and also that produced on commercial scale at Heydebreck, was free of graphite particles and required no filtration. This could be attained, it was claimed, in any decomposer of this type if the graphite packing were packed securely in place. This was necessary to prevent the pieces of graphite from moving and rubbing against each other due to gas evolution which resulted in erosion and the liberation of fine particles which then contaminated the caustic liquor. For this reason old graphite anodes are not a desirable source of graphite for decomposer packing due to its softness and lack of resistance to erosion. The packings at Ludwigshafen were tamped in place when the decomposer was first filled and once each month the packing was examined and retamped if necessary.

The installation of Huels-type vertical cells at Rheinfelden were originally laid out for the production of 70% NaOH. For this reason the hydrogen and caustic liquor had separate discharge openings in the decomposer. This was required because the caustic soda was to be kept heated above the crystalization point with steam-jacketed pipe lines immediately after leaving the decomposer and the additional heating of the hydrogen was neither economical nor desirable.

The production of 70% caustic solution to date has been carried out only in one vertical cell in this plant for a four-week period. This cell was operating at 24,000 amperes which was necessary to maintain the temperatures in the decomposer between 130° - 140°C. This was accomplished by:

1) Covering the outside of the decomposer with 30 mm. of glass wool.
2) Installing a tubular heat exchanger below the decomposer which transferred heat from the outflowing mercury to the inflowing amalgam. The outflowing mercury was then further cooled in a separate portion of the heat exchanger by the water feed to the decomposer. Under these conditions, the mercury entering the electrolyzer was 80°C and the amalgam leaving was at 85°C.



SKETCH OF TOWER DECOMPOSER AT RHEINFELDEN PLANT OF I.G. FARBENINDUSTRIE SCALE 1:10 M.C. FILE No. 325

EXHIBIT 7

Materials of construction for equipping all cells with heat exchangers were not available so the production of 70% caustic liquor was temporarily abandoned. The graphite packing in the decomposer was not impregnated during this period, but impregnation was considered advisable and the necessary equipment was being procured at the close of the war.

Electrical Connections.

The cathode connection on the Husls cell is made up of six copper bars of 17 x 160 mm. cross-section each. Three of these bars are bolted to the machined steel surfaces at each end of the bottom electrolyzer section previously described. Each copper bar is bent for 270 mm. of contact, and is overlaid by a steel plate approximately 10 x 170 x 270 mm., which serves to distribute the pressure from six 80 mm. studs to insure good contact. The contact surfaces of both steel and copper are tinned and thoroughly cleaned before making up the joints. At each end of the electrolyzer the contact area is 0.13 m.^{2} for normal passage of 12,000 amperes or half of the cell load. These three cathode bars at each end of the electrolyzer are connected to the horizontal main conductor bars of the same cross-section located below the cell room operating floor. These bars are mounted on porcelain insulators which are supported on brackets made up of steel angles. The normal current density through these bars is 147 amperes per square centimeter. The anode connections to each electrolyzer consist of six vertical lead bars which rise through openings in the floor in two groups of three bars each. Each group rises, close to, and at opposite ends of the electrolyzer. Above the floor a set of four bars, also vertical and of similar section, are clamped to each riser group. These four bar sets and their connections to the graphite anodes must be removed when access to the inside of the electrolyzer is required and are, therefore, made demountable. To these four bar sets at each end of the cell, and at the elevations of the upper and lower anode stem projections, are brazed four horizontal copper bars of 25 x 90 mm. cross section, each to conduct current to four anode stems normally 3000 amperes. Half of these bars extend only half-way across the ends of the electrolyzer to carry current to the nearest four anode stems in each row, and the balance extends completely across to conduct current to the farther four anodes in each row. The weight of these bars are carried by porcelain insulators which rest on brackets attached to the anodic end-plates of the electrolyzer. The current is carried from these bus bars to the copper rod, leaded into each anode stem, as previously described, by means of two flexible copper cables which measure 18 mm. in diameter and are 280 mm. long. The cables are soldered into holes drilled into the bus bar edges at one end and into a copper clamp at the other end. The clamp is secured to the 50 mm. copper rod projection of the anode stem by means of two 3/8" bolts. The connections were said to be very satisfactory for loads up to 28,000 amperes.

The anode bus bars in the "Drum Cell" are bolted directly to the anodic end-plates shown in M.C. Drawing No. 2171. The steel plates, rubber-covered on the undersides, thus are utilized to conduct current to the anode stems. The actual contact between the stems and the plates are made with a flexible copper cable as shown in the drawing referred to above.

Two short-circuiting switches are located below the floor under the ends of each cell. These are each of nominal 12,000 ampere capacity, and are connected between the copper risers from negative and positive connectors to the electrolyzer. The switch is the same at Huels, Rheinfelden and Ludwigshafen and is recognized to be of a poor design. The switches used on the horizontal cells at Hoechst, and described in FIAT Final Report No. 816, were stated to be more satisfactory. Operating handles for these switches extend through the floor. It was stated that this location of the switches was undesirable due to the inaccessibility for maintainance. At Rheinfelden and Ludwigshafen the short-circuiting switches were located above the floor. Three short-circuiting bars or "jumpers" can be connected to suitable extensions of the cell bus connectors, and are installed when the cell is to be shunted out of the circuit for more than one hour, or when a switch has to be removed for maintainance.

Due to the shortage of copper during the war, a considerable amount of cell room bus-bars were made of aluminum. Considerable difficulties were encountered with corrosion of these bars by mercury which leaked down on them. Some of these bus-bars at Rheinfelden were decreased approximately 50% in cross-section by this corrosion and it became necessary to build a protecting cover over all bars exposed to mercury drippage. All bus-bars were painted.

CELL OPERATIONS.

The Huels plant was the only operating vertical cell installation visited and, therefore, this section is devoted to a description of their methods.

Starting a Cell or Circuit.

When a cell is completely assembled and the critical items, such as electrolyzer leveling and the anode-cathode spacing are known to be correct, the cell is ready for operation.

In starting the cell, the operators and the cell maintainance men co-operate in performing the following duties:-

1) The cathode disk drive motor is started.
2) The amalgam pump is started.
3) Mercury is added to the cell through the top of the vessel in the pump suction line. As the mercury is added manually direct from flasks, it flows into the pump suction and is pumped into the decomposer from where it flows into the electrolyzer. When the mercury flows from the discharge weir of the electrolyzer back into the vessel in the pump suction line in sufficient volume, the addition of mercury is stopped. The mercury required to thus fill the system amounts to 2000 Kgs. for the Huels cell and 1200 Kgs. for the "Drum Cell".
4) The purified brine feed to the electrolyzer is now started by loosening the pinch-clamp on the feed line. The brine feed

should be warm to minimize hydrogen evolution, 60°C. being desirable.
5) Simultaneous with the starting of the brine feed the purified water feed is started into the amalgam decomposer.
6) When the electrolyzer is full of brine, as indicated through the sight-glasses on the brine overflow, the electrolysis is started by opening the two short-circuiting switches simultaneously. The effluent electrolyte and chlorine gas are directed through the waste chlorine pipe.
7) Brine and water feeds are now adjusted at the proper rates for the current flowing through the electrolyzer. The hydrogen formed in the decomposer is vented to the atmosphere by removing the rubber stopper, containing the manometer tube, from the decomposer cover. This venting is done for 15 minutes to guarantee that no air will be admitted into the hydrogen piping system.
8) During this same period the air in the electrolyzer has been displaced by chlorine and, after testing to make certain that the gas is 95% Cl_2 or higher, and that the H_2 content is not over chlorine and brine electrolyte flowing from the electrolyzer are diverted to the strong chlorine main.

This same procedure is followed when starting one cell or a circuit of cells except for the current load. With one cell, the starting amperage is the same as whatever load is being carried on the circuit, normally 24,000 to 28,000 amps. With the starting of an entire circuit of cells all the short-circuiting switches are in the open position and an initial load of 16,000 amperes is placed on the cells from the rectifier station. The amperage is increased as the chlorine gas concentration increases. This procedure is followed to minimize the wastage of the dilute chlorine which is absorbed in a packed tower by 10 to 12% solution of NaOH. A normal current load of 24,000 amperes on starting a cell circuit is usually reached within two hours after the current is first applied.

Duties of Cell Operators.

The operators in the cell room perform the following duties:

1) Analyse the gas in the four chlorine pipe headers below the corresponding cell rows every two hours by absorption in NaOH solution in a 100 ml. burette. If the Cl_2 plus CO_2 thus determined, is below 97% the gas from each individual cell in the row is similarly checked to locate the source of the low chlorine. This gas sample is taken through the manometer opening in the electrolyzer cover. When the cell with low Cl_2 is located the percentage of H_2 is determined by the method previously described in FIAT Final Report No. 816. If the H_2 is low the cell is examined for air infiltration; if high other checks, described later, are made to determine the cause and make corrections.

2) Determine the percentage of sodium in the amalgam leaving the

electrolyzer from each cell every 12 hours. This sample is secured with a glass tube dipper from the vessel in the pump suction line. With normal amperage of 24,000 - 28,000 amperes on the circuit the sodium content should be from 0.1% to 0.2%. If higher, the mercury entering the cell is checked similarly for sodium content to check the efficiency of decomposer operation. This sample is taken with the same glass dipper through the ½" wash-out pipe in the mercury feed weir but only after the pipe has been thoroughly flushed with water to displace the stagnant mercury contained in the pipe to assure a representative sample. The sodium content at normal loads should be 0 to 0.01%. The apparatus and method used for determining the sodium content of the amalgam is described in FIAT Final Report No. 816.

3) Check the density of the NaOH solution from each of the four caustic mains in the basement with a hydrometer every two hours. This should be such as to give 49% to 51% NaOH. If higher or lower each cell decomposer in the row is checked individually for the cause by sampling through the manometer opening in the cover and the required water feed adjustment is made.

4) By frequent inspection, insure that cathode disk rotation and amalgam pumping proceeds without interruption.

5) By periodic checking, insure that the positive pressure of the hydrogen in the decomposer and the chlorine in the electrolyzer are maintained at approximately 20 mm. H_2O.

6) By periodic checking, insure that the flow of brine to the electrolyzer is uninterrupted and is maintained at the proper volume as indicated by the rotameter.

7) By observation through the sight-glasses, make certain that the electrolyte discharge is flowing from the amalgam exit weir. If this flow is stopped the pipe should be flushed with water as later described.

8) By periodic inspection, make sure that the flow of purified water into the decomposer is maintained at the proper volume as indicated on the rotameter.

9) At least once every twelve hours, and more frequently if required, flush out the amalgam pipe lines with water to remove amalgam and crystallised caustic adhering to the pipe walls. This operation is done at two points. First, the discharge pipe from the pump to the decomposer and the suction pipe from the vessel in this line to the pump are flushed simultaneously by slipping a water hose over the 15 mm. pipe near the stuffing box on the pump and applying full pressure for a few minutes. Secondly, the amalgam pipe from the

vessel in the pump suction line back to the amalgam discharge weir, the weir itself and also the electrolyte discharge line from this weir up to the brine overflow, are simultaneously flushed by applying water pressure with a hose to the top of the stand-pipe inside the vessel in the pump suction line. This connection is made with a hose fitting equipped with a rubber stopper that fits tightly into the mouth of the stand-pipe. As previously stated, the amalgam pump is momentarily stopped for this operation. The efficiency of this washing is observed through the sight-glasses in the brine overflow.

10) Once each 24 hours, and more frequently if required, the mercury inlet weir and the mouth of the mercury inlet pipe to this weir are similarly flushed to dislodge adhering materials and to move them into the electrolyzer.

11) Periodically, visually check the amalgam circulation through the cell at the vessel in the pump suction line. Add mercury to the system if warranted.

12) Make periodic inspection of all cell joints for leakage and when found, take corrective measures to stop any leaks thus discovered.

13) Take voltage drops across each cell once every 24 hours.

14) Switch any cell or cells out of the circuit which cannot be maintained in good operating order. This should be done, for example, when the pump or rotor drive motor fails.

15) Keep written records on operating log sheets of all analyses made, irregularities in operations, corrective measures taken, and any other information essential to subsequent operators or plant supervisors.

Electrolyte.

The brine used at Huels is made by dissolving rock salt in depleted brine returned from the electrolyzers. The saturated brine thus formed is then purified for calcium, magnesium and sulphate removal. The equipment and methods used are similar to those described in FIAT Final Report No. 816 titled "Horizontal Mercury Chlorine Cells", and will not be repeated here.

A typical analysis of the purified brine as fed to the cells is as follows:-

NaCL	300 gpl	CaO	0.005 gpl
Na_2CO_3	0.2 gpl	MgO	0.003 gpl
NaOH	0.001 gpl	Cl_2	0.3 gpl
Na_2SO_4	2.0 gpl		

Experience has proven that the brine from the electrolyzers should

have a minimum NaCl content of 240 gpl to avoid excessive H_2 evolution and increased voltage requirements. The preferred concentration is 260 to 270 gpl NaCl. A typical analysis of the effluent brine is:-

NaCl ----- 265 gpl	CaO ----- 0.005 gpl
Na_2SO_4 --- 3.0 gpl	MgO ----- 0.003 gpl
NaOH ----- 0.02 gpl	

The above conditions require a flow of brine into each electrolyzer of 1200 liters per hour when operating at 24,000 amperes. With this flow and with approximately 45 cells in operation, the electrolyte temperatures are stabilized at 75°C., entering and 85°C. leaving the electrolyzers. These temperatures are ideal for good operation. When 100 cells were operated in 1944 and 1945 it was necessary to spray-cool the feed brine to attain these temperatures and prevent the boiling of the electrolyte in the electrolyzer. The principal effect of excessive temperatures in the electrolyzer is on the rubber-lining, the life of which is greatly reduced.

It was stated at Huels that impurities in the feed brine such as calcium and magnesium caused high hydrogen content of the chlorine gas by forming unstable amalgams which immediately decompose in the electrolyzer. Partial removal of sulfate was necessary to prevent an excessive accumulation of this impurity which would increase hydrogen discharge and the rate of anode wear. The generation of hydrogen in the Huels electrolyzers was stated to be less of a problem than with the evolution in other types of mercury chlorine cells. The fact that there has never been an explosion in the Huels cells would seem to substantiate this statement.

The circulation of electrolyte for resaturation at Huels was stated to result in the loss of 5 gms. of mercury per $m.^3$ of electrolyte circulated. The weak brine from the cells contains about 7 gms. of mercury per $m.^3$ which leaves about 2 gms. per $m.^3$ in the saturated brine returning to the cells.

The analysis of the filter cake from the Kelly-type filters used in the brine purification process has shown that the main loss of mercury occurs in this stage. It has been estimated that about 60 percent of the mercury normally lost can be attributed to the effect of filtration. No attempt, however, has been made to recover the mercury from the filter cake since it was not believed to be worthwhile in view of the fact that mercury was not expensive and sufficient quantities were available.

The greatest loss of mercury in filtration occurs when it exists in the metallic form. For this reason, the addition of sodium sulfite for removal of the last traces of available chlorine is kept at a minimum so as to avoid any appreciable reduction of the chloride to metallic mercury. Other aspects relative to mercury in the brine is discussed in the previous FIAT Final Report No. 816.

Electrolysis.

Electrolysis in both the Huels and Drum-type vertical cells takes place between the rotating faces of the cathode disks and the graphite anodes. The chlorine ions give up their charge on the faces of the graphite anodes and the gas thus formed rises through the body of the electrolyte to the chlorine space above. The sodium ions give up their charge on the surface of the film of mercury on the rotating cathode disks. The metallic sodium thus formed immediately combines with the mercury film to form sodium-amalgam. This sodium-amalgam is then swept from the rotating disks as those portions of the disk faces enter the main body of the mercury in the lower portion of the electrolyzer body. This removal of the amalgam from the disk faces was said to be both physical and mechanicl in nature. The amalgam having a lower density than the mercury bath, tends to be wiped from the disks by the bath, and secondly, the concentrated amalgams on the disks are removed by dilution with the mercury in the bath. The concentrations of the amalgams on the disks at any cell amperage were not known but sampling had indicated that the sodium content of the mercury in the bath increased uniformly as it flowed across the electrolyzer.

During the early development work on the vertical cell it was thought that the metallic sodium formed during electrolysis combined with mercury on the disk faces which was there due to amalgamation of the steel. Later this theory was disproven when experiments showed that mercury in a film approximately 1 mm. thick, is actually transported by the rotating disks. As the disk faces rise from the mercury bath the mercury tends to flow downwards due to gravitation and thus forms a fluid cathode surface. This surface or curtain of mercury must completely cover the steel disks to minimize hydrogen evolution. The disk surfaces were said to be incapable of transporting mercury in the above manner until electrolyzing current was applied and retained this property for only a few hours after electrolysis was stopped.

Experimental work has also proven that the speed of rotation and the diameter of the steel disks are controlling factors in cell operation. If the disks rotate too rapidly the mercury film is thrown off by centrifugal force; if too slowly the mercury is not lifted sufficiently to cover the entire disk. The maximum disk diameter which can be completely covered by a mercury film was said to be approximately two meters. The Huels plant operated with a disk rotation of 7.5 RPM and 7.0 RPM was used at both Ludwigshafen and Rheinfelden. The disks are always rotated in a clockwise direction when viewed from the drive side of the electrolyzer so that the concentrated amalgams are removed from the descending faces on the end of the electrolyzer to which the amalgam exit weir is bolted. This provides for rapid removal of the amalgams from the electrolyzer and thus minimized amalgam decomposition.

Both the Huels and Drum cells were designed for 24,000 ampere operation with current densities of 2400 and 1720 amperes per sq. meter respectively.

The range from 24,000 to 28,000 amperes was said to give satisfactory results at the Huels plant. Huels and Rheinfelden have both operated for short periods at 32,000 amperes. The "Drum Cell" was operated at 40,000 amperes, experimentally for two days. At their rated capacities both type cells have current efficiencies of 91% to 93%. Loss of current efficiency was stated to be due primarily to recombination of sodium and chlorine in the electrolyzer. Normal hydrogen content of the chlorine was 0.6% to 1.0% for the "Drum Cell" and 1.6% to 2.0% for the Huels type. It was stated that the volume of hydrogen evolution in the electrolyzers was essentially constant regardless of the amount of electrolyzing current flow. The principal objection to operating the cells above their rated capacities was the excessively high temperatures created in the electrolyzers and the deleterious effect of these temperatures on the rubber linings. When operated below 24,000 amperes the current efficiency of the cell is also lower. An experimental run on the Huels-type cells at Rheinfelden with 14,000 amperes gave an 85% current efficiency.

During the experimental work with mercury-displacers, as previously described, it was found that the magnetic fields set up in the electrolyzer had a braking effect on the cathode disk rotation. When operating with the present one-piece rubber-covered displacers at 24,000 amps., the disk drive motors require 200 watts. At 28,000 amps. these motors require 300 watts. With porcelain mercury displacers there was no change in the power requirements of the drive motors when the electrolyzing current was changed.

Anode Wear and Voltage Requirements.

At the Huels plant the voltages across the electrolyzer leads with new anodes, spaced 5 mm. from the cathode disks, are:-

3.9	to 4.0	volts at	24,000 amperes
4.0	to 4.1	" "	26,000 "
4.1	to 4.2	" "	28,000 "

As the anodes wear and the space between the anodes and cathode disks increases, the voltage also increases. With fixed anodes, at 24,000 amps., the voltage increases from 4.0 volts at the start to 5.0 volts, at the end of a 5 month period, when the anode-cathode gap has reached 30 mm. With present practice, the anodes are switched at the end of this five month period; this is done by exchanging the positions of the two anodes between any two cathode disks and thereby presenting essentially unworn anode surfaces to each disk. The cathode-anode gap is again set at 5 mm. during this exchange. When restarted, the voltage is 4.2 volts which increases to 6.0 volts at the end of a second five month period, when the anode-cathode distance has again reached 30 mm. After this total period of ten months, the anodes with approximately 35% of the original graphite still remaining are discarded. If the anodes were not exchanged after the first five months, the voltage would reach 6.0 volts in 7 to 8 months. Due to the present scarcity of graphite and labor, several cells have been permitted to operate for seven additional months after the first five-month anode exchange. At the end of this period, the voltage requirements were 7.0 volts and the temperature of the electrolyte leaving

the electrolyzer was 95°C. The anodes, when discarded, contained approximately 25% of their original graphite weight.

The anodic end-plates with oval shaped openings for the anode arms, giving some degree of adjustment as previously referred to, are in use on a few cells. The voltage requirements are lower. The cell at starting with new anodes at 24,000 amperes requires 4.0 volts and reaches 4.8 volts at the end of 3 months. The cover is then removed from the electrolyzer and the anodes over toward the cathode to again establish a 5 mm. gap. The cell is restarted and requires 4.3 volts. After a period of 2 to 3 months the voltage reaches 4.8 volts when the cell is again stopped and the anode plate positions are exchanged. The anode-cathode gap is again set to 5 mm. The cell starts again at 4.3 volts and reaches 4.8 volts in another 2 to 3 month period. Again the anodes are wedged over to make the anode-cathode gap 5 mm. and the cell restarts at 4.6 volts. At the end of a total period of 10 to 11 months the voltage reaches 5.0 volts when the anodes are discarded. This adjustable anode feature affects appreciable savings in energy at the expense of increased maintenance labor. It was claimed that when all cells are equipped with adjustable anodes, and labor and graphite are available that the average voltage requirements per cell will be 4.3 to 4.4 volts at 24,000 amperes compared to the present 5.0 volts. It was also pointed out that the war-time graphite now in use is inferior to graphite made from petroleum coke and, when available, should further reduce both voltage and graphite requirements.

During the months of December 1944 and January 1945, when operations were smoother, the average voltage across each cell was 4.50 volts at 24,000 amperes and 4.98 volts at 30,000 amperes.

At the Rheinfelden plant, discarded anodes from the vertical cells were further utilized in their Billiter cells. The anode-cathode gap was reestablished at 5.0 mm. and the anode positions were exchanged after 4 months of operation. At the end of a second four-months period, the anodes were removed. This total run of eight months in the vertical cells before utilization in the Billiter cells was said to give the greatest economy on overall graphite consumption. With the above, the voltage requirements per cell at 24,000 amperes are:-

Start with new anodes	4.00 volts
After 4 months	4.76 "
Restart	4.20 "
After a second 4 months	4.94 "
Average voltage per cell	4.46 "

A few cells have been operated with adjustable anodes using the same method described above for the Huels plant. When the anode-cathode gap was reset to 5 mm. every two months and the anodes removed at the end of four such periods, the average voltage requirements dropped to 4.33 volts at 24,000 amperes.

Amalgam Decomposition.

In operation, the amalgam decomposer packed with graphite pieces serves to bring the down-flowing amalgam in intimate galvanic contact with the up-flowing water or caustic solution. The NaOH and H_2 formed by the action, flow through the pipe connection near the top of the decomposer to the main in the basement as previously described. The operation normally requires no attention other than the maintaining of proper amalgam and water flows.

Caustic soda liquor strength of 49 to 51% are regularly produced at Huels. On only one occasion, for a short duration, have higher concentrations been produced. This was done experimentally and 55 - 60% NaOH solutions were made. It was claimed that 70% NaOH could be made in the decomposers, if desired. With the 49 - 51% NaOH and loads from 24,000 to 28,000 amperes, the temperature of the effluent caustic solution is 85 to 95°C.

If the graphite packing is not held tightly in place, erosion of the graphite occurs as previously stated. The fine particles of graphite thus formed are carried to the upper part of the decomposer by the caustic liquor, which it contaminates. The discharging NaOH solution is therefore very dark in appearance due to the suspended graphite particles. At Huels the total loss in graphite packing in this manner amounts to a layer of approximately 50 mm. every five months, when the electrolyzer is opened for anodic adjustment or replacements.

The treated graphite packing in the decomposers has become inactive only on rare occasions. One exception was shortly after the plant at Huels started, when many of the decomposers suddenly began to only partially decompose the amalgam. Investigation proved that the graphite packing had become inactive due to contamination of the sodium amalgam with lead and tin. The lead and tin contaminants were traced to the electrical connections to the anode plates in the electrolyzer, which were partially within the zone of electrolysis, as previously referred to. The lead and tin amalgams thus formed were decomposed in the decomposer and, it was thought, were deposited on the graphite packing of the decomposer as a skin. This skin of lead and tin eventually became extensive enough to materially reduce the area of active graphite surface and the decomposition of amalgam was retarded. On this occasion it was necessary to remove the cause of the contamination and also to replace the graphite packings in the decomposers. No serious difficulties have since been encountered with the graphite packings. Normally the activity of the graphite is said to have an indeterminately long life. Graphite packing is never reused; as much adhering mercury as possible is recovered by washing and the graphite is then discarded.

To remove the amalgam contaminants referred to above, it was necessary to remove all the mercury from the affected cells and distill it. The still was a small flame heated vessel equipped with a condenser and operated at atmospheric pressure. Normally the only distillations necessary are of accumulated thick mercury or so-called mercury butter, which is removed from the cells when cleaning. Ordinarily the only treatment given the mercury is

to wash it in a tub with a stream of water to remove graphite particles and other floating foreign materials.

Shutting down a Cell or Circuit.

At Huels when shutting down a cell the two short-circuiting switches are simultaneously closed. The brine feed to the electrolyzer is permitted to flow until the chlorinated brine is completely displaced, usually requiring 20 to 30 minutes. This is desirable to minimize the corrosion of the steel cathode disks, and also to prevent the liberation of chlorine when the electrolyte is drained out. The H_2O feed is similarly left flowing into the decomposer to strip the sodium still contained in the amalgam and to dilute the NaOH in the decomposer to a point where crystallization will not take place at room temperatures. After the above period, the amalgam pump and cathode drive motors are stopped. The chlorine-free electrolyte then drained from the electrolyzer into a steel tub to collect any entrained mercury, the brine overflowing the tub to the closest floor drain and to waste. The brine is drained through the top of the mercury inlet weir by loosening the cover bolts. This operation completes the shut down procedure.

If the entire cell circuit is to be shut down, similar procedures are followed, except that the flow of electrolyzing current to the cells is stopped at the rectifier station.

CELL MAINTENANCE.

In addition to the usual maintenance requirements on electric motors, drives and bearings, maintenance at Huels falls into the four major categories listed below:-

1) Adjustment or replacement of anodes.
2) Cell cleaning.
3) Rubber lining repair or replacement.
4) Prevention and stoppage of cell leaks.

These items will be discussed in the order listed above.

Adjustment or Replacement of Anodes.

With present practice each cell is stopped for anode adjustment or replacement approximately every five months. After the brine is drained from the electrolyzer, the cover and the two anodic end-plates are removed from the upper electrolyzer section. The cover is lifted off by the manually operated overhead crane after the cover bolts have been removed. The anodic end-plates can only be removed after the anodic copper glands and rubber sealing rings from around each anode stem have also been removed. The anodes are then replaced or their positions exchanged if only part of their life has been expended. Both these operations have been previously described.

The above, plus the reassembling and cell cleaning described below, normally requires a crew of four maintenance men working for an eight hour period.

Cell Cleaning.

Normally the cells are cleaned only when down for anode replacement or adjustment. The anodes may or may not be in position during the cleaning operation. After the cover and anodic end-plates are removed the mercury is drained from the electrolyzer through the valve in the bottom of the lower section. The mercury is drained into a portable steel tub in the basement and is subsequently washed with water as previously described. The interior of the electrolyzer, including the rotor assembly, is then flushed clean of clinging foreign materials such as pasty amalgams, graphite particles and precipitates from the electrolyte, with a stream of water from a hose. This flushing also drains through the outlet on the bottom of the lower electrolyzer section and passes through a steel tub to catch entrained mercury before overflowing the tub to a floor drain. During this flushing operation thin steel strips are worked back and forth between the cathode disks and the mercury displacers to dislodge materials that cannot be reached by the water jet. If the anodes are in position, the anode-catnode gaps are similarly cleaned.

The covers from the mercury inlet and amalgam-outlet weirs are removed and these devices are cleaned of foreign materials by scraping with a steel tool.

The cathode disks are now rotated and visually inspected to make sure tney are in good operating condition. Normally these disks require no attention. The only wear on these disks after years of operation is a slight pitting from contact with the electrolyte when the cell was not operating. No effort is made to remove the thin layer of rust from these disks which appears a few hours after shutting the cell down. This is also true if the cell is down for an extended period due to the need of major repairs. The rust from the disks is cleaned off only if it has become heavy and scaley and is relatively loose. This condition is normally found only in those cells that have been down for several weeks. When required, this cleaning is done with long handled wire brushes before the flushing operation.

During the electrolyzer cleaning, the decomposer cover is taken off and the upper layer of graphite packing is removed and replaced with new, treated graphite. The layer removed is usually 5" to 6" deep and consists of grapnite fines which have been eroded from the nut-sized chunks and carried to the upper part of the decomposer by the flow of sodium hydroxide. The removed fines are washed with water for mercury recovery and then discarded.

The electrolyzer and decomposer are now re-assembled, the mercury replaced thus completing the cell cleaning procedure.

On rare occasions, it becomes necessary to clean cells between anode changes or adjustments. These cleanings are usually made necessary by

thick amalgams which collect in the inlet or outlet amalgam weirs and which cannot be dislodged during electrolysis by the flushing methods previously described. On occasions these amalgams effectively dam the mercury flow through the electrolyzer to the point where the exit amalgams exceed 0.2% sodium and begin to decompose in the electrolyzer. This decomposition of the amalgam with the water of the electrolyte liberates hydrogen. The usual cause of the thick amalgams is iron, the source of which may be from the failure of the rubber covering which exposes steel electrolyzer parts to the electrolyte, or from the steel cathode disks if their continuous rotation is interrupted. This cleaning operation is performed without the removal of the anodic end-plates and requires the work of three men for four hours.

While the cell is being cleaned, the short-circuiting switches are checked by an electrician. If dirty or otherwise not in good operating order, the switch is removed for repairs. The switch can only be removed after the anodic and cathodic bus bars are joined by the auxiliary bus bars, or latches, previously referred to. Due to the poor location below the operating floor the switches become dirty and corroded in a short time and usually require attention each time a cell is taken out of operation.

Rubber Linings.

The failure of rubber linings on the electrolyzer parts results in extensive maintenance requirements at Huels. As the cells were constructed during war time there has never been any natural rubber available for use in electrolyzer linings. Various types of synthetic rubbers have been tried with lives of a minimum of three months to a maximum of three years; the average being approximately 18 months. It was claimed that linings of natural rubber will last 7 to 8 years.

Synthetic rubbers are manufactured in the I.G. Farbenindustries Huels Chemische Werke and therefore excellent opportunities prevailed for the experimental determination of which type was best suited for electrolyzer linings. The following mix was stated to be the best tried to date:-

100 parts Buna 85 (no styrene)
30 parts polyvinylchloride
25 parts sulphur

With the above mix dibensolthiacyldisulphide, known in Germany as "Vulkacit D.M." is used as an accelerator plus rubber dust as a filler.

Synthetic rubber with the above ingredients was not available at Huels a few months after the war started due to a shortage of polyvinylchloride.

The rubber linings on the electrolyzer cover: the middle section near the stuffing b xes, and the coverings on the mercury displacers, have the most frequent failures. When these or other rubber linings fail and steel is exposed to the electrolyte the presence of the failure is soon indicated

by a rapid increase in the hydrogen content of the chlorine being produced, and the cell is shut down. The electrolyzer is then dismantled and the affected part is usually sent to the Rubber Lining Division for repairs. Occasionally, small failures are cut away and patches applied in the cell building, using electric vulcanizers. Experience has proven that this type of repair has a very short life.

All parts sent to the Rubber Lining Division are first completely stripped of old rubber. Vulcanization of patches has been found to ruin any old rubber surfaces left in place. The stripping of old rubber is done by burning, where possible warpage of the steel part is not objectionable. If so, the rubber is chipped off mechanically. The areas to be covered are then sandblasted free of all foreign materials and a solution of "Buna S" and zinc oxide in benzene is immediately brushed on, to prevent further oxidation of the cleaned surfaces. This is allowed to dry for 6 hrs. Rubber cement made of "Buna S", benzene and a resin called "CORPESIN" is then applied with a brush to the surfaces and is also permitted to dry for approximately 3 hours. Additional coats of the latter are sometimes applied. The surfaces are then ready for rubber covering.

All electrolyzer surfaces are covered with 6 mm. of rubber except the mercury displacers which are covered with 10 mm., both thicknesses being applied in one sheet. After careful moulding of the sheet to the surface to exclude air, the covered area is tested with a high voltage spark for flaws. If no flaws are found the part is moved into a steel vulcanizing chamber. When the vulcanizer is sealed shut, saturated steam at 3 atms. pressure is admitted for a period of 2½ hours when vulcanization is complete. The vulcanized covering thus applied was said to have a Shore hardness of 90° to 95°.

All cell piping and fittings are similarly rubber covered. As previously mentioned the original rubber linings in the decomposers were found unnecessary and are not repaired or replaced.

Prevention and Stoppage of Cell Leaks.

The prevention and stoppage of leaks in the cells at Huels is a serious maintenance problem. The leaks develop at the flanged and gasketed section joints, the rotor stuffing boxes and around the anode-stem seal rings. The leakage consists of either mercury or electrolyte, depending on the location.

The stuffing boxes and the joint between the middle-bottom electrolyzer sections develop mercury leaks. The stuffing box packing found to give the best service is 20 mm. square, high pressure steam packing made of graphitized asbestos. The packing is obtained in 10 meter lengths and is cut with skived ends to form rings for insertion in the stuffing boxes. The gasketing materials for flanged joints have already been described.

Mercury leaks are the most serious. A small leak frequently drains sufficient mercury from a cell before detection so as to necessitate its

immediate removal from the circuit. For this reason, as well as the fact that finely divided mercury is difficult to completely recover from the floor, the cell room employees must be constantly on the alert to discover and stop leaks. As mentioned before, the leakage of mercury through the stuffing boxes was of such a serious magnitude as to warrant the installation of a complete interconnected piping system below the operating floor with funnel-like collectors below each stuffing box to collect the leakage.

Chlorine saturated electrolyte leakage from the joints between the top and middle electrolyzer section, the anodic end-plate joints, and the anode stem seals are also undesirable because:-

1) The electrolyte is corrosive to steel, copper and concrete with which it comes in contact.

2) Causes partial short-circuiting when dripping off the anodic end-plates.

3) Creates a nuisance in the building by liberating chlorine gas.

To prevent the leakages above, all the joining bolts at Huels are periodically tightened as the gaskets shrink upon ageing. All packing gland bolts on shaft stuffing boxes are tightened one full turn each week. Flanges have been stiffened on sections to make more rigid joints, new bolt holes have been drilled to place the joint bolts on closer centers; yet it was stated that the leakage problem is still not solved and continues to be a major fault with the Huels cells.

CELL BUILDING.

The cell room and allied buildings in the chlorine plant at Huels was specifically designed for the use of vertical type cells. The general layout of plant buildings is shown in Exhibit No. M.C. Drawing No. 278.

The cell building proper is approximately 23 m. wide, 16 m. high at the eaves and 105 m. long. The walls and roof beams are of concrete construction. There are two concrete floors; the basement at grade level and the operating floor approximately 5⅜ m. above. The building was designed to house 136 cells in 4 parallel rows of 34 cells each. Only 120 cells have been completely installed, the remaining floor area being used primarily for maintenance work on cell parts. It is doubtful if this area could economically be used for any other purpose. The rectifier room is located adjacent to one end of the cell building and houses 5 Brown-Boveri mercury arc rectifiers, each with 24 electrodes, 6 phase, rated at 8000 amperes and 600 volts, having at full load a conversion efficiency of 92% - 93%.

In the building design, ventilation was given paramount consideration to thus keep mercury concentrations in the atmosphere at a minimum and to maintain reasonable room temperatures for the employees. Toward this end the

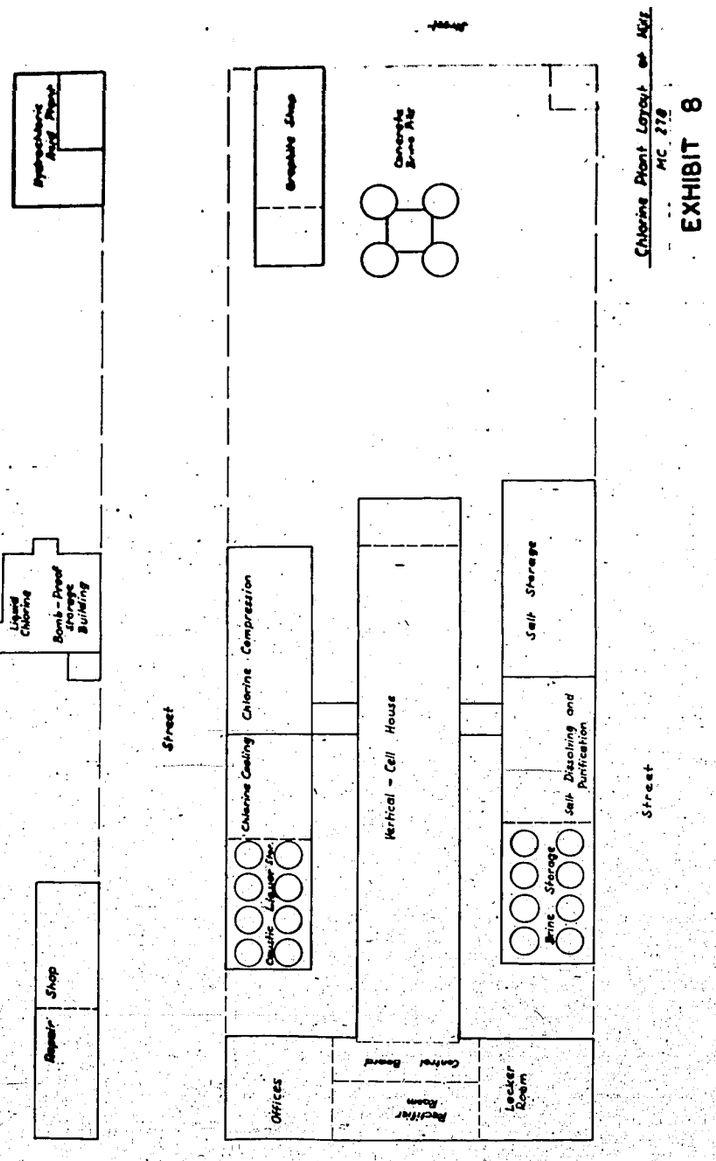


EXHIBIT 8

building was made long and narrow and with high ceilings on both floors. Three sides of the building were kept free of appendages to permit a maximum of window area on both floors, which was further increased by a monitor-type roof. The cell room plan is shown in M.C. Drawing No. 277.

With this design it was stated that with 100 cells in operation the natural ventilation of the room amounted to 200,000 cubic meters of air per hour with all windows open. Under these conditions the mercury vapor concentration in the cell room atmosphere was said to range between 30 to 60 micrograms per cubic meter. Cell room temperatures under the same conditions varied between 30°C in the winter and 40°C in the summer months.

The concrete floors were pitched toward two drainage gutters running the length of the building for the accumulation and removal of spilled mercury and electrolyte. Experience has proven this design to be inadequate as the floors have cracked and spalled resulting in the absorption of considerable amounts of mercury. The collection of spilled mercury has become so difficult in the basement that one area of this floor, approximately 10 m. x 12 m. has been covered with 6 mm. steel plates, welded together to form an impervious floor covering.

QUALITY OF PRODUCTS.

Average analyses of the three cell products at the Huels and Rheinfelden plants have not been kept during the war years due to labor shortage and the press of other work. The following analyses were said to be typical. All analyses are of the products as they leave the cell except the sodium hydroxide liquor which is taken after the suspended graphite particles are removed by filtration.

Caustic Liquor.

$NaOH$	50.25%	Fe_2O_3	0.0016%
Na_2CO_3	0.33%	Al_2O_3	0.025%
Na_2SiO_3	0.00%	Pb	nil
$NaCl$	0.004%	Cu	nil
Na_2SO_4	0.031%	As	nil
$NaClO_3$	0.00%		

Chlorine from the Electrolyzer.

Cl_2	96% to 98%
CO_2	1.0 to 1.7% (as low as 0.3% with new anodes and as high as 2.0% (with badly worn anodes.)
O_2	0.02% to 0.09%
CO	0.01% to 0.06%
H_2	0.6% to 1.9%
N	0.02% to 0.20%

H_2 from the Decomposer.

H_2 - 99.5% to 99.8%
Air - 0.2% - 0.5%
Hg - 0.2% - 0.5%

LABOR, MATERIALS, and SERVICE REQUIREMENTS.

The operating requirements at the Rheinfelden plant were never definitely established because 16 out of the 20 vertical cells were placed in operation less than six months before operations ceased in November 1944, and also because these cells were operated in Billiter cell circuits. Operations at Ludwigshafen never reached a commercial stage. This section is therefore devoted solely to these requirements at the Huels plant.

Operating requirements at the Huels plant have covered a wide range. Operation with a new type cell, previously untried on plant scale, were started during war-time with the accompanying scarcity of good labor and materials. Since the end of the war and Allied Occupation, the conditions of labor and materials was stated to be even worse than before. The plant, therefore, has never experienced a period of what might be termed normal operations.

During late 1944 and early 1945, essentially all cells were in operation and 3000 metric tons of chlorine per month, or 100 tons per day, were being produced. The operating requirements discussed in the following paragraphs are for this period of operation, representing only the cell room and graphite shop.

Labor.

A total of 66 people were employed each of whom worked 56 hours per week. Six of this group were electricians and ten general mechanics who worked days on general maintenance work. The remaining 50 employees were divided between shift and day work on operations and allied work. This group is segregated into shift and day employees below with their job duties:-

Workers per Shift	Workers per Day
1 Leader	2 Day Leaders
5 Cell Attendants	6 Anode Manufacturers
1 Mercury Collector & floor cleaner.	6 Anode installers or changers
1 Locker Room Attendant	7 Generals
	2 Mercury Collection & clean up
8 Total Workers per Shift	1 Supply Room Attendant
	24 Total Workers per Day.

The total operating plus general maintenance requirements per metric ton of chlorine produced was:-

$$\frac{66 \text{ Employees} \times 56 \text{ hrs./wk.}}{100 \text{ tons } Cl_2 \times 7 \text{ days per wk.}} = 5.28 \text{ manhours per metric ton chlorine.}$$

Repair labor requirements for this period such as rubber lining, etc. were not available.

Materials

During this same period mentioned above, 6000 metric tons of raw salt, 2 metric tons of mercury and 20 metric tons of anode graphite were consumed per month. Unit consumptions would be:-

$$\frac{6000 \text{ tons Salt}}{3000 \text{ tons } Cl_2} = 2.0 \text{ metric tons raw salt per metric ton chlorine}$$

$$\frac{20 \text{ tons Graphite} \times 1000 \text{ (Kg per ton)}}{3000 \text{ tons } Cl_2} = 6.67 \text{ Kgs. graphite per metric ton chlorine.}$$

$$\frac{2 \text{ tons Hg} \times 1000 \text{ (Kgs per ton)}}{3000 \text{ tons } Cl_2} = 0.667 \text{ Kgs. mercury per metric ton chlorine.}$$

It should be noted that the war-time graphite was considered to give 80% of the life of high quality petroleum coke graphite.

The large mercury consumption was due primarily to cell leakages. During this period an average of 1200 Kgs. of mercury per day was collected from traps, floor drains, and general floor areas. Only a fraction of the 2 tons of mercury lost monthly were accounted for; 7 kgs. in the sodium hydroxide, 18 kgs. in the hydrogen and 500 Kgs. in the brine. The balance of the lost, or 1475 Kgs. per month, was unaccounted for.

Services.

Overall energy consumption in the cell room including A.C. and D.C. was 16,000 K.W. per hour or $\frac{16{,}000 \text{ K.W.} \times 24 \text{ hrs.}}{100 \text{ tons } Cl_2 \text{ per day}}$ = 3840 KWH per metric ton chlorine.

Purified water for the amalgam decomposers was consumed at the rate of 7 $m.^3$ per hour.

COMPARATIVE DATA ON HUELS AND DRUM TYPE VERTICAL CELLS

	Ludwigshafen Drum Cell	Huels Cell
Rated capacity in amperes	24,000	24,000
Kg. Cl_2 per day at 92% current efficiency	700	700
Construction Data		
Length of assembled cell complete,	2.8	2.75
Width " " " " "	2.1	2.45
Height " " " " "	2.2	2.18
Height above floor,	1.65	1.53
Number of disks	5	4
Disk diameter	1.845	1.8
Drum diameter	0.617	-
Cathode area, S	13,91	10
Disk thickness	20	20
Disk spacing, center to center mm.	110	200
Depth of disk immersion in Hg.	0.65	1.0
Anode to cathode distance (New anodes)	5	5
Number of anode plates	6	8
Thickness of new anode plates, mm.	80	78
Number of anode leads	48	32
Mercury requirements, Kgs.	1200	2000
Anode graphite weight in cell, Kgs.	1170	1600
Weight of electrolyte in cell, Kgs.	400	600
Velocity of disks, rpm.	7	7.5
Electrical Data		
Cathode current density, amperes per sq. meter	1720	2400
Voltage, new anodes	3.75	4.00
Voltage, 11 months old anodes	4.90	6.00 (10 months)
Chlorine Analysis		
$Cl_2 + CO_2$	98.7-99.2%	96.0-98.0%
CO_2	0.6- 1.0%	1.0- 2.0%
H_2	0.6- 1.0%	0.6- 1.9%
Amalgam Concentrations		
Na in Hg entering electrolyzer	0.0%	0.0%
Na " " leaving "	0.1- 0.2%	0.1- 0.2%
Brine		
Sp. Gr. of feed to cell (corrected to 20°C.)	1.195	1.195
" " " outlet from " (" " ")	1.170	1.170

APPENDIX I

LIST OF GERMAN PERSONNEL INTERVIEWED

Name	Position	Location
Dr. Oswin Nitzschke	Supt. Inorganic Division	I.G. Farbenindustrie Plant at Huels.
Dr. Werner Honsberg	Director of Electrolysis	I.G. Farbenindustrie Plant at Ludwigshafen.
Dr. Werner Künzer	Engineer-Chemist Chlorine Dept.	
Dr. Albert	Manager of Chlorine Dept.	I.G. Farbenindustrie Plant at Rheinfelden.

APPENDIX II

LIST OF TARGETS VISITED

Name	Location
I.G. Farbenindustrie Plant	Huels
I.G. " "	Ludwigshafen
I.G. " "	Rheinfelden

APPENDIX III

BIBLIOGRAPHY

Copies of the reports, documents and microfilms listed below were transmitted to Washington, D.C. Requests for this information should be addressed to:-

Office of Publication Board
U.S. Department of Commerce
Washington 25, D. C.

Note: M.C. Drawings are listed in Appendix IV.

1. Related Reports Published by the Joint Intelligence Objectives Agency.

FIAT Final Report No.	Title
431	Survey of the chlorine and caustic plants in Western and Southern Germany.
816	Horizontal mercury chlorine cell, I.G. Farbenindustrie, A.G.

2. Related Reports Published by the Combined Intelligence Objectives Sub-Committee.

CIOS File No.	Title
XXVI - 62	The German chlorine industry with particular emphasis on I.G. Farbenindustrie, A.G. and the war influence.
XXVII- 85	Miscellaneous chemicals, I.G. Farbenindustrie, A.G. Ludwigshafen and Oppau.

3. German documents containing information on mercury chlorine cells.

M.C. No.	Subject
247	Operating data and costs - I.G. Chlorine plants 1942, 43, 44, "Chlor-Uko", 816-W.
284	Technical experience exchange of electrolysis departments. (Technischer Erfahrungsaustausch auf dem Elektrolysen Gebiet) Reports of four I.G. plants, 1939.

	Subject
306	Technical experience exchange of electrolysis departments. (Technischer Erfahrungsaustausch auf dem Elektrolysen Gebiet), average for I.G. plants, 1939.
313	Mercury cell data average for all I.G. plants for 1938 and 1st quarter of 1939, including 1939 average for Hoechst plant.
331	Minutes of the January 1942 meeting of the chlorine sub-commission (Chlor-Uko) report on vertical cells at Huels.

4. Microfilms of papers related to vertical chlorine cells from I.G. Farbenindustrie Chlor-Fako meetings.

Subject covered	J.I.O.A. Reel No. C-86 Frame No.
Development of the vertical mercury cell	245 - 260
The vertical round cell	261 - 266
Experiences with the vertical mercury cell at Rheinfelden.	267 - 270
Experiments and results with the vertical mercury cell at Ludwigshafen.	271 - 289
Further research and experience with vertical mercury cells at Ludwigshafen.	635 - 670
An amalgam cell with inclined cathode	671 - 674
Comparison of the cost and space occupied by vertical and horizontal cells.	679B- 738

APPENDIX IV

LIST OF M.C. DRAWINGS ON VERTICAL CELLS*

M.C. Drawing No.	Detail	Plant Section	I.G. Drawing No.
217	Vertical Cell	Assembly General	Ludwigshafen	L 6255 - 1
217 a	" "	Cell Assembly	"	L 5749 - 1
217 b	" "	Anode and Pin	"	L 14838 b-2
217 c	" "	Top Section	"	L 14624 b-2
217 d	" "	Mercury Washer	"	L 14716 - 2
217 e	" "	Center Section	"	L 5755 e - 1
217 f	" "	Shaft Bland	"	L 13611 c - 2
217 g	" "	Amalgam Outlet	"	L 14652 b - 2
217 h	" "	Mercury Inlet	"	L 14643 a - 2
217 i	" "	Anode Connection Plate	"	L 14700 e - 2
217 j	" "	Drum - Disc - Shaft	"	L 14803 - 2
217 k	" "	Amalgam Pump	"	F 8049 - 8
217 l	" "	Amalgam Decomposer	"	L 5863 - 1
217 m	" "	Mercury Displacer	"	L 14610 b - 2
217 n	" "	Bearing Bracket	"	L 13590 a - 2
217 o	" "	Shaft - Sleeves Bearings	"	L 5272 d - 1
217 p	" "	Drive Wheel	"	52178
217 q	" "	Caustic Sampler	"	SK 484
217 r	" "	Principle of Operation	"	SK 457
217 s	" "	Flow Sheet	"	SK 458
217 t	" "	Sight Glass - Hg. Outlet	"	L 3497 - 16
217 u	" "	Graphite Packing Ring	"	L 3017 - 16
217 v	" "	Bottom Section	"	L 13567 c - 2
267	" "	Assembly General	Huels	L 4973 - 1
268	" "	Decomposer	"	H 1282 - 1
269	" "	Mercury Inlet Weir	"	H 2105 - 2
270	" "	Bottom Section	"	H 1936 a - 2
271	" "	Rotor Details	"	H 1939 - 2
272	" "	Center Section	"	H 1937 b - 2
273	" "	Mercury Displacer	"	H 2085 a - 2
274	" "	Top Section	"	H 1938 - 2
275	" "	Mercury Exit Weir	"	H 2109 - 2
276	" "	Rotor Bearing & Boxes	"	H 2336 - 2
277	" "	Cell Building Lay-out	"	L 4456 - 1
278	" "	Chlorine Plant Lay-out	"	SK IV 34-4
279	" "	Side Cover-plate	"	H 2607 - 2
280	" "	Assembly Cross Sections	"	H 1207 - 1
314	" "	Amalgam Pump Details	"	-----
324	" "	Amalgam Pump Curves	"	-----
325	" "	Tower Decomposer	Rheinfelden	-----

* Filed with Joint Intelligence Objectives Agency, (J:I:O:A:), Room 2213, Munitions Building, Washington, D.C.

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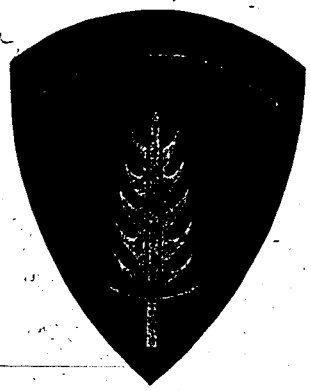
FIAT FINAL REPORT NO. 834

PRODUCTION OF CAUSTIC POTASH IN MERCURY CHLORINE CELLS



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FIAT FINAL REPORT NO. 834

PRODUCTION OF CAUSTIC POTASH IN MERCURY CHLORINE CELLS

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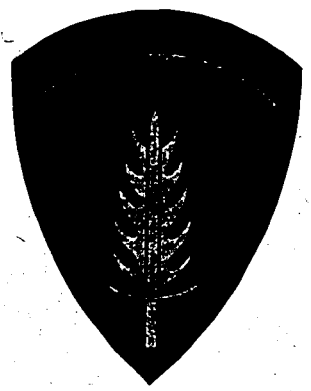

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FIAT FINAL REPORT NO. 834 18. June 1946

PRODUCTION OF CAUSTIC POTASH IN MERCURY CHLORINE CELLS

I. G. FARBENINDUSTRIE, A. G. — SOUTH BITTERFELD

BY

THE U. S. CHLORINE INDUSTRY TEAM,
TECHNICAL INDUSTRIAL INTELLIGENCE BRANCH,
U. S. DEPARTEMENT OF COMMERCE.

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Mr. Arthur D. Tucker, TIIB

ABSTRACT

Potash has been made commercially in only one mercury cell plant in Germany. The operation is similar to NaCl electrolysis but is more critical with respect to brine purity, current density limitation of 2400 amperes/m², and increased electrode spacing of approximately 2 mm. Current efficiency averages 93 percent, cell voltage 4.3 and hydrogen 1.8 percent. Cost data are tabulated for the first quarter of 1945.

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INTRODUCTION

Objective:

The purpose of the investigation was to determine the main differences in design and operation of mercury cells in the production of caustic potash liquor, as compared with that already described for the production of caustic soda, in FIAT Final Reports Nos. 732 and 816.

Evalution:

Operation of horizontal mercury cells on KCl and NaCl brine was found to be remarkably similar in most details, brine preparation being the most outstanding difference.

Guide to the Reader:

This report summarizes the findings at the South Bitterfeld plant of the I. G. Farbenindustrie, A. G. through personal interview, in the field, with the Russian Technical Officers in Charge, also comments on production of mercury cell potash by a German chemist who worked there from 1923—1940, and was in close contact with the initial mercury cell production of potash at Bitterfeld 10 to 12 years ago. At present the mercury cells are operating on NaCl brine, for producing the needed quantity of pure caustic soda, the potash production being confined to the Billeter diaphragm cells located in the same building.

Unit consumption and cost details are available in the "Chloraustausch" records of I. G. for 1942—1943, which may be refered to in MC File No. 247. Cell details, or subsequent operations for handling the chlorine and hydrogen are not elaborated, since they are completely covered in FIAT Final Reports No. 732 (Bitterfeld Plant) and No. 816 (Horizontal Mercury Chlorine Cell)

HISTORICAL

Prior to the past decade, all caustic potash liquor made in Germany was produced in Billeter diaphragm cells. A high purity grade, for particular uses such as for Edison type storage cells, was obtained from the diaphragm cell liquor by osmosis, which began about 1930. After two years of experimental electrolysis of KCl brine in two mercury cell units, carried on in the South Bitterfeld plant, eighty-four — 12,000 ampere cells were installed and first put into commercial operation in February 1936, supplementing the existing Billeter cell production.

Bitterfeld is the only plant in Germany where potash has been produced commercially in mercury cells. However, at Zscherndorf, near Bitterfeld, Kali-Chemie started experimental operation in 1939, of two 14 meter Leverkusen type cells. At Rheinfelden, one vertical 24,000 ampere cell is being prepared at present, with auxiliary equipment, for experimental operation on KCl brine. At Hoechst, consideration is also being given to experimental potash operation.

In 1940, potash liquor was being produced commercially in seven German plants, all of which were members of a Potash Pool, for interchange of information. These included the following:

Company	Location	% of Total Sales
I. G. Farben	South Bitterfeld	34)
Alkaliwerke	Westergehn	17) 68
Kali-Chemie	Zscherndorf	17)
Feldmueller	Luelsdorf Stettin	

CONSTRUCTION NOTES

The 84 mercury cells which are installed at South Bitterfeld for the electrolysis of KCl brine are very similar in general to the preferred Hoechst 7 meter design, fully described in FIAT Final Report No. 816. This is made from a steel 800 mm. I-beam, laid on one side, with hard rubber lined sides, the lining being held in place on the bottom by longitudinal steel strips, leaving the major portion of the horizontal mercury bed surface bare. The active amalgam area is approximately five square meters.

Each cell is equipped with 37 graphite anodes of conventional size, supported from two steel cover sections rather than one as at Hoechst. The only difference pointed out in cell assembly, for potash vs. soda operation, was the initial spacing of graphite to mercury, which is 7 mm. and 5 mm. respectively. This is done to decrease contact of chlorine in the brine with potassium in the mercury with resultant loss in current efficiency. A number of cast iron covers were observed which were lined with poly-vinyh chloride, apparently quite successfully.

The decomposers consist of long, bare, welded steel troughs of rectangular section, approximately 250 mm. wide, inside. The graphite grids were formerly made up of untreated strips, bolted together. At present blocks used are 55 mm. X 218 mm. wide X 165 mm. long, each of which is grooved with 13 slots about 5½ mm. wide and 27 mm. high which are parallel with the 165 mm. diameter. These blocks are previously treated by soaking in a 7 % FeCl solution for 24 hours, without subsequent baking.

The mercury content of each cell is 750 to 800 Kg. The flowing mercury sheet was said to be 5 mm. thick, by measurement. The slope in 7 meters was approximately 15 mm., but was set by the velocity of mercury as measured by timing the travel of a floating object from one end of the electrolyzer th the other. The optimum rate is considered from 45 to 50 seconds.

Each cell is equipped with two lights — a red one which lights when the mercury pump motor stops, and a green one which lights when the cell is cut of the circuit. There is only one connecting lead between cells for the 12,000—16,000 ampere load. A cut out switch of excellent design is provided for each cell; this is closed pneumatically but must be opened manually with levers.

The cells are arranged longitudinally in the cell room rather than in the usual crosswise arrangement, largely due to the original substitution of mercury type for Billeter diaphragm cells. Electrically, they are connected in series with the Billeter cells, and the overall voltage supplied by the rectifiers with all the cells in operation is about 830 volts. The floor has an adequate slope for drainage of wash water. Part is tiled, but the greater portion is covered with a very smooth, hard bituminous material.

All pipe lines are rubber lined.

BRINE PREPARATION

Unpurified potassium muriate, mined at Salzfurt — about 200 kilometers distant, is transferred from the cars to a large bin inside the building by means of conveyors. This material normally consists of the following:

KCl	90 per cent
NaCl	57 per cent
MgCl2	0.05 per cent
CaCl2	0.003 per cent
Insolubles	balance

From the bin, the muriate passes into a long rectangular steel tank equipped with a puddling conveyor. An equal weight of water is also added to this tank and the resultant slurry is transferred continuously to an elevator and thence into the top of one of two steel tanks, which serve in the same manner as a Buchner funnel for removing the free solution and washwater from the salt bed. Each tank is about 2.5 meters in diameter by 8 meters deep and is equipped with a shallow conical section on the bottom, at the top of which is located a steel screen for supporting the undissolved salt bed. Vacuum is applied to the cone bottom as the tank is being filled, and when filling is completed, 2.5 m³ wash water are added for each of two successive washings, after which air is drawn through the bed for two hours.

The resultant batch consists of 18 to 19 m tons of moist solid containing only 0.5 percent NaCl and representing 85—90 percent of the original KCl content of the muriate. The liquids drawn off are used in another operation. The potassium chloride is then removed through a chute in the bottom of the tank into one of two dissolving tanks. A vertical cylindrical opening is made through the salt bed above the chute by drawing up a 300 mm. diameter cone-topped steel cylinder. The damp solid falls through this shaft into the chute as it is progressively removed from the top by means of a rotating skimming plow.

The dissolving tanks are made of steel, brick lined, and are cylindrical in shape. Each is equipped with a heavy agitator and has a capacity of 20 m³. As the solid salt is discharged into a dissolving tank, depleted brine from the cells is also added both in sufficient quantity to make a final 20 m³ batch of brine containing close to 350 g. p. l. KCl at the solution temperature of 70°—75° C. (The brine from the cells is first freed of its chlorine content by a method which is described later.) KOH, K_2CO_3, and $BaCO_3$ are then added to the brine in sufficient quantities to give aproximateley the analysis as listed in the next paragraph. These two tanks are operated batchwise, each on an hourly cycle.

From, the dissilving tanks, the brine is pumped each half hour to one of three 180 m³ brick lined steel, cylindrical tanks, by means of a cast iron centrifugal pump. It takes 4 to 5 hours to fill each tank, batchwise, and during this period the agitator is continuously in operation. A reaction period for precipitation of the impurities is thus provided. When filled, the contents of the 180 m³ tank are carefully checked and additional reagents added, as required. The tyical composition of the brine is represented by the following:

KCl	345	— 350	g. p. l.
K_2CO_3	0.5	— 0.6	„
KOH	0.1	— 0.15	„
K_2SO_4	3.	— 4.	„
$KClO^3$	2.	— 3.	„
CaO	0.4	— 0.5	„
NaCl		— 0.8	„

The unsettled brine is passed through a Kelly type filter which is equipped with a single layer of polyvinyl chloride cloth. The life of this filter cloth is said to be 5 to 8 months. Cotton filter cloth lasts only 5 to 6 weeks. The filtrate is passed into one of two intermediate storage tanks, also 180 m³ capacity brick lined steel tanks, without agitators. From here the brine passes through the second Kelly type filter, from which it goes to a 200 m³ brick lined storage tank and thence to the cells.

It was stated on several occasions that brine quality was of the utmost importance for good cell operation. It should be crystal clear and must contain no magnesium, chromium, or vanadium. Iron, aluminum, etc., must be low, and are automatically taken care of. Calcium is not particularly detrimental in the electrolyser, but will result in an inactive scale on the decomposer graphite. The KCl content and temperature of the brine must be watched to avoid crystallisation and plugging of pipes and tubes.

The depleted brine from the cells is dechlorinated by a novel method, based on the following reactions:

(1) $Cl_2 + 2KOH = KClO + KCl + H_2O$

(2) $_2KClO + C = CO_2 + 2KCl$

In accordance with the first reaction, KOH is added in sufficient amounts to the depleted brine to convert the available chlorine to KOCl. The brine contains 0.5 to 0.6 g. p. l. of chlorine. The brine temperature is approximately 75° C. For the second reaction, the neutralized brine is passed through two 30 m³ steel, rubber lined tanks in series, each of which is filled with 30—35 mm. lumps of non-impregnated graphite, obtained by breaking up used cell anodes. The brine enters the bottom of each of these tanks below a false bottom which supports the graphite bed, and overflows from the top. Samples are withdrawn from the discharge line of the pump, located between these tanks, and must test from 0.1 to 0.15 g. p. l. KOH. The brine flow through these tanks is continuous at 35 to 40 m³ per hour and available chlorine is said to be entirely removed by this process. The KCl 03 remains constant at 2 to 3 g. p. l. and requires no special consideration. The graphite fill never needs to be removed, but washing with water at 5—6 month intervals is necessary. Additions of graphite lumps are made from time to time as required.

Up to 1940 at least, "activated" carbon was used for chlorine removal in these tanks. This was treated at Leverkusen. After sizing to 3—4 mm. the carbon particles were placed in a tank under high vaccum (4 mm. absolute pressure) and then covered with zinc chloride solution. Soaking in this solution vas continued for several hours at atmospheric pressure. This was followed by roasting to 800° C. The transition from this special carbon to cell graphite was not explained, but the latter is said to work well and should be much cheaper.

OPERATION AND MAINTENANCE

Although 84 mercury cells were in position to operate on potassium chloride brine, they were all operating on sodium chloride brine at the time of our visit. Potash production was being continued in the Billeter diaphragm cells.

It was stated that there were practically no differences in operating characteristics between caustic potash and soda electrolysis in these mercury cells, the following being mentioned specifically:

Current load on cells	12,000 amperes
Cathodic current density	2,400 amps./sq. m.
Anode life	7—8 months
Temperature of exit brine	75—80° C
Decomposer cleaning cycle	2—4 months

Differences mentioned were:

	Potash	Soda
Spacing between graphite and emalgam, mm.	7	5
Average cell voltage, at 12,000 amperes	4.3	4.5
Current efficiency, percent	92—94	94—96
Hydrogen content of chlorine gas, percent	1.5—2.0	1.0—1.5

At least 1 percent of the difference in current efficiency was attributed to the method above described for removal of chlorine from the depleted brine. It was said that more thickened amalgam "butter" was formed in caustic potash operation than in caustic soda perhaps three to four times as much, but that the 34 hour removal schedule for either operation was adequate. Brine quality is much more critical in the case of KCs electrolysis.

According to Dr. Wagner, in 1940 the caustic soda cells were operated at 16,000 amperes, but the current load on the cells when producing caustic potash was strictly limited to 12,000 amperes = 2400 amperes/m². Potash operation was at that time considered appreciably much more critical than soda, the hydrogen content of the chlorine gas varying between 2 and 6 percent, according to condition of brine and cell. For soda cells, the hydrogen varied from 1 to 2 percent. Brine feed temperature was maintained at 70° C., minimum to result in a discharge temperature of at least 80° C. He stated that potassium amalgam reacted with water in the decomposer much more easily than sodium amalgam and that no amalgam "butter" was formed. (At that time the decomposer grids were made up of untreated graphite strips, bolted together). Very little trouble was experienced with leaks through decomposer welds, and if repairs were required, welding could be successfully carried out on old joints — both points quite different from caustic soda experiences. He also stated that anode life was about 7 to 8 months in either operation, but that due to the greater current load on soda cells, graphite consumption per unit of chlorine produced was one third greater in the case of potash.

The following table summarizes operating data (a) for potash and (b) for soda, both at 12,000 amperes and for present experience, and (c) for soda at 16,000 amperes, around 1940.

Type of Operation	Potash	Soda	
Current load — Amperes	12,000	12,000	16,000
Cathodic current density — Amps/m²	2,440	2,440	3,250
Anodic current density — Amps/m²	2,660	2,660	3,550
Brine concentration (Feed)	345—350	310	310
in g. p. l. KCl or NaCl (Discharge)	270—280	250	—
Brine flow per cell — L/Hr	400—450	400	450
Temperatures (Brine feed)	55— 60	60	60
°C (Brine discharge)	80	80	90
(Decomposer liquor)	80— 90	80	90
Voltage per cell-for new anodes	4.1	4.3	—
Average	4.3	4.5	5.0
Current efficiency, per cent	92— 94	94— 96	94— 96
Hydrogen in chlorine gas, percent	1.5—2.0	1.0—1.5	1.— 2
Anode life in kiloampere hours per set	60,000	—	80,000
Percent K or Na increase in amalgam	0.20	0.15	—

When a complete circuit of cells is put into operation about 4,000 amperes is first applied. The current is gradually increased to the normal load of 12,000 amperes, depending upon the hydrogen content of the cell gas, full load being reached in 10—12 hours

The chlorine averges 95—97 percent and CO_2 2 percent for either operation. No particular difficulty said to be experienced with excessively low current efficiencies on potash. Low current efficiency values occur in either operation if the cells are allowed to become excessively dirty or if the specified brine feed quality is not maintained. Anodes and electrolyser are cleaned every 2 to 4 months for either operation, and at this time if the decomposer has not been operating normally the grooved graphite blocks are removed. These are rinsed with water, soaked in hydrochloric acid and again rinsed with water. Following this, the graphite blocks for a potash cell are soaked 24 hours in 7 percent ferric chloride solution, after which they are replaced in the decomposer, without heating. A solution of NaOCl is used for the graphite blocks for a soda cell.

Explosions are rare in either operation and have occurred only when pieces of graphite break off the anodes and fall into the amalgam. The overall circuit e. m. f. of around 830 volts maximum is not considered very hazardous, and no serious accident has ever occurred from this cause. The workmen always wear rubber gloves, but not rubber footwear. The floor surface is of insulating material and drains rapidly after becoming wetted. The supporting beams for the operating aisles are electrically insulated, as well as the cells.

Condensate from the Billeter cell liquor evaporators is used as feed water to the decomposers. The caustic potash liquor analysis was given as follows:

Total alkalinity, as KOH	50.0 —50.5%
Actual KOH	49.7 —50.4%
K_2CO_3	0.1 — 0.4%
NaOH	0.2 — 0.4%
KCl	0.01 — 0.02%
K_2SO_4	0.001— 0.01%
$KClO_3$	0.001— 0.005%
Fe_2O_3	0.002— 0.05 %

Of the 750 to 800 Kg. mercury requirement per cell, annual loss was stated to be about four to five percent. No difficulty has been experienced from mercury poisoning. The customary double locker room with intermediate shower facilities were believed to provide adequate prevention measures. The mercury "butter" skimmed from the cells is only washed with water or hydrochloric acid to recover fluid mercury. No mercury still is employed at this plant in connection with electrolytic cell operations.

The rubber lining of the header pipes was said to last five to seven years when natural rubber was used, but only two years for Buna. Cell and cover linings last about one-third as long.

COST SHEET FOR MANUFACTURE OF CHLORINE AND CAUSTIC POTASH

Mercury Cell Installation South Bitterfeld Plant

First Quarter, 1945

Item	Quantity Kg. (Total)	% Yield or Kg per 100 Kg.	Price per 100 Kg.	Total cost in R. M.	Unit cost of 100 Kg KOH & Cl_2
Potassium Chloride, purified	5,201,000	81.84	15.22	791,643	12.46
Storage cost for raw material				1,572	0.02
				793,215	12.48
Salt-credit	4,078,624	74.18	1.0	40,786	0.64
Net cost for potash				752,429	11.84
Potassium Chloride				40,786	0.64
Direct current, K. W. Hrs.	9,369,250	147.43	1.65	154,593	2.43
Mercury	825	0.01	654.78	5,402	0.09
Electrode consumption:					
Preparation of graphite	19,100	0.30	93.19	17,799	0.28
Sulfuric acid, as SO_3	31,400	0.49	5.96	1,871	0.03
Graphite residues				220,451	3.47
Hydrogen	771,200	12.14	1.38	10,671	0.17
				209,780	3.30
Shipping cost				069	—
Totals-Chlorine & KOH	6,355,000			209,849	3.30
Labor costs: Wages-hours	4,121	0.17	0.85	3,521	0.15
Charge				310	0.01
Salaries				965	0.01
Charge				016	—
Social Security				360	0.01
Power costs: Millwater, m³	10,231	0.42	3.0	307	0.01
Tap water, m³	8		26.0	2	—
Low pressure steam, mt.	1,044	0.04	200.0	2,087	0.09
Electricity-motors	72,814	2.98	1.65	1,202	0.05
Hydrogen	2,087	0.09	2.90	61	—
Repair costs-hours	2,923	0.12		14,239	0.58
Materials				2,519	0.10
Hydrogen peroxide	1,662	0.07	104.3	1,733	0.07
Transportation				1,198	0.05
Overhead: Charge on wages				1,584	0.06
Charge on salaries				252	0.01
Fire protection				205	0.01
Office costs				275	0.01
Investment charges: Depreciation				9,479	0.39
Interest on plant				4,050	0.17
Taxes				1,342	0.05
Miscellaneous costs				614	0.03
Totals - chlorine	2,445,000			46,321	1.90
Production — (KOH)	3,910,000				
Amt. & Cost (Clorine)	2,445,000			127,037	3.26
Sum	6,355,000				

APPENDIX I

List of Russian Personnel Interviewed

Name	Position	Location
Major M. Glakov	Supt. of Cell Plant	I. G. Farbenindustrie, Bitterfeld.
Captain Z. Nefatova	Chemist-Engineer	I. G. Farbenindustrie, Bitterfeld.

German Personnel Interviewed

Dr. Albrecht Wagner	At present Asst. Supt. Chlorine Plant.	I. G. Farbenindustrie, Leverkusen
	1923—1940 Several important positions.	I. G. Farbenindustrie, Bitterfeld.

APPENDIX II

List of Targets Visited

Name	Location
I. G. Farbenindustrie	Bitterfeld (South Plant)
I. G. Farbenindustrie	Leverkusen

APPENDIX III

Bibliography

Copies of the reports and documents listed below were transmitted to Washington, D. C. Inquiries should be adressed to:

Office of the Publication Board
U. S. Departement of Commerce
Washington, 25, D. C.

1. FIAT Final Report No. 816 — Horizontal Mercury Chlorine Cell I. G. Farbenindustrie A. G. by the U. S. Chlorine Industry Team.

2. FIAT Final Report No. 732 — Electrochemical Operations at I. G. Farbenindustrie, A. G. Bitterfeld by R. B. MACMULLIN.

3. M. C. File No. 247 — Operating Data and Costs, 1942, 1943, 1944 I. G. Chlorine Plants.

4. M. C. File No. 346 — Flow Diagram — Caustic Potash Equipment at the South Bitterfeld, I. G. Plant.

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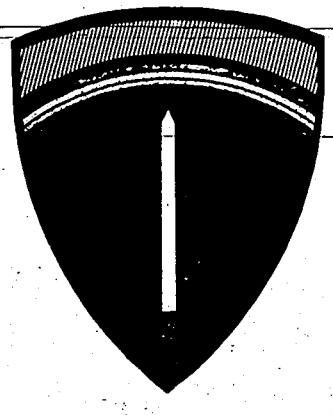
FIAT FINAL REPORT 725

HIGH PRESSURE, HIGH TEMPERATURE HEATING 250 ATM

Halbach, Ernest W.



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FIAT FINAL REPORT NO. 725 20 March 1946

HIGH PRESSURE, HIGH TEMPERATURE HEATING 250 ATM

BY

Ernest W. HALBACH

Joint Intelligence Objectives Agency

FIELD INFORMATION AGENCY TECHNICAL

ABSTRACT

Report covers general description of use of water up to 250 Atm. pressure for high temperature heating. It discusses "Samka" piping (steel pipes welded externally around vessels), forced and natural methods of circulating the water, and arrangements for protection of pump. 5 pages of description and 5 sketches.

TABLE OF CONTENTS

I. INTRODUCTION

Other investigators have reported that high temperature kettles were generally heated by high pressure water in Germany rather than oil or Dowtherm as is usual in the United States. Samesreuther, Butzbach leads in building kettles and many other types of apparatus for high temperature heating and for pressures up to 300 atm. Vessels may also be lined with nickel, copper, stainless steels (VA) etc. For its own installations, pumpless hot water heating is used.

High pressure hot water heating gives good heat transfer and allows the use of simple boilers, but specially developed welding technique is necessary for the kettles. These systems, with or without a pump, are generally used in Germany in preference to oil, Dowphen (Diphenyl) or Dowtherm. This was partly because of higher heat transfer but largely because high pressure vessel fabrication technique was well developed so that the the special equipment was available.

I. G. Farbenindustrie produced about one hundred kg. "Dinyl" (Dowtherm) annually, although approximately 130 tons/Mo were produced during the last war-years when glycerine was lacking. The phthallic anhydride plant of I.G. Ludwigshafen contained the largest Dowtherm heating system.

II. DESIGN OF KETTLES

Increasing requirements for higher temperatures caused a new vessel design in which double wall construction was replaced by welding steel piping directly to kettle walls, Fig. 1, and called SAMKA-piping. In using a heavy wall steel pipe directly welded to the kettle wall, pressures could be increased to 300 Atm., tested at 500 ATM. Maximum temperatures of 400° can be obtained and still kettle walls may be made comparatively thin. This is important for instance, in the case of expensive nickel or silver-lined shell construction. The Samka-piping is especially adopted for hot water heating, because there is only a little flow resistance even at high velocity with good heat transfer. Piping may be subdivided so that temperature drop can be reduced to a minimum. It is also possible to heat the lower parts of a kettle and simultaneously to cool the upper section.

In case of thin wall kettles and heavy wall piping an intermediate copper or soft metal section is used and completely welded in, see Fig. 1. This assists in welding and provides a good contact with the vessel wall.

Samesreuther has also developed another interesting type of kettle, the riveted or welded staybolt design, called "Warzenschweissung" (Nipple-welded-kettle). This design is for steam-heating only and for pressures up to about 75 Atm., see Fig. 2. It is not so expensive as Samka-piping and is useful for difficult designs like stirring-dryers, evaporators, etc.

Furthermore, this welded vessel-wall provides increased strength in the case of internal pressures. This allows smaller thickness of the inner shell as well as nickel, copper, aluminum or VA platings.

References:

Vessel Walls, Z.V.D.I., Beihefte Verfahrenstechnik 1937, Nr. 1, page 27-33 (I.G.)

Welding, Z.V.D.I., Beihefte Verfahrenstechnik 1937, Nr. 2, page 68-71 (Sa.)

III. HEAT TRANSFER

Hot water heating is also preferred when uniform temperatures are to be kept. For welded on heating pipe coils (Samka-piping) the heat transfer rate compared with usual double wall kettles is relatively low, or about

$$450 - 850 \text{ KCAL/M}^2_{hr}C^\circ \text{ @ 250 Atm.}$$

For welded staybolt design (Nipple-kettle) it is about 30% higher than for double wall kettles, or about

$$1100 - 2200 \text{ KCAL/M}^2_{hr}C^\circ \text{ @ 75 Atm. max.}$$

It is stated that heat transfer rates for Dowtherm (Dinyl) is considerably lower, about one half of the above cited values. The latter is almost inflammable, has odor, and is poisonous, but requires only equipment designed for low pressures (100 lbs/sq. inch at maximum temperatures of 700° F). However, it is expensive and according to the general opinion in Germany, losses through stuffing-boxes and flanges are unavoidable.

References:

Chem. Fabrik 1934, page 421-429 (I.G.)
Ind-Engng. Chem. 1937, page 910-912 (Badger).

IV. HEATING SYSTEM

In high pressure water heating two methods of circulation are used, with and without a pump.

(a) Heating Without Pump

This extremely simple type, Fig. 4, is used by Samesreuther, Butzbach, also Bamag, Berlin and other firms. It requires no pump, but there must be a considerable level difference to get sufficient circulation and good process heating.

The difference in level between furnace and heater required is about 10-15 feet. A temperature difference of 10° min. between heating water inlet and outlet is normal. Above the unit, a compensating vessel must be provided. This is similar to those used in central heating systems for allowing for the expansion of water and for the removal of gas and steam bubbles. Its valve is only closed during process heating (Thermosyphon).

Of great importance is the disadvantage that every heater requires its own furnace in close vicinity. The circulation force in the pumpless heating is so low, that it is impossible to control more than one unit connected to one boiler.

(b) Heating with Pump Circulation (Fig. 3)

This system allows any arrangement of furnace and kettles, and closer temperature control (5° differential at kettle) with a high heat transfer. One furnace may supply a number of large apparatus. The modern Buna-Plant (1939) of I. G. Schkopau for 30,000 tons annually uses for the butadiane synthesis (dehydration of buthyleneglycol) a forced circulation hot water heating system designed by Opitz & Klotz, Leipzig. It is the oldest and best firm for such plants and has developed the "Kaltes Gestaenge", i.e. cold plungers. By a skillful arrangement of valves it is impossible for hot water of the circuit to damage the plungers of the piston pumps. The actual pump operates with cold water and a cold water column is used to move the hot high pressure water through valve controls. See pages 13 and 14. These sketches are merely schematic and the sizes shown are not of the volumetric capacity of the respective items of equipment; e.g. the equalizer. Further, the necessity for using a separate suction and discharge line on each side of the pump may be unnecessary.

Undoubtedly the great progress made in Germany during the last few years in designing equipment for high pressure power plants has permitted improved combinations. In many power plants

centrifugal pumps are working, feeding hot water at 125 Atm. 325° with 2900 r.p.m. German experts believe that it is practical to apply centrifugal pumps of the types used in power plants. Such pumps are produced by Klein, Schanzlin & Becker, Frankenthal/Pfals.

An investigation was made January 22, 1946, of Samesreuther, Butabach. Director Richard Samesreuther and Dr. Siegfried Kiesskalt (now a consulting chemical engineer) were interrogated. Samesreuther has been among the leaders in developments and applications of welding technique to kettle and vessel design. As he stated, his whole plant was therefore slated to be evacuated for reparations. The plant and equipment are not modern, but the value of the plant is represented by experienced and specialized personnel.

According to Dr. Kiesskalt, extensive studies have been made by I. G. Farben comparing German high pressure water applications with Dowtherm in United States. High heat transfer rate and low operating cost have resulted in applying high pressure water systems in Germany almost exclusively. It also was stated that the complete control of Dowtherm pumping has eliminated all former objections except lower heat transfer rate. In late years some high pressure water systems were converted to the use of "Dinyl" (Dowtherm). Two such converted units were seen at I. G. Farben plant, Hoechst (visit of Target, January 31, 1946, Dr. Spangler). Dowtherm is considered for new installations if the temperatures required are below 350°.

Kettles, condensors, autoclaves, heat exchangers are fabricated complete with heating coils or double wall according to design. For heating, a pumpless high pressure system is used. Furnaces are designed by Samesreuther and built locally at each place of installation.

SUMMARY:

A temperature of 350° and below the development of "Dowtherm" technique (control of leakage) makes it unnecessary to operate with high pressure water, where design of apparatus becomes expensive.

However, at temperatures above 350° only high pressure water systems are applicable. Dowtherm decomposes at a rate of 3% per month or more at 400°. Actually installations have been carried out for 400° and 450° with high pressure water heating, using Opitz & Klotz circulation pump. One instance is known

(melting kettle) where 500° temperature was applied and successfully operated according to Dr. Spangler.

Operation beyond critical temperature is fully possible.

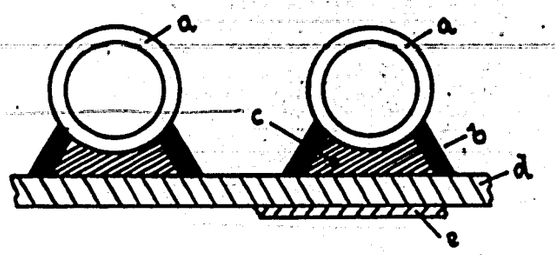
Pumpless systems (as Samesreuther) may be used without limitations of temperature provided sufficient level differential is available and provided that vessels are operated with individual furnaces.

Fig. 1.

"Samka"-Piping

Esp. for hot-water-heating!

High-pressure-steam > 75 at
till 250 at (test.pr. 400 at)



More expensive than Fig. 2!

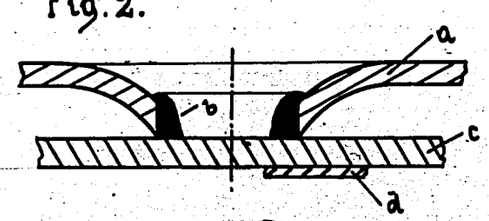
a .... pipes
b .... weld
c .... copperstrip
d .... inner-part
e .... nickel-plated (copper, VA...)

Fig. 2.

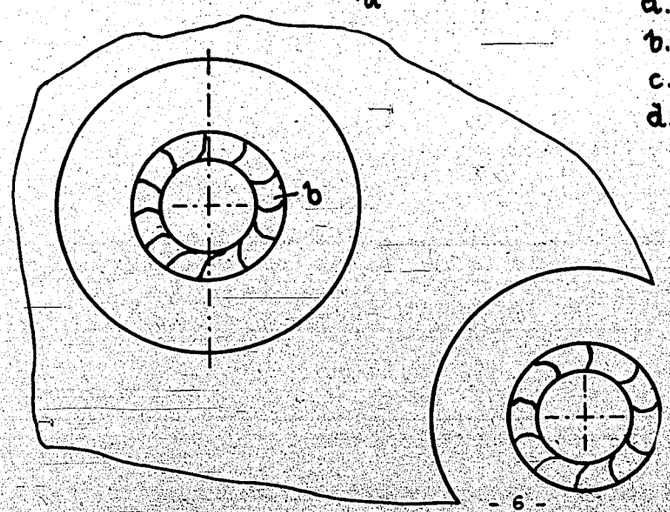
Double-wall-welded-kettle.

"Nipple-(w.)-Kettle".

!Only f. steam, not f. hot water!



a .... outer part (punched/hollowed)
b .... annular weld
c .... inner-part
d .... plated (Ni, Cu, VA...)

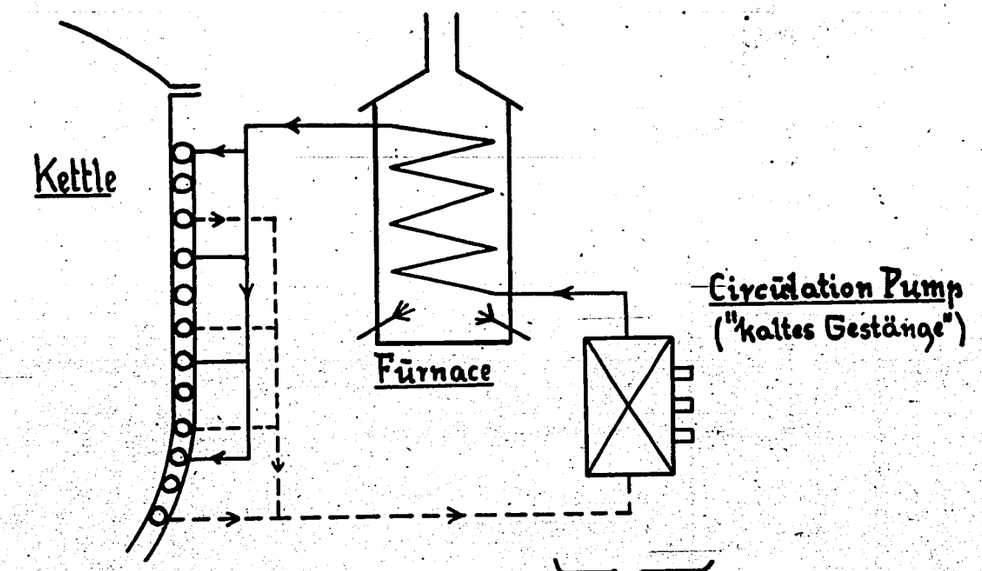


For all types
of apparatus!

Fig. 3.

Forced-Circulation / Hot-Water-Heating.

"Opitz & Klotz"



Instead of:

normal high-pressure
Feed-pumps
[e.g. Klein-Schanzlin & Becker, Frankenthal]

Also several Kettles -
Only one circulation plant!

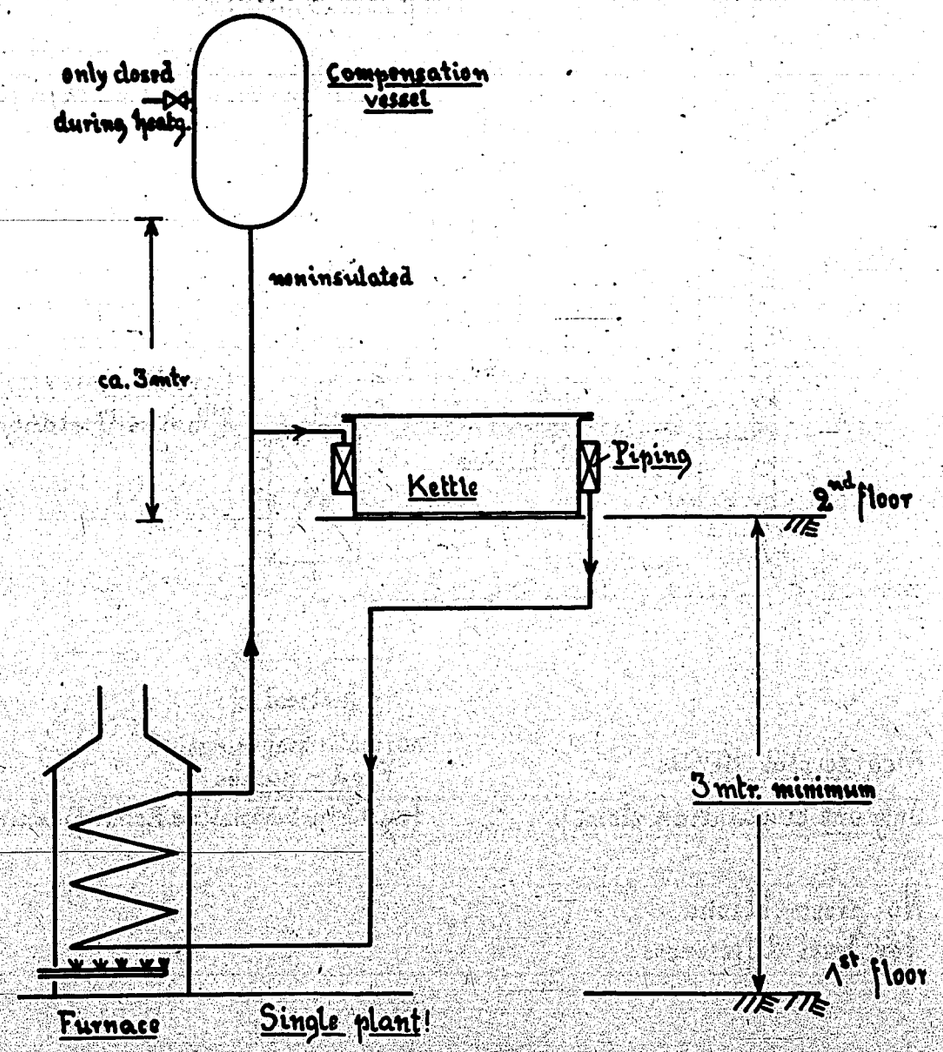
No prescriblions
for level differences!

Fig. 4.

Hot-Water/Pressure Heating

without pumps.

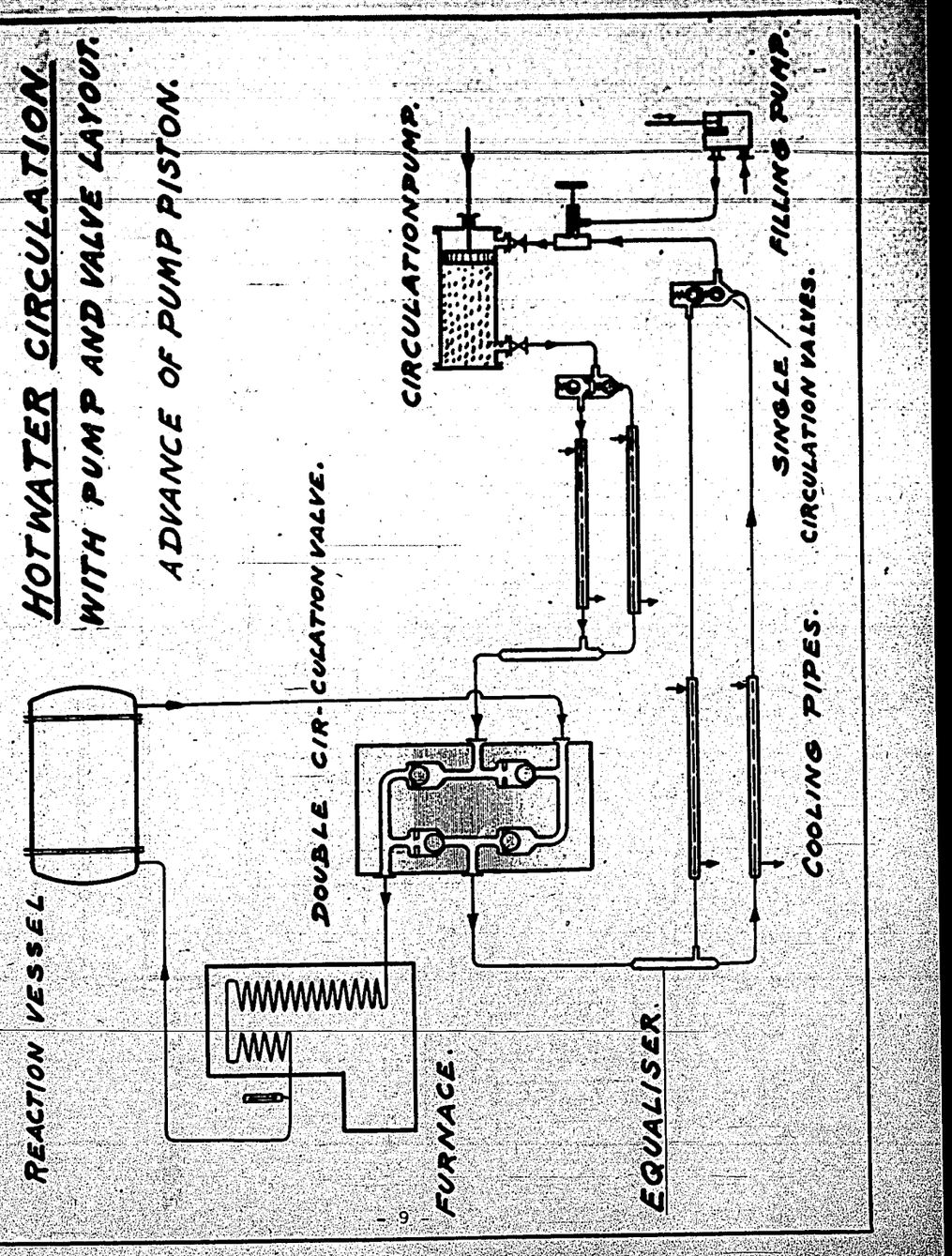
("Thermosyphon" or "Gravity Heating")



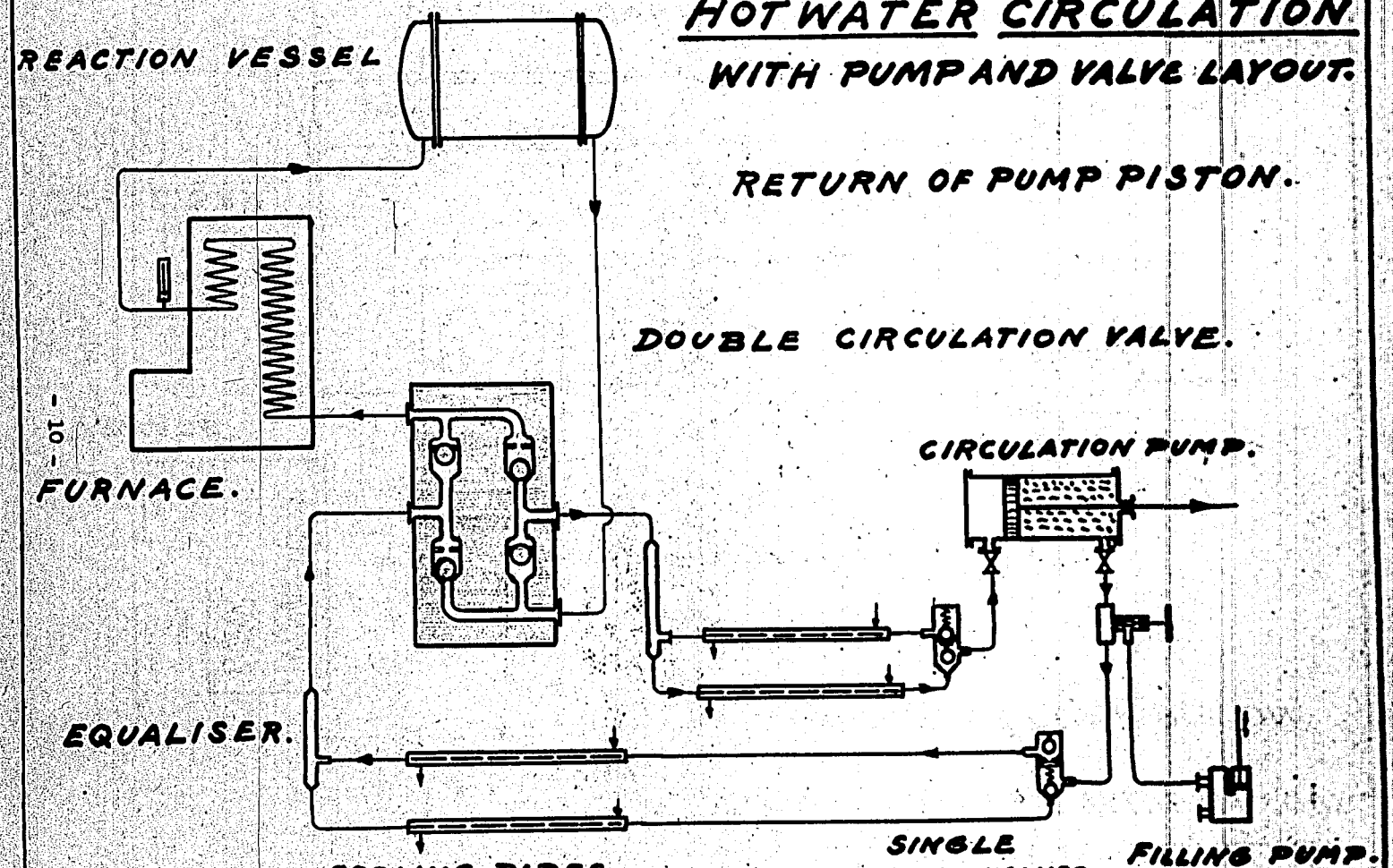
HOTWATER CIRCULATION.

WITH PUMP AND VALVE LAYOUT.

ADVANCE OF PUMP PISTON.



HOT WATER CIRCULATION
WITH PUMP AND VALVE LAYOUT.



RETURN OF PUMP PISTON.

DOUBLE CIRCULATION VALVE.

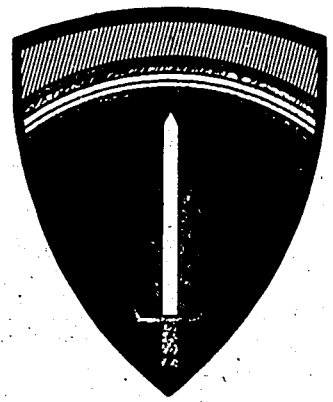
CIRCULATION PUMP.

Co-bus 1

FIAT FINAL REPORT 724

MISCELLANEOUS CHEMICAL PROCESSES AND PLASTICS MACHINERY

Halbach, Ernest W.



OFFICE OF MILITARY GOVERNMENT

FOR GERMANY (US)

FIELD INFORMATION AGENCY TECHNICAL

OFFICE OF MILITARY GOVERNMENT FOR GERMANY (US)

FIAT FINAL REPORT NO. 724 — 7 June 1946

MISCELLANEOUS CHEMICAL PROCESSES AND PLASTICS MACHINERY

BY

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FIELD INFORMATION AGENCY, TECHNICAL

ABSTRACT

The report is in four parts, (1) Polymerization of Styrene, (2) Polystyrene Moulding Compounds, (3) Polyvinyl Chloride Sheeting and (4) Plastic Zippers. Report is in detail showing compositions, molecular weights, labor requirements, equipment required, and methods of controlling polymerization.

TABLE OF CONTENTS

PART 1. POLYMERIZATION OF STYRENE

I N T R O D U C T I O N

Polymerization methods in U.S.A. and Germany have produced several types of pure polymers as well as copolymers of styrene. Only type III has gained considerable volume of production in Germany (400 TO/MO).

Objective:

The following report represents essentially a comparison of the two important Ludwigshafen styrene types, type III and type IV polymer, giving consideration also to the question of most economic coloring of the product. This latter question will be further dealt with in the following section of this report in connection with the manufacturing of Polystyrene moulding powder.

MANUFACTURING OF STYRENE POLYMERS

At I.G. Farben in Ludwigshafen seven types of styrene polymers and copolymers were manufactured, among them three Emulsion types. (E = prefix for Emulsion). Type EF was eventually transferred to Schkopau to avoid concentration. The various polymers are in the order of their importance:

Type III Mass polymerized, then continuously tower polymerized.

K = 70 - 72

MW = 90 - 100,000 (Staudinger)

MW = 150,000 (ULTRA CENTRIFUGE METHOD)

Capacity: 400 TO/MO

Main application: Standard injection moulding

Type IV Mass polymerized same as Type III, then remaining monomer removed by double roll vacuum dryer.

K = 80 - 85

MW = 250,000 (Staudinger)

MW = 370,000 (ULTRA CENTRIFUGE METHOD)

Capacity: 25 TO/MO

Main application: Injection moulding for articles requiring greater strength and heat resistance.

Type L. Towerpolymerized in same equipment as Type III without prepolymerization.

K = 58

MW = 60,000

Capacity: 20 - 50 TO/MO

Main application: Lacquers.

Type B. Copolymer of: 70% styrene, 30% Butylacrylate

K = 40

Capacity: 100 kg/MO

Application: Electrical lacquers

Type EF. Emulsion type. Transferred to Schkopau.

K = 125 - 130

K Max. = 145

MW Max. =1,000,000

Capacity: 50 TO/MO (Schkopau)

(120 TO/MO at Ludwigshafen before transfer of plant)

Main application: Same as type IV. Special injection moulding.

Type E.H. Emulsion copolymer.
Prepared as type E.F.

50% Styrene
25% Acrylonitrile
25% Vinyl carbazole

Replaced by type EN.

Type EN. Emulsion copolymer.
Prepared as Type EF.

70% Styrene
30% Acrylonitrile

K = 100 - 105

MW = 500,000

Capacity: 2 TO/MO

Application: Injection moulding of type letters to replace metal.

Of the above polymers Type III and IV especially were investigated at Ludwigshafen. For type EF a report in German is added, obtained by Dr. Rhodes at a recent visit (Jan. 46) in Schkopau. For type EN completed colored moulding powder was manufactured at Ludwigshafen.

TARGET REPORT

I.G. Farben plant Ludwigshafen was visited December 27 1945, January 17, 18, 1946. Dr. Ohlinger and Dr. Bülow were interrogated.. Polystyrene type III polymerization plant consisting of 14 units was badly damaged, 10 units being completely destroyed, while 4 units remain operative with a capacity of approximately 100 to 120 TO/MO of polystyrene. Monomer plant was severely damaged, but remaining capacity was in operation. All styrene monomer produced for months to come was reserved for synthetic rubber production so that polymerization plant will remain idle.

One unit of 25 TO/MO capacity for type IV polymer was set up in the same building on the fourth floor. This unit is completely destroyed and could not even be located in the wreckage. Type EF units had been transferred to Schkopau before the bombing.

Investment of plant was about 2,000,000 R. Marks for 14 units type III including buildings (500,000 RM) with total capacity of 400 TO/MO. Investments for machinery and equipment were therefore:

Type III: 3,750 - RM per TO/MO

Type IV 2,000 "

Type IV installation cost (one unit) was 60,000 - RM at 30 TO/MO Capacity.

Building requirements are said to be about only half of

type III installation. Beside the much lower investment cost and reduced space and building requirement, the type IV polymer represents an improved product of higher molecular weight. Injection moulding industry utilized largely type III and prefers this type for ease of moulding. In case of type IV, 15 - 20° higher moulding temperatures are necessary with subsequent longer cycles in injection moulding.

On the basis of monomer cost of .80 RM/KILO, prices were as follows:

Monomer	Polymer	
Cost RM/KILO	Type III 400 TO/MO RM/KILO	Type IV 25 TO/MO RM/KILO
.80	1.00	1.40
1.00	1.20	1.60

.20 RM/KILO differential between monomer and polymer type III appears safe, as Dr. Ohlinger gave normal cost as:

15 - 18 RM per 100 KILO for normal production on 400 TO/MO basis

Steam consumption: 220 kg/100 KILO type III

Electric power: 25 KW/100 KILO type III

At operation platform for polytowers one man or woman was necessary to control 8 prepolykettles and 4 polytowers. A second man was required for the operation of 3 to 4 grinding and bagging units at bottom level. Labor requirements therefore were:

1 man or woman (3 shifts) - 4 day ton output

and 1 man (1 shift) - 3 - 4 day ton output

No comparative details for type IV polymer were available. It was stated, however, that present cost price of 1.40 to 1.60 RM/KILO for type IV was the result of rather experimental and small-scale operation. Any larger scale production on type IV method will automatically bring cost of type IV to equal that of type III product.

MANUFACTURING PROCESS FOR TYPE III POLYMER

For mass prepolymerization 2 kettles are used, built of aluminum, covers and paddles are made of silumin. Volume is 2000 liter each containing 1400 Kilo of styrene. At a production rate of 22 Kilo/hr. styrene, which is added continuously via a Sihi measuring pump (22 Kilo/hr. for each kettle), the polymer remains in the tank about 65 hrs. This comparatively long time allows slow prepolymerization at low temperatures. Kettles are equipped with aluminum heating coils with warm water circulation about 72° - 78° As heat is released during polymerization, actual temperature in kettle is 78° - 82°. Paddles are operating at 60 RPM. Paddleshaft is made of V2A. Silumin paddle is flanged to shaft. The pipelines, exhaust and nitrogen lines are of Aluminum. Packing ring between cover and kettle was finally made of felt paper impregnated with Igamid paste with good results. At packing of paddle nitrogen is introduced into stuffing box, as otherwise, styrene monomer vapour will polymerize on packing shaft and stop the paddle.

It was stated that after sufficient experience was gained, the installation of a double prepolymerization kettle was no longer considered necessary. Original packing difficulties are now under control, to warrant single kettle operation.

The prepolymerized product (33 to 35% polymerized) then enters a cylindrical tower 6.2 meters high built in six separate rings made of V2A steel. Sections are about 1 m. high 750 mm. in diameter. Lower section has internal heating coil only, 2nd, 3rd, 4th and 5th sections have external double wall heating and internal heating coil. Top section has external double wall heating only. Coils are 50 cm. in diameter. All sections of mantel or of coils may be individually operated with reduced steam (Max. 10 ATM = 180°), hot water of 74° - 78° or cold water. The tower is filled up to about 1/2 of 5th section, and is kept under a nitrogen atmosphere. (N_2-50 L/hr.). To effect complete polymerization in the tower 0.02% glacial acetic acid is added at the storage of monomer. With the addition of acetic acid without explanation why, the volatile content is kept below 0.5%. Otherwise 1% or more. Requirements are both for type III and type IV product of 0.5% maximum volatile content.

Four thermometers are introduced through top cover of tower. Also vision glass is installed in the top cover so that height of tower content and observation of material together with automatic temperature recorders for all stations of tower allow complete control of tower conditions.

All packings are of "Klingerit" except top section of tower, where still hot monomer is present. The same packing as at prepolykettles, felt impregnated with igamidpaste, is applied there.

Tapered end section at bottom of tower is equipped with screw-extruder. (This section may be electrically heated when necessary). The screw delivers through two openings (60 mm. long, 4 mm. wide) two continuous parallel running strips on a conveyor 8 m. long at a rate of 44 kg/hr. Styrene strips are cooled with 6 water-cooled rollers, then cut into 1 inch long pieces dropped into an Alpine grinder, ground to 2 - 3 mm. granulation size and bagged.

All clear type III polymer was shipped to Troisdorf. No coloring of material was done in Ludwigshafen. Dynamit A.G., Troisdorf processed Type III material by coloring on mixing rolls, or sold clear polymer direct without any processing for injection moulding.

TEMPERATURE REGULATIONS

In case monomer purity is not properly controlled, polymerized material is retained at the joints of the section of the vertical tower. Gradually additional quantities are deposited, and it has become necessary to entirely dismantle the vertical tower, in order to restore unhindered flow of the polymerisat. After control of monomer purity was perfected (99.5% pure by refractive index - less than .1% Divinyl Benzene, less than .1% Methyl Styrene), it has not been necessary again to dismantle the vertical tower units. It is therefore considered that in a new installation, longer tower sections may be used, possibly 2 only. This will reduce the possibility of forming undesirable deposits of high polymerized material. Steam is used as follows:

For the 3 lower tower sections	180°
For the 4th " - "	150°
For the 5th & 6th " "	100°

In case polymerization flow in the tower is retarded, steam temperature is brought up to 180° in the 5th section. Further regulation is possible at the lowest section of the tower where temperature at the outside mantle is kept at 140 - 150°. At the funnel connection at the end of the tower to the inlet for the feed of extruder-screw, temperature is kept at 245 - 255° by electrical heat applied at the mantle. The extruder screw itself is heated to 210° by electrical cartridge. Speed of the screw and therefore output of polymer can be regulated by a PIV reduction gear which allows infinite regulation. Two continuous parallel strips of polystyrene are transported over a conveyor belt whose speed is regulated by a PIV infinite reduction.

The possibility of regulating temperatures separately at each point from the pre-polymerization kettles to the extruder mouth, together with the final regulation of extruder screw and transport belt speed results in a very close control at each point of operation. As total time to pass through the entire process approaches 100 hours, changes at each phase are extremely slight and can be immediately corrected. If monomer

is used at 99.50 purity volatile contents do not exceed 1/2 of 1%. A constant K-value of 70 - 72 is obtained, corresponding to a molecular weight of 90,000 - 100,000. According to Dr. Ohlinger's statement, the operation of the unit was absolutely fool-proof.

The normal operation temperature at Prepolykettles was kept absolutely constant. Likewise all temperatures at vertical tower unit were kept constant for all sections, so that regulations of condition was limited to:

1. Temperature control at top section of tower (normally 100° steam).
2. Temperatures at (max. 180° steam) - Extruder mantle and screw. (Electrical heat)
3. Speed of extruder screw and conveyor (Controlled by infinite PIV reductions)

MANUFACTURING PROCESS FOR POLYSTYRENE TYPE IV.

In order to obtain a better quality of high molecular weight it was found that a good product is obtained by immediately separating monomer from polymerized material at the end of the pre-polymerization period, as described for type III product. 35% of the entire mass is polymerized to a molecular-chain of fairly even length, as polymerization takes place at comparatively low temperatures with sufficient time (65 hours). Monomer during the additional polymerization time of approximately 33 hours in the tower is exposed to higher temperatures from 150 - 250°. Undesirable chain lengths are obtained which impair the quality of the final product. In the process for type IV polymerization the mixture of 35% polymer and 65% monomer as derived from pre-polymerization kettles is charged directly upon a set of steam heat rolls. (No acetic acid is added).

These rolls are heavily chromium plates, slow moving 1½ - 2 revolutions per minute and have a surface temperature of 200° at about 14 atm. internal steam pressure. Roll spread allows a film thickness of about 1½ mm. The entire machine should operate under 10 mm. vacuum; however, in actual operation 15 - 20 mm. was the best which could be obtained. The travel time for the polymer on the roll surface over an arc of 200° is about 15 seconds. In this short time interval no essential change takes place in the polymer, while the monomer is immediately evaporated, condensed and returned to the pre-polymerization kettles. The polymerized sheet which adheres to the hot rolls is stripped off by a brass knife; both roll and knife have to be perfectly fitted in order to remove the entire hot viscous

film from the roll surface. Temperature of styrene sheet on roll was about 140° - 150° and was immediately reduced to 75° - 80° after leaving roll surface. In the beginning the film was as wide as the entire machine, namely approximately 1200 mm. It was found, however, that by subdivision better results were obtained. Separating strips were added to the brass knife so that 6 separate continuous strips are taken off from the rolls on either side. These drop into suitable containers placed below vacuum.

Every 3 hours the container cars fill up. The vacuum is broken, the atmosphere filled with nitrogen, the cars removed and replaced by empty ones. Container cars are located within vacuum and are heated by a double wall casing to 60° to prevent monomer condensation. This machine which represents a vacuum double roll dryer was built by Venuleth & Ellenberger, Darmstadt. Roll diameter 500 mm., width 1,300 mm. Special chromium plating was done by Krupp, Essen. Production capacity of the unit was about 25 TO/MO. Installation cost was RM 60,000 for the unit. Polystyrene type IV showed a high molecular weight 370,000 (ultra centrifuge method) and a better mechanical strength as well as higher heat resistance than type III. Type IV material was equal to type III in water-clear quality of product and was equal to type EF (emulsion type), as far as physical properties and heat resistance are concerned. It was stated by Dr. Ohlinger, however, that the operation of type IV was not as yet under full control. The double roll vacuum dryer was the first unit designed and may still be improved.

Due to insufficient vacuum control the type IV product was not uniform in volatile content and mechanical properties.

Type EH Emulsion copolymer consisting of:

50% Styrene
25% Acrylonitrile
25% Vinyl carbazole

was replaced by Type EN

Type EN This emulsion copolymer consisted of 70% styrene and 30% Acrylonitrile. 2 TO/MO were produced for a special application in injection moulding of type replacing metal type for printing.

Type EN polymer was colored gray at Ludwigshafen (all other coloring operations were done at Troisdorf). Mill mixing (400 x 1000 mm. rolls), 10 minutes at 150°C, drove off extra monomer, and color was added. Because of lack of mill capacity coloring was later done by extruder also. Single screw 80 mm. diameter Kleinwefer extruder was used. EN polymer was premixed with dye

and fed into screw, 650 mm. long, threads 30% progressive. Practically, coloring by extruder was as good as mill mixing. However, volatile content was reported not quite uniform in extruder coloring.

Type L This type of polymer was produced in regular Type III equipment using tower only without pre-polymerization in prepolykettles. Acetic acid is used. K = 58. MW = 60,000. Quantity 20 to 50 TO/MO was produced at expense of type III for lacquer use.

Type B Small quantity of 100 kg/MO only was produced for electrical lacquers. K = 40.

Type B represents a copolymer: 70% Styrene, 30% Butylacrylate.

Type EF This emulsion type polymer was produced at Ludwigshafen at a rate of 120 TO/MO until moved to Schkopau, where 50 TO/MO capacity was relocated. This type was not investigated but both Ludwigshafen and Schkopau extracts are added.

LUDWIGSHAFEN REPORT: (a) Type EF was essentially pure polystyrene prepared in the following manner. A jacketed enamelled kettle of 1200 gallon capacity was charged with two parts of water and one part of styrene monomer. The mixture was stirred with a paddle type stirrer, and there was added (based on styrene) 0.1% potassium persulfate catalyst and 0.5% $Na_2H_2P_2O_7$ as regulator plus 1.0% of the emulsifier Amfoseife 18. The mixture was heated to 70°C for two hours and then heated quickly to 95°C and maintained at this temperature for an additional two hours to complete the polymerization, leaving less than 0.1% free monomer. The emulsion was finally drum dried on rolls to produce a powder which was used for injection moulding purposes.

SCHKOPAU REPORT: (In German)

Beschreibung und Fahrweise der Anlage zur Herstellung von

Polystyrol EF. (I.G. Farben, Schkopau)

Chemischer Vorgang:

Styrol wird in einer schwach alkalischen Seifenlösung mit Kaliumpersulfat als Aktivator 100% polymerisiert. Das Polymerisat wird aus dem Latex durch Ansäuer mit Ameisensaure ausgefällt, filtriert, gewaschen und getrocknet.

Die Polymerisation und Fällung von Polystyrol EF wird in Bau B 39a durchgeführt.

Polymerisation:

In einem 10 m^3 Rührwerks-Kessel (1) wird nach folgendem Ansatz polymerisiert:

5 400 l wofatiertes Wasser
7,2 kg. (0.4% auf Styrol) Natronlauge 100 %ig
18 kg. (1 % auf Styrol) Paraffinfettsäure

werden auf 50° aufgeheizt und durchgerührt, bis klare Lösung eintritt.

Das wofatierte Wasser wird in einer geschützten Leitung von B 30 angeliefert und in einem 20 m^3 Kessel (2) gestapelt. Der Pm-Kessel (1) ist innen verchromt und mit einem Wasser-mantel versehen, der mit Heiss-und Kaltwasser beschickt werden kann.

Von der Emulgator-Lösung wird das freie und gebundene Alkali durch Titration kontrolliert.

Dann werden 1800 kg. monomeres Styrol zugepumpt und Aktivator 1,8 kg. (0,1 % auf Styrol) Kaliumpersulfat zugegeben. Die Luft wird durch Stickstoff verdrängt und unter anfänglichem Aufheizen auf 70° wird die Polymerisation bei 80 - 85° in 2 - 3 Stunden zu Ende geführt. Das vollständige Auspolymerisieren des Styrols erkennt man daran, dass eine Probe mit Kochsalz-lösung gefällt eine krümelige Ausscheidung ergibt.

Fällung:

Gefällt wird durch Ansauren mit Ameisensäure und Alkalischstellen durch 20% iges Ammoniakwasser. In filtrierbarer Form wird die Fällung durch Erhitzen auf ca. 80-85° gebracht. Man lässt den Latex in eine verdünnte Ameisensäure laufen. Die für die Fällung nötige Ameisensäure wird im Laboratorium wie folgt bestimmt:

In einem Erlenmeyer - Kolben von 500 cm^3 werden in 100 cm^3 Wasser, 0,3, 0,4, 0,5 etc. cm^3 konzentierte Ameisensäure 100 cm^3 Polystyrol-EF-Latex geschuttelt. Dabei fällt Polystyrol aus. Die Fällung wird mit 20 %igem Ammoniakwasser schwach alkalisch gestellt und aufgekocht. Man steigert die vorgelegt Säuremange solange, bis das Filtrat klar abläuft. Die für die Fällung der Betriebscharge, die in 3 Teilen vorgenommen wird, benötige Säure-menge wird entsprechend berechnet. Für loco 1 Latex werden normalerweise 500 - 600 l. Wasser mit 3 - 4 kg. konzentrierter Ameisensäure vorgelegt.

Ausführung der Fällung:

In einem Fällkessel (3), einem emaillierten Kessel mit Gitter-Rührer von 8 m^3 Inhalt und Kühlmantel, werden ca. 1500 l Wasser vorgelegt und die berechnete Monge konzentrierte Ameisensäure zugegeben. Dann werden

unter Rühren 1/3 des Pm-Kesselinhaltes langsam zugedrückt. Um das nicht filtrierbare, käsig abgeschieden Polymere in filtrierbare Form zu bringen, wird nach dem Neutralisieren mit 20 %igem Ammoniakwasser durch Einblasen von Dampf auf 90-95° aufgeheizt und solange bei dieser Temperatur gehalten, bis das Polymere eine filtrierbare Form angenommen hat. Die Fällbrühe wird dann einen phnytalisierten Vorratsbehälter (4), der mit einem Rührer versehen ist und 8 m^3 Inhalt hat, bedruckt. Von hier wird das Prodnkt mittels Pumpe (5) der Filtration und Waschung zugeführt. Auf 2 Saugzellen-Drehfiltern (6, 8) von 0,35 m^2 der Firma Imperial Meissen, die durch eine Wasch-Schnecke (7) verbunden sind, wird das Material von der Mutterlauge befreit, gewaschen und trocken gesaugt. Das Vakuum für die Saugzellenfilter wird von einer Wasserringpumpe (9) erzeugt. Das trocken gesaugte Material fällt durch einen Schacht auf eine Dampf-beheizte Rillenwalze und wird hier in Stäbchen verformt. Das in Stäbchen verformte Polymere wird von Hand auf Sieben gesammelt und in 4 Imperial-Trockenschränken, bei ca. 100° getrocknet. Das trockene Material kommt in Papiersäcken (25 kg) zur Abgabe an die verarbeitende Industrie. Kapazität der Anlage: 50 Moto Polystyrol EF.

Description of Process and Tests (German)

I.G. Farbenindustrie A. G. - Werke Badische Anilin - u. Sodafabrik-
Ludwigshafen/Rh.

L.K. - Abteilung 13 August '45
Dr. Chl/W.

Betriebsbeschreibung der Styrol-Fabrik
Polystyrol

Zur fabrikatorischem Herstellung von Polystyrol III dienen zwei Vorpolymerisationskessel in Form von Ruehrbehaltern und ein Haengekessel in Form eines senkrechten Turmes für die Nachpolymerisation. Die Ruehrgefaesse (Inhalt ca. 2000 l) sind aus Aluminum die Deckel und die Ruehrer aus Silumin guss. Die Ruehrerwelle besteht aus VA-plattiertem Stahl und ist an das Ruehrblatt angeflanscht. Die Drehzahl des Ruehrers betraegt ca. 60 U/Min. Saemtliche Rohrleitungen, Belueftungsleitungen und Stickstoffleitungen sind aus Aluminum gefertigt. Die Beheizung der Vorpolymerisationskessel erfolgt durch einem Warmwasserkreislauf, der die Ruehrkessel aus einem Reservoir ueber eine Pumpe in den von unten in die Ruhrbehaelter eingefuehrten Heizschlangen aus Aluminum durchlaeuft. Als Dichtungen des grossen Flansches zwischen Deckel und Behaelter haben sich bis jetzt Pappeinlagen, die mit Igamidpaste bestrichen sind, am besten bewaehrt. Die Packung der Stopfbuechse an der Ruehrwelle besteht aus Asbestschnur mit Talkum. Da eine Ölschmierung nicht in Frage kommt wird die Asbestschnur waehrend des Zusammenbaues mit Talkum eingepudert. Um zu vermeiden, dass Styroldaempfe in die Stopfbuechse eindringen, dort kondensieren und durch Polymerisation den Ruehrer zum Stillstand bringen,

ist eine Vorstopfbuechse angebracht in die dauernd durch eine kleine Zufuehrungsleitung etwas Stickstoff eingefahren wird. Die Dichtungen an den Produktleitungen für Zu und Ablauf, sowie an den Beluefteungsleitungen bestehen ebenfalls aus igamidimpraegnierter Pappe.

Der Haengekessel, der als ca. 6 m. hoher zylindrischer Turm in sechs Einzelschussen ausgefuhrt ist, besteht aus remanitplattiertem Schmiedeeisen. Er kann ebensogut oder noch besser aus V_2A Material hergestellt werden. Die einzelnen Schuesse besitzen je eine Mantel-und Schlangenheizung. Die Beheizung erfolgt durch Hochdruckdampf über eine Dampfreduzierstation, mittels welcher entsprechend dem eingestellten Dampfdruck die für die Polymerisation benoetigten verschiedenen Temperaturen reguliert werden. Der unterste Schuss besitzt lediglich eine Heizschlange. Der Mantel, Trichter und die Auslaufschnecke werden elektrisch beheizt. Der 2, 3, 4 und 5. Schuss haben Mantel-und Schlangenheizung der oberste Schuss nur Mantelheizung. Ein auf dem Deckel aufgesetzter kleiner Rueckflusskuehler (V_2A-Rohr) verhindert, dass monomeres Styrol durch die Beluefteungsleitung abdestilliert. Die Polymerisation im Turm wird ebenfalls unter Stickstoff-Atmosphaere vorgenommen. N_2-Anschluss mit Messscheibe sind an Deckel angeschlossen (ca. 50/1/h). Durch das ebenfalls auf dem Deckel befindliche Schauglas kann der Verlauf der Polymerisation, sowie die Standhoehe im Turm verfolgt werden. Das polymerisierende und das fertig polymerisierte Produkt fliesst infolge des Eigengewichtes durch die einzelnen Schuesse des Turmes zur Auslaufschnecke, die das Polystyrol durch eine mit zwei Schlitzen (60 mm. lang, 4 mm. breit) versehene Duese auf das Transportband befoerdert. Es hat sich als zweckmaessig erwiesen, die Thermometerhuelsen im Turm durch den Deckel einzufuehren, da jede nicht beheizte Querverbindung des Fluss des zaehen Polymerisates einen unerwünschten Widerstand bietet.

Als Dichtungen für die einzelnen Schuesse des Turmes, die in der Hauptsache nur mit Polystyrol gefuellt sind, können gewoehnliche Klingeritringe verwendet werden. Der oberste Schuss dagegen, wo noch relativ viel heisses Monostyrol vorhanden ist, ist an saemtlichen Flanschen mit igamidimpraegnierten Pappdichtungen versehen.

Temperatur- und Durchsatzverhaeltnisse.

Die Vorpolymerisationskessel sind mit je 1400 kg. Styrol gefuellt. Die Temperatur im polymerisierendem Produkt betraegt 78-82° und wird auf einem Multithermographen registriert. (Alarmsignal bei Temperatur zu hoch). Der Einlauf in die Vorpolymerisationskessel erfolgt aus einem Vorratsgefaess über eine Sihipumpe, Diephragmafilter, Messuhr und Rotamesser. In jeden Ruehrkessel laufen 21-22 kg/h monomeres Styrol ein, sodass das Material in den Ruehrbehaeltern eine mittlere Verweilzeit von 65-68 Stunden hat. In Verlauf dieser Zeit verwandelt sich das Styrol unter staendigem Ruehren zu ungefaehr 33-35% in Polystyrol, der Rest besteht aus unveraendertem.

monomerem Produkt. Der Umsatz wird durch refraktometrische Messung im Abbe- Refraktometer bestimmt.

Es ist noch zu erwaehnen, dass dem in die Polymerisation einlaufenden Styrol vorher im Vorratsgefaess 0,02 % Eisessig zugesetzt werden. Dieser Zusatz ist notwendig, um eine restlose Durchpolymerisation des Styrols im Hauptkessel zu bewirken.

Die Temperatur des Warmwasserkreislaufes liegt etwas unter der oben angegebenen Temperatur des Produktes bei ca. 74-78°, da bei der Polymerisation Waerme frei wird, die abgefuehrt werden muss.

Die Warmwassertemperatur kann am zweckmaessigsten durch automatische Regulierung eingestellt werden.

An den Zugangsleitungen des Kreiswassers sind noch Dampf zum Anwaermen beim Anfahren und Kuehlwasser zum Abkuehlen des Vorpolymerisates angeschlossen, sodass im Bedarfsfalle der Warmwasserkreislauf durch entsprechende Ventilstellung abgestellt und Dampf oder Kuehlwasser durch den Kessel gefahren werden kann. Um nun bei einer solchen Massnahme eine Temperaturveraenderung des Warmwasserkreislaufes an anderen normal laufenden Ruehrgefaessen zu vermeiden, besteht an jeder Rueckfuehrungsleitung aus dem Ruehrgefaess zum Reservoir eine Ablaufmoeglichkeit zum Kandel, die durch einfache Ventilstellung geoeffnet werden kann.

Das, wie oben beschriebene, vorpolymerisierte Produkt laeuft nun in Form einer zaehfluessigen Loesung ueber einen regulierbaren Ablaufhahn zum Polymerisationsturm, der ebenfalls bis zur Haelfte des 5. Schuesses mit polymerisierendem Material gefuellt ist (ca. 1400 kg.). Die mittlere Verweilzeit im Turm betraegt ungefaehr 33 Stunden. Die Heiztemperaturen sind folgende:

Die unteren 3 Schuesse sind mit 180° Dampf
der 4te " " 150° "
" 5.u.6" " 100° 100° entspanntem Schleichdampf beheizt.

Man geht im 5ten Schuss lediglich bei erlaehmender Polymerisation auf gespannten Dampf ueber oder wenn infolge zu weitgehender Auspolymerisation im 5ten Schuss und des dadurch herabgeminderten Fliessvermoegens des Produktes die Gefahr einer Blockbildung besteht. In diesem Falle wird der Ablauf aus den Vorpolykesseln unterbrochen und das Material durch Temperaturerhoehung (gespannten Dampf 150 - 180°) heruntergeschmolzen. Alsdann stellt man wieder auf die normalen Fahrbedingungen um.

Nachem das Produkt den Turm durchlaufen hat, ist die Polymerisation vollstaendig beendet.

Die elektrischen Heizungen am untersten (1) Schuss des Turmes

werden durch einen elektrischen Regulierschrank eingestellt. Am Mantel betraegt die Aussentemperatur 240-250°, am Trichter 245-255°, an der Foerderschnecke herrscht eine Innentemperatur von 200-210°.

Das Polystyrol fliesst als zaehe plastische Masse zur Austrittduese. Die Foerderleistung der Schnecke ist durch ein PIV-Getriebe regulierbar. Das Polystyrol tritt in der jeweils gewuenschten Bandstaerke aus den Duesen und wird auf dem Transportband unter den wassergekuehlten Fuehrungswalzen weitergefoerdert. Die Laufgeschwindigkeit des Bandes und des vorne angebrachten Abschlaegers ist ebenfalls durch ein PIV-Getriebe regulierbar.

Auf dem Transportband kühlt das Material soweit ab, dass es durch die Schlagmesser des Abschlaegers in Kleine Stueckchen zerkleinert werden kann. Diese fallen in einen Auffangbunker und laufen von da kontinuierlich einer Schlagkreuzmuehle zu, wo sie zu dem für den Spritzguss direkt verwendbaren oder zum Einfaerben auf Mischwalzen geeigneten Pulver gemahlen werden.

Am Einfallschacht des Bunkers befindet sich eine Umstellklappe mit Fallrohr, sodass stueckchenfoermiges Polystyrol auch direkt in Faesser abgefüllt werden kann.

Das Mahlgut wird aus dem unter der Mühle befindlichen Silo ueber ein Schuttelsieb in Holzfaesser mit Papiersackeinlagen oder direkt in Papiersäcke abgefüllt.

Das in der Polymerisation eingesetzte monomere Styrol muss einen Reinheitsgrad von mindestens 99, 3 - 99.5% haben, da sonst der Gehalt an fluechtigen Bestandteilen im Polystyrol ueber die zulaessige Grenze von 0.5 - 0.7% ansteigt.

Unter Beachtung der obigen Fahrbedingungen wird das Polystyrol III in stets gleichbleibender Beschaffenheit mit einen absolut konstanten K-Wert von 70-72 Einheiten, entsprechend einem Molekulargewicht von 90 - 100,000 erhalten.

Anfahren eines Polymerisationsaggregates

Bei Inbetriebnahme einer vollstaendig neu erstellten Apparatur kocht man am zweckmaessigsten den Hauptkessel mit 200 - 300 l. Aethylbenzol, mit dem man vorher die Ruhrbehaelter gespuelt hat, einige Stunden aus, um die von der Montage herruehrenden Schmutzpartikel möglichst weitgehend zu entfernen. Das Aethylbenzol laesst man unten wieder ab. Anschliessend spült man mit 200 l. Styrol nach und polymerisiert das Styrol im untersten Schuss durch Erhitzen auf 120 - 140° rasch durch und erhitzt das Produkt nach 10 Stunden auf 180°. Man hat dabei Gelegenheit die elektrischen Schaltungen auszuprobieren und mit dem erhaltenen Material nach Entfernen des an der Austrittsduese angebrachten Blindflansches das Foerderband genau einzuregulieren. Das Polymerisat wird nicht restlos ausgefahren, sondern man laesst

im Trichter des Turmes einen Propfen aus Polystyrol zurueck, der als Abschluss bei der naechsten Füllung Verwendung findet.

Um nun die kontinuierliche Fahrweise in Gang zu bringen, erhitzt man die mit je 1400 kg. Styrol gefuellten Vorpolymerisationskessel ca. 48 Stunden auf 80 - 82°. Nach dieser Zeit ist das Styrol zu ungefähr 30 - 35% in Polystrol verwandelt, (refraktometrische Bestimmung!) wobei die Viskositaet stetig ansteigt. Aus den Vorpolykesseln hat man vorher die Luft weitgehend mit Stickstoff verdraengt. Aus den beiden Ruehrbehaeltern laesst man anschliessend gleich viel vorpolymerisiertes Produkt in den Haengekessel einlaufen und zwar in einer Menge, wie sie dem normalen Zulauf an Monostyrol in jeden Vorpolykessel entspricht. Gleichzeitig mit dem kontinuierlichen Ablauf aus den Vorpolykesseln wird der Kontinuierliche Zulauf von monomerem Styrol 20-22 kg./h je Vorpolykessel eingestellt.

Das in den Hauptturm einlaufende vorpolymerisierte Produkt wird durch Beheizung des jeweils zu fuellendem Schusses mit gespanntem Dampf von 110 - 120° kontinuierlich weiterpolymerisiert und auf diese Weise wird der Turm von unten allmaehlich bis zur Haelfte des 5ten Schusses mit Polystyrol gefuellt. Waehrend die obersten Schuesse noch befahren werden und in Polymerisation sind, erfolgt in den unteren Schuessen (1, 2 und 3) durch Beheizung mit 170 - 180 graedigem Dampf (9 - 10 atue) bereits die restlose Durchpolymerisation, die bei dieser Temperatur nach 10 Stunden beendet ist. Gegen Schluss dieser Zeitspanne schaltet man auch die elektrischen Heizelemente ein und beginnt bei ca. 220 - 240° Aussentemperatur an Mantel und Trichter und 190 - 210° Innentemperatur in Schnecke mit dem Ausfahren des Polystyrols.

Die Apparatur befindet sich nunmehr in vollstaendig kontinuierlicher Fahrweise, indem monomeres Styrol in die Vorpolykessel einfliesst, das vorpolymerisierte Produkt in den Hauptturm ablaeuft und das auspolymerisierte Produkt als fertiges Polystyrol aus dem Kessel ausgefahren wird.

Analysenmethoden der Polystyrol III-Fabrikation

1. Divinylbenzolbestimmung.

Das zur Polymerisation gelangende monomere Styrol muss vollstaendig frei sein von Divinylbenzol, da man nach unseren Untersuchungen bei Mengen von ueber o,o3% Divinylbenzol im monomeren Styrol bei der Polymerisation teilweise unloesliche, vernetzte, nicht mehr vollkommen thermoplastische Polymerisate erhaelt. Der Divinylbenzolgehalt kann quantitativ nur durch Intensitaetsmessung einer U.V. Linie ermittelt werden. Diese Bestimmungen werden im Physikalischen Laboratorium durchgefuehrt. Im Betrieb sind die Destillationskollonnen des Aethylbenzols und Reinstyrols so eingestellt, das Divinylbenzol ausserhalb der zulaessigen Grenze mit Sicherheit ausgeschlossen bleibt.

2. Kontrolle der Vorpolymerisation

Zur Kontrolle des Polymerisationsverlaufs bei der Vorpolymerisation des monomeren Styrols kommt ebenfalls die refraktometrische Methode zur Anwendung (Berechnung Polystyrol in Monostyrol).

3. Untersuchungen von Polystrol III.

Die Fabrikation von Polystyrol III wird durch nachstehende Untersuchungsmethoden laufend geprueft:

(a) Viskositaetsmessung (K-Wert)

(b) Schlagbiege - und Biegefestigkeit

(c) Bestimmung des Gehaltes an fluechtigen Anteilen

ad (a) Die Viskositaet der polymeren Produkte wird innerhalb der I.G. durch die K-Wert-Bestimmung charakterisiert = Literatur: Fikentscher, Cellulose Chemie 1932, Seite 58 und 71. Im Betrieb wird die Bestimmung in Capillar-Viskosimeter nach Ubbelohde durchfuehrt und zwar mit einer 1 %gen Loesung von Polystyrol in Benzol. Ig Substanz wird in einem geeichten Mebkolben auf 100 ccm mit Benzol aufgefuellt und auf einer rotierenden Schuettelmaschine in Loesung gebracht. Die Kappillare des Viskosimeters wird mit einem Teil der Loesung gefuellt und die Durchflusszeit (t) abgestoppt. Fuer das Viskosimeter nach Ubbelohde gilt die Formel.

Va (absolut Viskositaet) = Vk Sp

$Sp = \frac{\text{gramm}}{\text{cm } 3}$ = spez. Gewd. Loesung bei 25°

Vk = kinematische Viskositaet
= Ausflubzeit (t) Konstante der Kapillare (k).

Der Druckfaktor ist durch die Konstruktion der Ubellohde schen Kapillare ausgeschaltet.

Absolute Viskositaet Vac = Vk Sp = Poise $\left(\frac{g}{cm \cdot sec}\right)$

Die relative Viskositaet erhaelt man aus der absoluten Viskositaet der Loesung durch Dividieren mit der absoluten Viskositaet des Benzols (Vb = 0.00611)

Relative Viskositaet $Z = \frac{Vac}{Vb} = \frac{t \cdot k \cdot Sp = t \cdot 0.01 \times 0.8785}{Vb \qquad 0.00611}$

Die Tabelle der K-Werte ist zu den z-Werten in Beziehung gesetzt aufgrund der folgenden empirischen Gleichung:

$$\log \frac{Vac}{Vb} = \log z \ldots \left(\frac{75\,k^2 \quad k}{1 \quad 1{,}5\,k.c}\right) .c$$

z = relative Viskositaet der Loesung bei der Konzentration c

c = Prozentgehalt in Volumprozentent, also c gramm in 100 ccm.Loesung.

k = Parameter der Kurve, also die von Konzentration c unabhaengige Groebe, die wir mit Eigenviskositaet bezeichnen, weil sie jedem Produkt eigen und fuer dieses charkteristisch ist.

ad (b) Zur Bestimmung der Schlagbeige- und Biegefestigkeit werden Pruefstaebe aus gemahlenem Polystyrol gespritzt. Die Pruefstaebe haben folgende Dimensionen:

55 x 6 x 4 mm.

Im Schopper-Schlagpendel werden die Schlagbiegefestigkeiten $\frac{cmkg}{cm^2}$ bestimmt.

Die Biegefestigkeiten $\frac{kg}{cm^2}$ erhaelt man durch entsprechende Bestimmungen im Biegepruefer (Schopper - Apparat).

Die Berechnung der Biegefestigkeit geschieht folgendermaben:

	b	h	e	p	f	kb
	mm	mm	mm	kg	mm	kg/cm^2
	Probenbreite	Probenhoehe	Auflageentfernung	Biegekraft	Durchbiegung	Biegebeanspruchung
Beispiel	6	4	40	10		

Die Formel lautet:

$Kb = \frac{p \cdot 4 \cdot 6}{4 \cdot b \cdot h^2}$ kg/cm^2 (alle Masse in cm. eingesetzt)

$Kb = \frac{P \cdot 4 \cdot 6}{4 \cdot 0.6 \cdot (0.4)^2} = 62.5\ p$

Kb = 62.5 10 = 625 kg/ cm²

Schlagbiegefestigkeit errechnet sich wie folgt:

	b	h	l	A	KS
	mm	mm	mmkg	cmkg	cmkg/cm²
	Proben-Proben breite	höhe	Auflage entf.	Schlagarbeit nach Tabelle	Schlagbiegefestigkeit
Beispiel	6	4	-	5	-

Schlagarbeit A = KS in $\frac{cmkg}{cm^2}$ (Masse in cm. eingesetzt)

$KS = \frac{A}{b \cdot h} = \frac{5}{0.6 \quad 0.4} = 20.8, \frac{cmkg}{cm^2}$

ad (c) Die Bestimmung der fluechtigen Anteile des Polystyrols geschieht nach folgender Methode:

Die in Plaettchenform anfallenden Polystyrolstueckchen werden in einer Schlagkreuzmuehle gemahlen. Das Mahlgut wird sodann durch ein Din-Sieb Nr. 1171 mit 2 Siebsaetzen geschuettelt. Das oberste Sieb Nr. 8 hat hebenstehende Dimensionen

0,75 mm lichte Maschenweite
0,50 mm. Drahtstaerke
64 Maschen / pcm;

das zweite Sieb hat:

0,30 mm. lichte Maschenweite
0,20 mm. Drahtstaerke
400 Maschen / pcm.

Zur Bestimmung der fluechtigen Anteile wird der auf dem zweiten Sieb Nr 20 durchgehende feine Staub nicht zur Bestimmung herangezogen. Eine auf einer analytischen Waage in einer Kristallisierschale (80 mm. ∅) genau abgewogene Menge (z.B. 0,5 g) wird 24 Stunden in einen Trockenschrank auf 95° erhitzt und nach dem

Abkuehlen in einem Exsikkator wieder zurueckgewogen.

(% Gehalt an fluecht. Anteilen) = $\frac{b}{a}$ 100

b = Gewichtsverlust in gr. a = Einwage (gr.)

Dr. Ohl/W 19 Januar 1946

Betriebsbeschreibung der Polystyrol IV Anlage Lu 615 Leistung 25 moto.

In dem Bestreben, eine gegenueber Polystyrol III verbesserte Polystyroltype zu entwickeln, wurde gefunden, dass man ein sehr gutes Produkt erhaelt, wenn die aus der Vorpolymerisation (vgl. Polystyrol III Betriebsvorschrift) stammende viskose Loesung von Polystyrol in Monostyrol in geeigneter Weise in festes Polymerisat und fluessiges Monostyrol zerlegt wird. Das hierbei gewonnene Polystyrol IV stellt also ein bei 80° polymerisiertes Produkt dar und setzt sich infolge der absolut konstanten, relative niedrigen Polymerisations-Temperatur aus Polystyrolmolekuelen von weitgehend einheitlicher Kettenlaenge zusammen. (Das Mol. Gew. betraegt ca. 370 000 gemessen nach dem Prinzip der Ultra-Zentrifuge von Svedberg.) Da die Bildung von niedrig polymeren Anteilen, die sonst bei hoeherer Temperatur entstehen, bei diesem Verfahren ausgeschaltet ist, besitzt Polystyrol IV groessere mechanische Festigkeiten und hoehere Temperaturbestaendigkeit, aber das gleiche wasserklare Aussehen wie Polystyrol III.

Man kann, kurz zusammengefasst, sagen: Polystyrol IV entspricht hinsichtlich Festigkeit und Waermebestaendigkeit dem Polystyrol EF (Emulsions-Polymerisat), hinsichtlich Transparenz dem Polystyrol III.

Als geeignetste Apparatur fuer die Trennung des Polystyrole und Monostyrols aus obiger Loesung, wurde ein Vakuum-Doppelwalzentrockner (Lieferfirma: Venuleth & Ellenberger, Darmstadt) befunden. Diese Methode hat folgende Vorzüge:

(1) Das Polymerisat faellt in Form eines trockenen Filmes an, kann leicht zerkleinert und unmittelbar fuer Spritzgusszwecke eingesetzt werden.

(2) Infolge der kurzen Verweilzeit auf den mit 14 atue Dampf beheizten Walzen ist das Polystyrol bei 1½ - 2 Umdrehungen pro Minute nur kurze Zeit auf hoeherer Temperatur. Ein Abbau der langen Kettenmolekuele ist dabei ausgeschlossen.

(3) Das Abdestillieren des Monostyrols unter Vakuum und anschliessender Kondensation zeigt die geringsten Materialverluste und liefert ein

Rueckstyrol, das ohne weiteres wieder in dem Polymerisationsprozess eingesetzt werden kann.

POLYMERIZATION IN COLOR

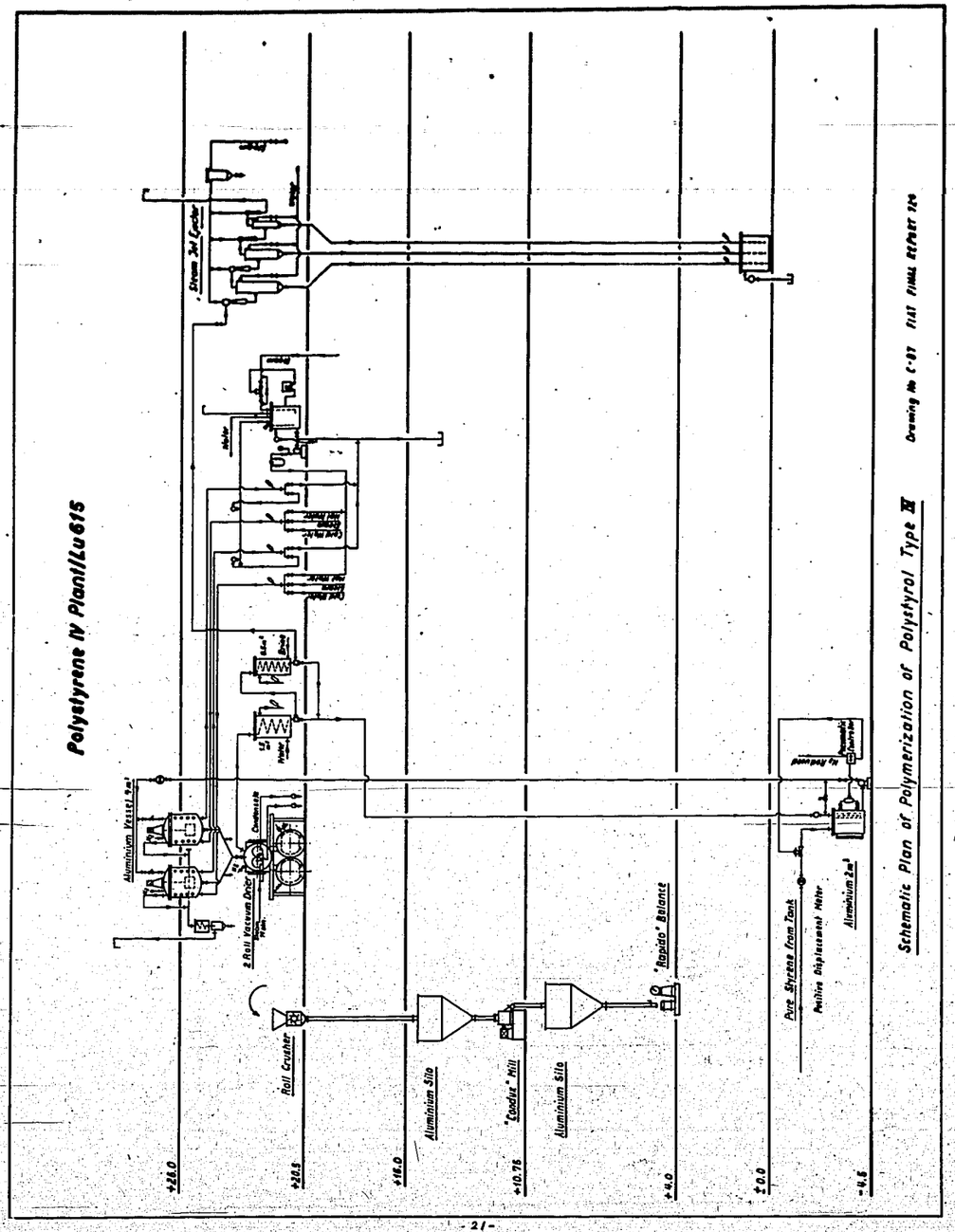
Due to the set up at I.G Farben, all coloring of polystyrene was done at Dynamit A.G. - Troisdorf. There was often discussion, according to Dr. Ohlinger, concerning the operation of one polytower unit by polymerization in standard color, either black or white, as for both colors sales outlet is sufficiently large to warrant operation of one tower unit (output 25 TO/MO) continuously on one color. According to Dr. Ohlinger this is entirely practical without additional cost over the clear product type III. Present cost at Troisdorf is 60 RM. per 100 KILO for coloring only against 20 RM per 100 KILO for polymerization of monomer. U.S.A. cost for mill mix coloring amounts to 5 - 7 cents/pound. In the set up for new polymerization capacity, it is extremely important to consider polymerization in color for standard colors for sake of cost as well as quality of polymer.

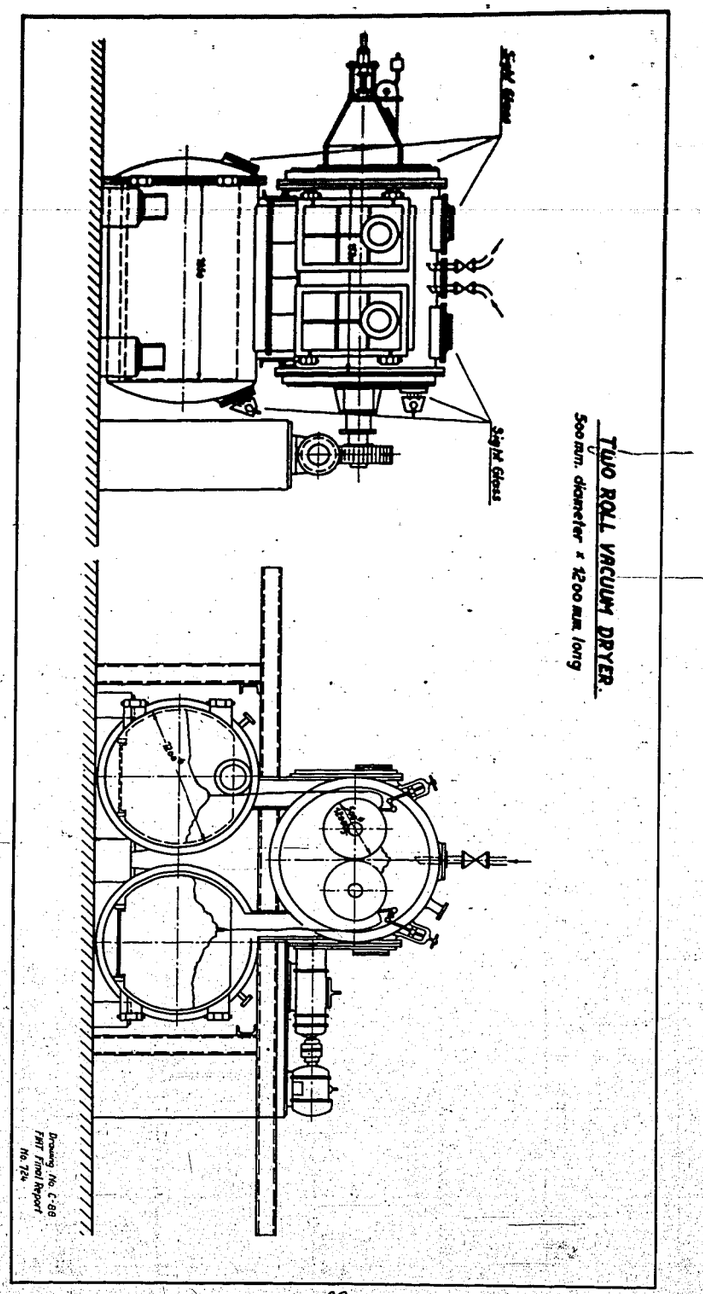
SUMMARY

In present tower method no higher molecular weight polymer than type III can be produced. Less viscous polymer will not flow satisfactorily in the vertical tower.

Output of tower unit (one ton per day) is at upper limit, as increase in diameter of polytowers is objectionable for sake of heat transfer. Double roll vacuum dryer for type IV requires improvements, namely larger roll diameters and improvement of vacuum in order to obtain more consistent operation and better control of properties.

Improved vacuum dryer should result in compact installation and low cost, high molecular weight polymer. As for tower method, polymerization in color is practical also for vacuum dryer.





PART 2. MANUFACTURING OF POLYSTYRENE MOULDING COMPOUND

I N T R O D U C T I O N

Various types of Polystyrene as Type III, IV (clear) and EF (tinted) were further processed at Dynamit A. G., Troisdorf for use in injection moulding. Apart from Rheinische Gummi and Celluloid Fabrick, Mannheim, which processed their own requirements in similar manner as Troisdorf, Dynamit A. G. was the only source of Polystyrene moulding compound in Germany.

Objective:

Manufacturing of Polystyrene moulding powder essentially consisting of coloring by mill mixing represents an expensive and uneconomical process. German process was investigated with a special view to experience gained in new methods of coloring by extruding.

TARGET REPORT

Dynamit A. G. was visited Jan. 10, 11. Dr. Mienes, Dr. Roehm, Dr. Eisemann, Dr. Scholz, and Ing. Tensi were interrogated. Coloring of Polystyrene is done on mixing rolls 1000 x 400 mm. operated at 18 and 20 R.P.M. These are located in separate enclosed rooms. Clear polystyrene powder and colors are dry mixed and loaded on mill rolls.

15 KILO batches for type III

10 " " " " EF

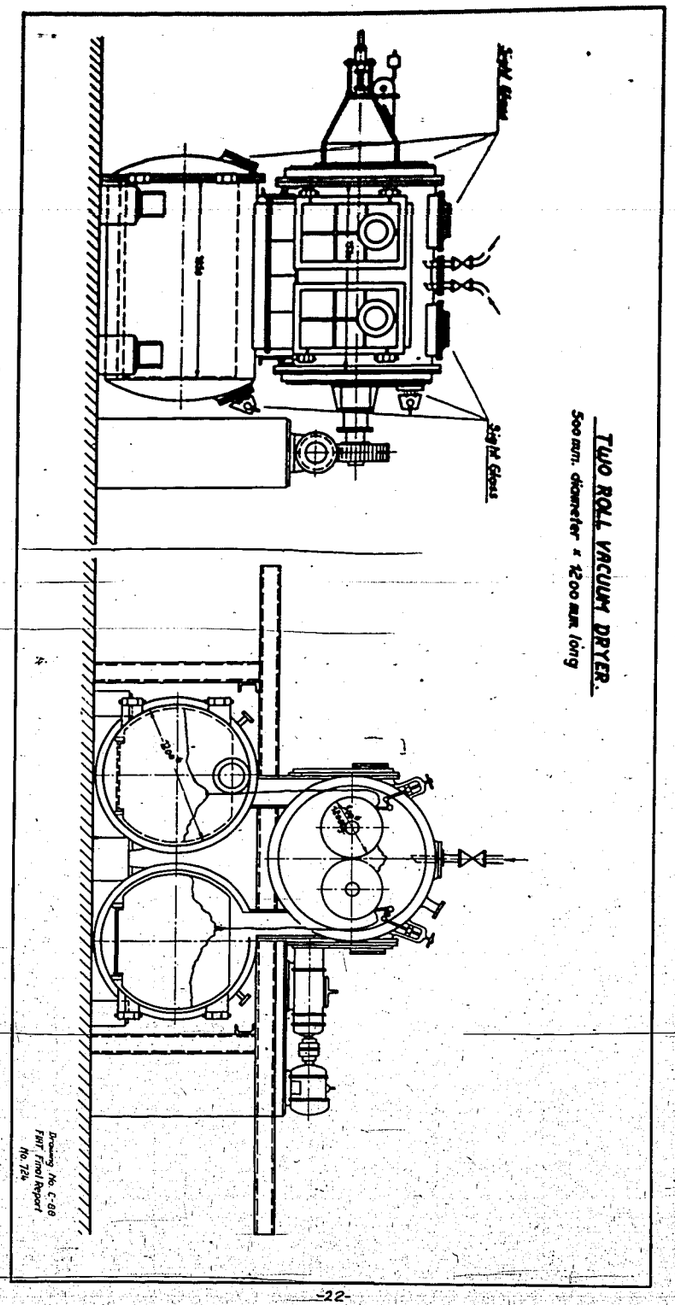
Mixing cycle is about 20 minute average, varying about 5 minutes with color. Roll temperatures were 110° - 120° type III, 150° - 160° for type EF.

Capacity of mills:

25 TO/MO for type III
18 " " " EF

at 3 shift operation.

Blanket drawn from mill was folded, broken in half, (when cooled off),



TWO ROLL VACUUM DRYER

500 mm. diameter x 1200 mm. long

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Blanket drawn from mill was folded, broken in half, (when cooled off),

rough cracked in a star cracker to 1 - 2 square inch size, and granulated either in M.A.G. or Excelsior grinders. M.A.G., Augsburg, #4 mill was used with an output of 100 Pds/hr. Each granulator was housed in a fully separated room. The rotating grinding disk was studded with a varying number of hammer bolts (12 to 30) which move between a series of fixed bolts. The machine was operating at 2500 RPM at 15 HP. The product of this grinder contained fines, which were put back on mixing mill.

The Excelsior grinder represents a fairly slow operating, screenless machine with 600 mm. wheel diameter and 650 RPM. One center ring is fixed on axle, one side ring each is mounted on either side of travelling center ring. The side rings remain stationary during operation of mill, but may be adjusted horizontally. Thus the distance between travelling center wheel and stationary side wheels determines the granular size without the use of a screen. Material is fed at center of wheel and travels in radial direction. Surfaces of center wheel on both sides and surfaces of side wheels facing center wheel are equipped with hardened rough grinding sections. This mill produces a granulation with minimum of fines. Capacity is about 30 - 35 TO/MO on styrene per grinder.

Total volume per month:

Type III Colored - 200 TO/MO

" Clear - 50 - 100 TO/MO

" FF - 60 - 70 "

10 standard colors were mixed, among them Black 30 - 40 TO/MO, White 25 - 30 TO/MO.

Polymer was purchased from Ludwigshafen at 2.50 RM per KILO and moulding powder was sold at 3.50 RM per KILO.

Color concentrates were produced, mixed with clear powder, but injection moulding still showed streaky, uneven colors. Chloramin bottles for army use were produced: 1 part, red; 9 parts, clear, but showed poor color distribution. Finely ground colored polymer mixed with clear transparent also shows uneven distribution of color.

Coloring costs were about 60 RM/100 KILO Average.

To reduce cost of coloring, extrusion with single and double screw extruder was experimentally carried out. Single extruder built by August Novrack, Bautzen was used with screw 240 mm. diameter 3½' long. This did not produce satisfactory coloring effect. Material was not sufficiently mixed. Further experimental unit for 75 ton pressure was built at Kuemmel,

Hamburg (Division of Troisdorf) and Troisdorf Extruder screw was sent there. Double extruders were more successful. Only one small machine was available for trial. This was built by the Italian firm L.M.P., Lavarationo Materie Plastici, Turin. At first screws were turning in opposite directions. Maximum mixing effect was obtained when both screws were operating in same direction. Screws were 30 mm. diameter, 500 mm. long operating at 30 R.P.M. with screw centerline 20 mm. apart. First section of screw consists of 3 coarse threads, 25 mm. each, then follow 25 mm. open spacing, further 4 semi-coarse threadturns at 15 mm. width each, again a 25 mm. spacing and the last section consists of 20 turns of 15 mm. width each. Both screws have outside bearing at extruderhead. Extruder was successfully operated 600 hours on coloring of Igamid at a rate of 3000 KILO/MO. It was stated by Dr. Eisemann that styrene will be easier to color by the same process.

SUMMARY

Coloring of styrene by mill mixing will be replaced by extruder, as soon as larger double screw extruders are developed. The war has held up this development. These machines were to be built by Eckert & Ziegler, Wessenburg, Bavaria and Kleinewefers, Krefeld.

Even if extrusion coloring will result in lower costs than mill mix coloring, it still requires heating and softening of styrene for incorporation of color. This intermediate and undesirable heating operation cannot be eliminated for small volume colors, but for all large volume standard colors, coloring in the polymerisation process itself should be contemplated.

PART 3. POLYVINYL CHLORIDE SHEETING

I N T R O D U C T I O N

Specialized sheeting methods of P.V.C. material were investigated. Unplasticized P.V.C. sheeting 0.0012 - 0.0016" made by the "Luvitherm" process as well as thin plasticized sheeting such as "Mipolam" have been investigated and described previously. See Kline's report (a.c.): file # xxix6" Page 20 - 25.

Investigation of German Plastics De Belle a.c. (Quartermaster).
The German Plastics Industry.

Pages 13/1 - 13/3 and 34/1 and 34/3

The evacuation of one Luvitherm calender unit has been effected and operation of the actual machine by U.S.A industry will allow full study and application of this process.

Objective:

Manufacturing of sheeting (P.V.C.) of various thicknesses by special methods were investigated.

TARGET REPORT

(A) C.F. Roser, G. m. b. H. Stuttgart - Feuerbach.

This plant was visited December 12, 1945 and Dr. Hans Roser was interviewed. One part of the plant (40% of capacity) was severely burned.

For P.V.C. capacity 300 TO/MO could still be produced equal to about 1.2 million pair of soles.

200 TO/MO may be added in 6 months if destroyed factory is repaired.

Formulation for P-soles: (Polyvinylchlorid soles)

45% Vinylchlorid H. H (wacker)
36% Plasticizer
10% Organic filler (woodflower)
2% Cotton flock
7% Inorganic filler
100%

or: 50% Igelit (vinylchlorid)
40% Plasticizer
8% Organic filler (woodflower)
2% Cotton flock
100%

They prefer Wacker H. H. Resin, as the higher polymerized resin (H. H.) allows higher percentage of fillers.

For plasticizers they use:

1st choice: Plastomol KF. (Ludwigshafen)
Triglycol ester of ft. fatty acids
2.50 RM/KILO

2nd choice: Palatinol H. S. (Offenbach)
Dioctyl Phthalate

or: Palatinol K (Offenbach)
Dibutoxyethel Phthalate

3rd choice: Mesamoll I (Leuna)
Mepasin Sulfophenolate
(cheapest) 1.30 RM/KILO

During war time any suitable plasticizer or combination of plasticizers was used, as obtainable.

Palatinol C (Ludwigshafen)
Dibutyl Phthalate 1.90 RM/KILO

was used, but was not found to be satisfactory.

Vinnol H. H. cost 1.60 RM/KILO
Igelit base price 1.50 " (old price)
2.50 " (new ")

Sole stock sold as: 3.20 RM/KILO. Their process of making P.V.C. sheeting was unusual, in that no calender was used and press operation was only used for embossing. Mixing mill roll surfaces had to be perfect; actually the finished sheet was pulled off the mill.

Milling time was 10 minutes at 160° roll temperature. Back roll journals were fitted with motor driven screws, so that fine adjustment and absolutely uniform closing of mill rolls is possible. After uniform mixing is obtained, the operator closes mill rolls to about 2 mm. (motorized screws).

Then the full sheet thickness is gradually built up. Every 15 seconds the operator opens up the mill rolls further by 1/4 mm. Electric timers control exactly the roll movement by motorized screws. In this way even quantities of material are built up every 15 seconds until the bank has almost disappeared. During the last turn the surface of the sheet is cooled by brushing on cold water, the mill is stopped, leaving a minimum bank, immediately reversed and the sheet pulled off. The portion of the bank remaining (about 6" long 2" thick) at the beginning of the sheet is cut off and returned to the mill.

For surface roughing an embossing operation was added. Total cycle at embossing press was 30 seconds with 10 seconds under heater.

The Roser P-sole was reputedly the best P-sole manufactured in Germany. P-soles made by Deutsche Linoleum Werke, Bietigheim or by Spohn and Knoll, St. Georgen were considerably softer.

For attaching P-soles to the shoe a cement was developed by Roser which is put on the whole hot sheet immediately after it is pulled off the mill. Vinnol H-40 (mixed Polymer) is used.

At Salamander Shoe Co. (Dr. Zigle) the soles were wetted with solvent and attached quickly. Dr. Zigle there stated that both stitching and cementing was done and that stitching will not be omitted until a better cement is developed.

For P-soles fillers give soles leather characteristics, while the absence of fillers as in P.C.U. - paste soles results in rubber characteristics. P-soles stand up under actual road test for 3000 kilometers against 800 - 1000 kilometers for leather.

Roser expects to produce a breathing upper leather, incorporating a cotton sheet impregnated with P.V.C. paste. So far no paste material has been produced in the American zone.

TARGET REPORT

(B) Spohn & Knoll St. Georgen (Baden)

This plant was visited December 14, 1945 and Ing. Ludwig Hemmel was interviewed. They are plastic fabricators and do impregnation and coating. Items produced were P.C.V. soles, sacking, paper creping, laminated with asphalt into bags ("caschiert" air and watertight).

P.C.V. soles were made from paste and consumption was 60 - 70 TO/MO. Paste arrived ready mixed from Bitterfield in drums. Production was practically stopped except for using remnants of paste stock. As no supplier of paste was left in the American zone, negotiations took place with I. G.

plant at Rheinfeld to produce paste with results unknown.

Four machines developed in their own shop, were available for casting P.V.C paste on a conveyor to form sole stock without use of mills, calenders or presses. See attached sketch on page 30.

Paste as received is filled into a trough fastened at one end of a belt 72' long, 3½' wide. This conveyor picks up the paste while passing the trough. Special chrome-nickel steel is used for the basket weave conveyor, made by Krupp. If properly mounted, the belt lasts for several years. Frame design is executed so that one piece belt can be taken out by removing frame sections, supporting rolls on one side. The belt pattern is impressed at one side of the P.V.C. sheet and serves as wearing surfaces. The exposed side of the sheet is quite smooth until last layer is built up, when woodflower is brushed on the surface for roughening so that cementing of soles becomes easier. The sheet is gradually built up in layers of 3/4 mm.= .030" for one complete cycle. A doctor blade at the trough admits an even quantity of P.V.C. paste and is so regulated that at each cycle additional .030" material is built up, until full thickness (normal ¼") is obtained. After leaving the doctor blade, the belt travels horizontally through a chamber, heated by gas-air mixture, entering at 260° temperature cooling off to 90° at the outlet. (See sketch). Paste dries to solid sheet and combines readily with new paste at the following passage. Belt travels at a rate of 3½' per minute and takes 22 minutes for one layer cycle at 0.030" thickness for each layer. One ¼" thick sheet takes 8 hours to build. Minimum thickness sheet built is 0.7 mm. = 1/32", max. is 8 mm. = 5/16". If heavier sheet is produced, it loosens itself from the belt by its own weight while belt returns. One girl operates 2 units, attending to paste trough and doctor blade regulation. Each machine can produce 800 to 900 KILO/day sole material according to thickness.

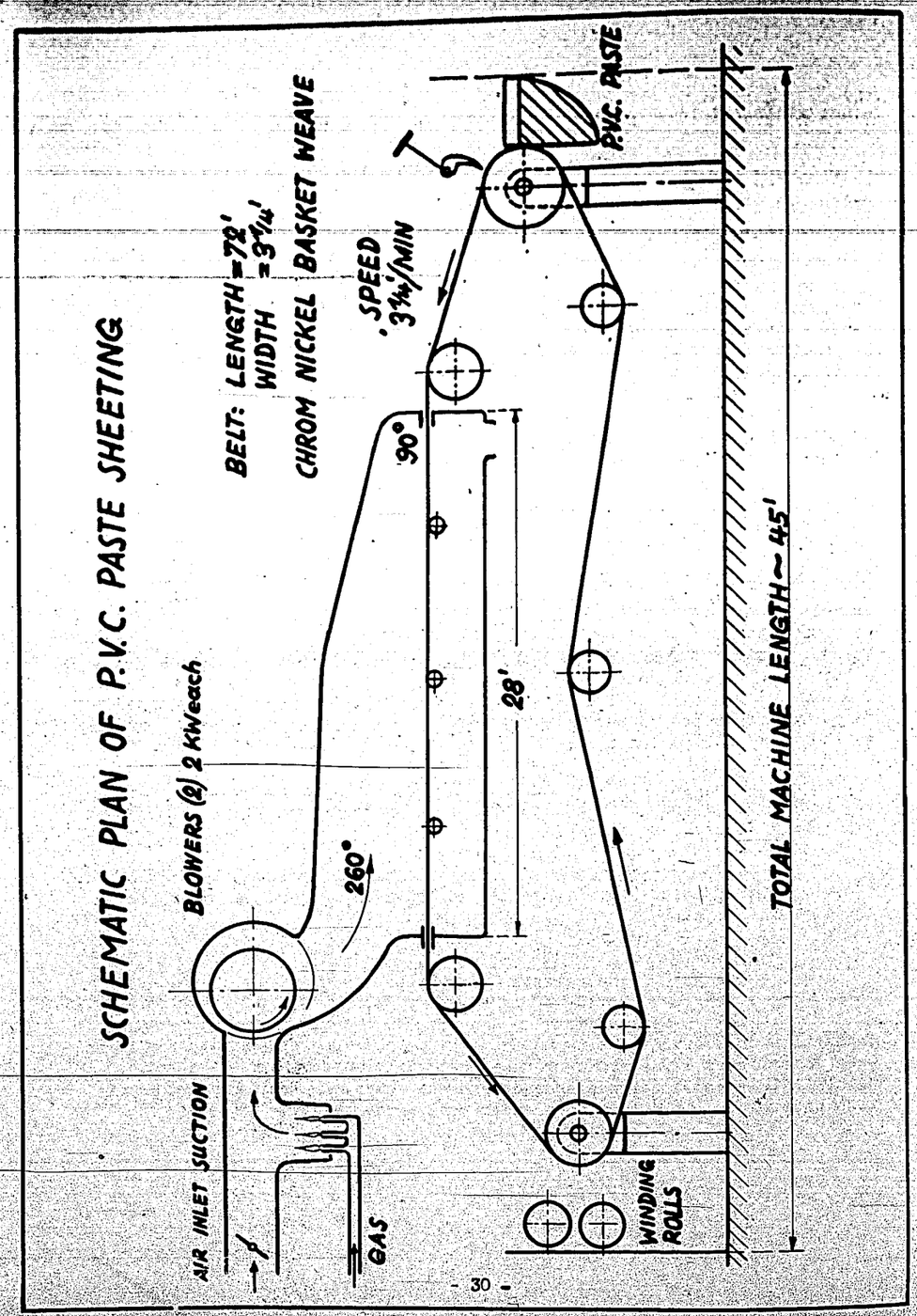
No filler is used except small quantity of woodflower. After the last layer is put on, cooling roller is applied, and sheet pulled off. Sole stock is sold at 3.50 RM/KILO.

This process represents the simplest setup seen to produce P.V.C. sheeting material. It depends entirely on procurement of selected grade of P.V.C. paste.

TARGET REPORT

(C) Hutchinson Gummi Werke Mannheim

This plant was visited January 21, 1946 to investigate their production on P.V.C. sheeting materials. Dr. Hasslacher and Ing. Hollmann were interviewed. The plant produces primarily rubber (Buna) products, mainly sole sheets, calendered and pressed. Part of plant and equipment were destroyed, but mill and calender room were intact.



Several mills and 2 calenders also 1 out of 3 extruders (3") were used for P.C.V. production.

3000 to 4000' of P.V.C. sheeting were made at 800 to 1000 KILO/ day (8 hour) consumption. Sheeting was produced 1.20 m. wide. Thicknesses produced were:

0.12	mm.	thick	for	thin raincoat stock
0.2	"	"	"	white hospital sheeting
0.25	"	"	"	heavy rain coat stock (black and dark gray)
4.5	"	"	"	for P. sole stock

Extruder tubing P.V.C. was made 50 mm. diameter and 0.2 wall thickness.

Mill and calender were operating at 160°. After leaving calender, sheet was passed over 16" diameter cooling drum to winder. Calender was operating with little friction producing 400 m/hr. at 0.12 mm. and 300 m/hr. at 0.2 mm. thickness.

P.V.C. extruder was operating on a tubing 50 mm. diameter 0.2 mm. wall delivered at a rate of 200 m/hr. Mantel was steam heated, while head was provided with electric heater band.

Typical formulations are:

	KILO	KILO	KILO
Igelit (Schkopau)	40	40	65
Vinnol H. H.	25	20	
Mesamoll	10	10	
Mollit S.B.	10		
Palatinol H.S.	10		
Trycresyl phosphate	5	15	
Palatinol F		15	20
Plastonmall KF			15
	100	100	100
Then added T_1O_2	5	5	
	Hospital Sheeting		Other Sheeting

On the basis of 2.45 RM for Igelit their average formulation cost was:

2.20 - 2.40 RM/KILO

Cost per 100 m^2 of sheeting was:

0.12 mm. thick 62 RM per 100 m^2
0.3 mm. " 142 RM " " "

Thickest sheet produced as 0.08 mm. thick.

P. soles were not as yet produced but were to be made shortly. Their production on synthetic rubber soles (20% new buna, 60% regenerate, 20% fillers) was 1800 KILO/8 hr. shift.

Buna mixing capacity was 3 Ton/ day max. Two 7 deck 250 Ton presses handled 900 KILO/8 hr. shift sole sheet of 1000 x 1000 mm. at 3½ - 4 kilo per sheet using black iron plates. Press polishing on these presses is contemplated for P.V.C. sheeting.

TARGET REPORT

(D) Schlieper & Baum G. m. b. H. Wuppertal - Elberfeld

This company was visited January 9, 1946 and Director Hans Baun was interviewed. The company normally does cloth printing. The greater part of the enterprise was totally demolished, both machinery and buildings. No work was possible at present. They had done work in the past for Dynemit A.G. Troisdorf, printing for their account mipolam sheets 0.1 to 0.15 mm. 950 mm. wide. Printing pattern was used as for regular raincoat material. Special engraves rolls were necessary and special color formulation. No particular difficulties were encountered. Standard 6 - 12 - 16 roll printing textile machines were used.

SUMMARY

Production of P.V.C. sheeting as mipolem at Troisdorf is identical with U.S.A. calender practice. Special type sheeting as Roser mill process and paste casting on belt for thickness of .015" - 5/16" deserves attention.

PART 4. PLASTIC ZIPPERS

I N T R O D U C T I O N

Plastic Zippers in Germany were produced according to two methods:

1. Single element method:

   Elements were shaped from extruded plastic stock and cemented to tape.

2. Injection method:

   Multiple teeth were injected over a bead into the tape (Winterhalter patents)

The second method was largely used for Igamid zippers on war applications.

Objective:

The industry was investigated primarily with a view to evaluate its war use application.

TARGET REPORT

(A) Ri-Ri Werk Reissverschluss A.G., Wuppertal-Wichlinghausen

This plant was visited January 3rd and 4th, 1946. Director Alfred Wieferhaus and Director Dinger were interviewed.

Condition of Plant:

The metal zipper producing portion was completely burned out and machines were ruined beyond repair. Plastic injection machines were not damaged, but were not operating for lack of tape. Some stock of Igamid moulding powder was still available.

Capacity:

Five special built Injection Machines were available for production of chains at a rate of 2500 feet/day each Army size, 3000' - 4000' feet/day each, for standard civilian size.

Four Standard E & Z injection machines were available for accessories.

Applications:

During the war the entire plastic productive capacity was used for the army, primarily for the Luftwaffe. Igamid only was used.

Lengths required were as follows:

Summer combination:

20, 25, 35, 70, 75 cm.

Fliegerschutzanzuege: (Protection combination)

20, 25, 40, 59, 60, 62, 64, 66 cm.

Jackets for Marines:

20, 25, 70 cm.

Handgrenade bags: 20 cm.

Furlined flyer's boots: 32, 35 cm.

Sleeping bags: 90 cm.

Parachute covers: 20 cm.

Trousers: 25, 38, 40 cm.

Landing Strips:

For quick preparation of landing strips on sandy soil (Africa) the Luftwaffe experimented with 40 M^2 cotton-duck sections, with zippers on all sides. First trials were made with steel tape, with holes punched in and die cast elements. Sections were entirely too heavy (Executed by William Prym, Stolberg near Aachen).

Further experiments with Standard army size igamid zipper proved successful until the end of the African campaign stopped further developments.

Requirements:

Army standard requirements for strength were 25 kg/cm (about 135 Pds/1"). All zippers applied in army clothing were alike in size, type of element and tape used.

Types:

For army size only Igamid was used. Size of closed zipper was 7-1/2 mm. x 4 mm.

Tape width 17 mm., 3/4 mm. thick with 2 mm. bead.

For civilian size (6 mm. x 2-1/2 mm.) Polystyrol type E. F. was used.

The army finally adapted the igamid zipper after two years of experimentation and trials in all zones of combat.

Method of Manufacturing:

Ri-Ri-Werk manufactured zippers after the Winterhalter patents of multiple injection. 5 vertical type injection machines were used, of 1 ounce shot size. In actual operation chain moulds were not fastened to the die plates of the machine.

To insure absolute position of dies, the machines were installed slanted 30°. Zipper chains were injected up to 10° length in one shot. Two strings of tape cut to size were inserted into the open mould outside the machine. Then the mould was closed and pushed into the machine. The machine operator placed the mould correctly without fastening, closed the press, injected and after 10^2 cooling time allowance, opened up and pushed the mould out to his left. By another operator mould was taken apart, zipper removed and mould returned to loading station. Four moulds of one type were necessary to maintain a cycle of about 15 seconds. The army zipper required this method of handling injection moulds on account of an undercut in the element. An extra metal strip insert had to be loaded together with the tape.

Beside multiple moulds this method required three operators, one man and two girls, for each machine.

Redesign of tooth element by the Licencor Winterhalter A. G., Zuerich (not available to Ri-Ri-) made normal injection operation possible by fastening dies to machine plates.

Standard Ecka t and Ziegler air operated injection machines provided necessary end pieces for separable zippers also sliderbodies. Important is the proper funnelling of inlet into the sliderbody openings, so that openings will not catch in any position.

Trials were made with injection of igamid elements on igamid tape. It was found that under the necessary high injection temperature

(220° C at nozzle) igamid tape was softened sufficiently that no consistent tape strength could be obtained. The company was not permitted during the war to carry out a development program for larger injection machine units for contemplated 50 cm. long chains.

Ri-Ri carried on their own toolshop, in which chain dies were produced by hobbing element cavities with single tooth hob.

TARGET REPORT

(B) Bolta Werk, G. m. b. H., Nuernberg

This company was visited December 5th and 6th, 1945. Director A. Vonau and Director Willy Diezel were interviewed.

Twenty-five percent of the buildings were destroyed and partially rebuilt, but injection machine capacity was intact. The company operated 11 full automatic Isoma and 3 air operated Eckert and Ziegler machines. War items produced were:

Igamid condensers for radio
Trolitul battery covers
Trolit igniter caps for Luftwaffe M.G.

No parts for Army zippers were produced.

Total capacity was about 20 TO/MO moulding powder consumption.

For civilian zipper production, 100,000 sliderbodies complete were produced at peace time for Zipp Werk G. m. b. H. with two cavity moulds. All plastic production at Zipp Werk was halted at the beginning of the war. Their capacity was 50,000 m/week on plastic civilian zippers (single element method).

TARGET REPORT:

(C) Eckert & Ziegler, G. m. b. H., Weissenburg (Bavaria)

This company was visited December 10th, 1945 and Dipl. Ing. Thilenius was interviewed.

In the plastic zipper field this company developed and built the special injection machines for Ri-Ri, Barmen. Their general line of injection machines is well known. Of late some larger units their type E.H. 400 have been built (400 gramm shotsize and 800 mm. stroke). These were delivered to:

1. Dynamit A.G., Troisdorf

2. Freudenberg, Weinheim
3. Rhein Westf. Spritzguss, Kettwig
4. A.F.A., Hannover

Former machines built were operated from one central air system; now with the availability of German built vein type pumps new machines were to be built self-contained with hydraulic pumps.

No special design of further larger plastic zipper machines was contemplated.

It was stated that the Czechoslovakian firm:

J. VLTAVSKY A. G., HAKONITZ

was building three sizes

35 g. - 100 g. - 250 gramm

shotsize injection machines with horizontal clamping mechanism and vertical, hydraulic operated injection cylinder as Lester (U.S.A.), except that injection shot is made directly into parting line of die.

SUMMARY

Apart from igamid army production at Ri-Ri Werke, no war production in Germany was carried on in plastic zippers. Metallbesatz and Zippwerk, both Nuernberg, had completely stopped all civilian work. Consequently development in the U.S., where production was not halted, has exceeded in injection machine size and production, any development which has taken place in Germany. The non-availability of Nylon moulding powder in the U.S. was the reason why zipper applications for the air corps were not further advanced. With the new tooth design of Winterbalter A.G. available in the U.S.A., the application of strong nylon army zippers produced on larger machines will become fully feasible. The light weight of nylon zippers has been the deciding reason for full application of this zipper in the German Luftwaffe.

VISIT TO THE NORDDEUTSCHE SEEKABELWERKE, NORDENHAM 1. OLDB.

At the request of General Clay in order to arrange to ear-mark and guard certain extrusion machines at the Norddeutsche Seekabelwerke, Lt. Col. J. J. MacFarland and Mr. M. N. Elias visited this plant.

This plant manufactures various types of cable including cable suitable for submarine use. However, from a chemical point of view, the most interesting operation carried out at this plant was the extrusion and subsequent two-way expansion of styrene to form films having considerable tensile strength and flexibility. Film thicknesses as small as one hundredth of a millimeter have been successfully produced.

The principle on which the extrusion operation is carried out is old, the extrusion machines having been produced by the firm of Berstorf near Hannover and being at least ten years old. However, the method of orienting the film is new. This consists in extruding a tube of polystyrene containing no plasticizer and drawing the tube over a somewhat "Y" shaped spreader fitted with small rollers along each branch of the "Y". The polystyrene is drawn over this and the portion between the initial diameter as it comes from the orifice of the machine and the widest portion of the "Y" is in the ratio of one to five. The little rollers in each branch of the "Y" assist in reducing the friction of the extruded tube as it passes over the "Y" and is laterally expanded. The direct tension on the tube is maintained at 0.450 kilograms per square millimeter of the cross section. As the tube comes off the expander, the edges are slit forming two separate sheets which are then rolled up separately on suitable rollers. The largest practicable width of sheet which has been produced thus far is 300 millimeters. The thickness of the sheets can be varied from 0.15 millimeters to 0.01 millimeters. The film which is called styroflex is reported to have a breaking strength of 700 kilograms per square millimeter as compared with ordinary polystyrene which has a breaking strength of approximately 400 kilograms per millimeter.

Experiments were made by this company also in extruding fine threads of polystyrene and these had a tensile strength of about 900 kilograms per square millimeter. The threads however were brittle. Cloth had been woven from the threads but the cloth was brittle and the only suggested use for the material was as a filter cloth at relatively low temperatures for solutions which do not attack polystyrene.

The chief use of the film was in making a new type of electric cable in which narrow strips of the styroflex were wound about a copper wire in an endless helix, the strips being built up of many layers and the outside then covered to form a tube with wider strips of styroflex. Such a cable had considerable flexibility and for certain uses was extremely satisfactory. It was especially satisfactory for television but had also been tested out for submarine use in which case it was enclosed in a flexible, steel tube. We were informed that the United States Signal Corps had shown interest in this product.

The expander was made at the plant. A rough sketch of the expender is shown below. Blue prints of the machine were requested, but due

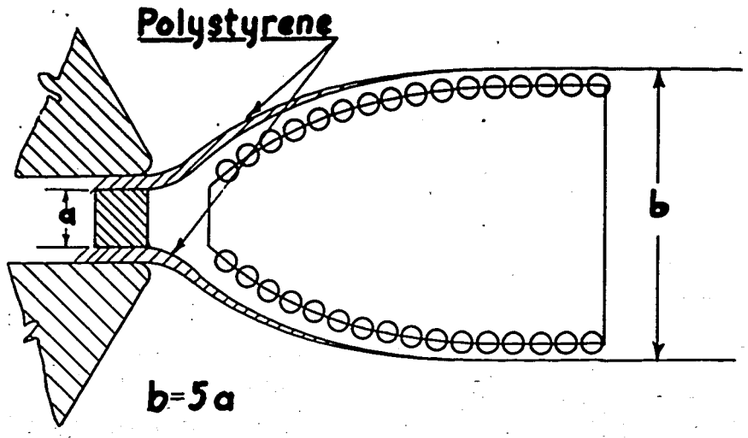
to the shortage of blue print paper they could not be immediately procured. Arrangements were made, however, with the local Army group to provide a sufficient quantity of blue print paper so that these prints could be made and as soon as they are completed they will be sent to this office and should be made a part of this report.

Another use for the styroflex film which has been developed at this plant has been the production of collapsible tubes lined with the film. Because of its chemical resistance this provided a suitable substitute for tin tubes during the war. The process consists in using an aluminum or zinc foil at the edge of which, by means of adhesive, is attached a film of styroflex. This produces a sheet composed half of styroflex and half of metal foil. Adhesive is applied to the edges of the double sheet and the whole of this is rolled up so that the styroflex sheet comes on the inside of the tube. A shoulder provided with a threaded outlet is then moulded to one end of the tube.

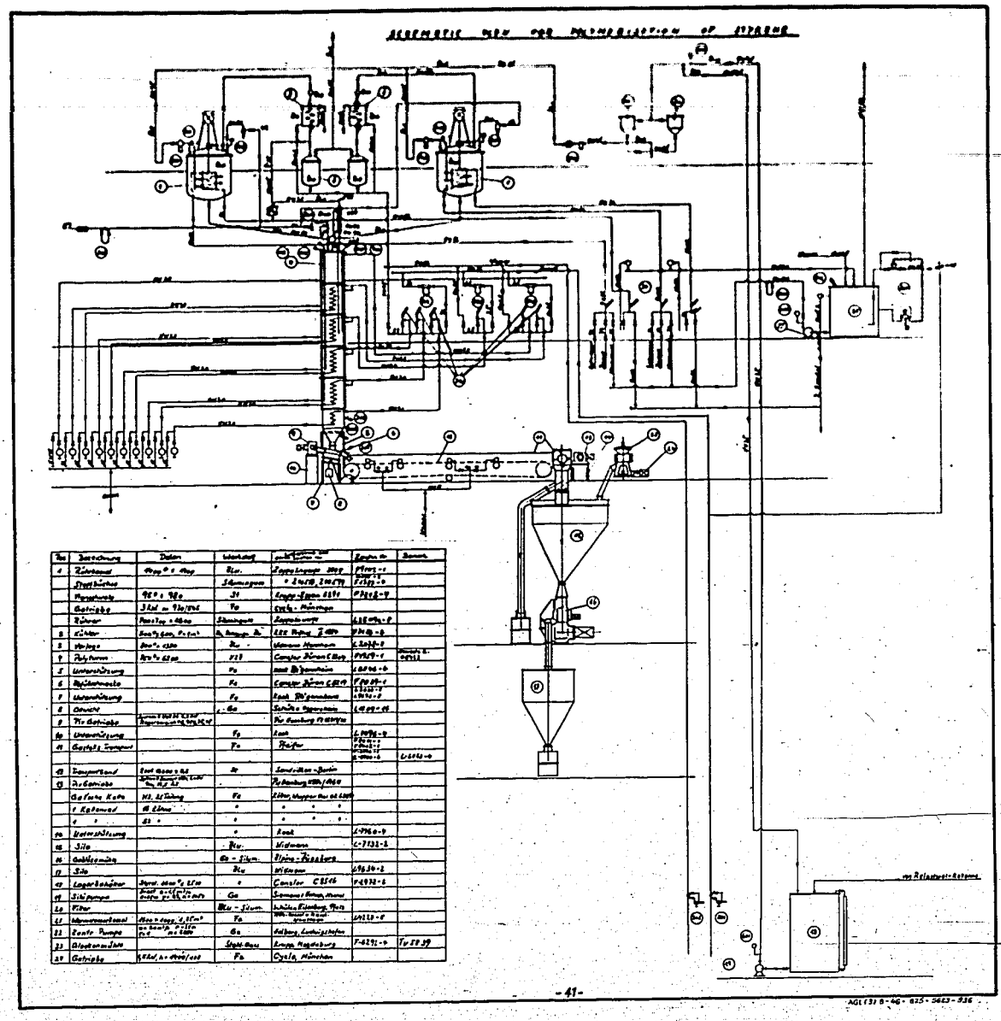
The weight of each machine, including the extruder, the spreader, and the rolls, is probably in the neighborhood of three tons. The length of the set-up, complete with rolls, etc. would be about twelve feet, the width about three feet, and the height about six feet.

Samples of the styroflex sheet and the collapsible tubes as well as polystyrene thread were obtained and forwarded to the Washington office of JIOA.

Sketch 'A'



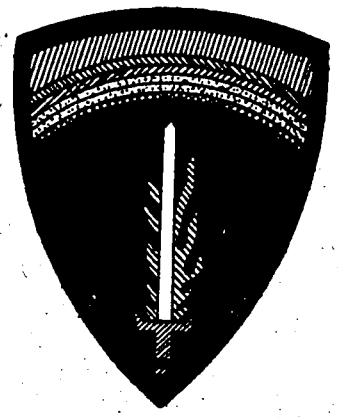
Plan view of Spreader for lateral orientation of Polystyrene to produce Styroflex.



FIAT FINAL REPORT No. 836

THE PRODUCTION OF ACRYLONITRILE IN THE I. G. FARBENINDUSTRIE PLANTS AT LUDWIGSHAFEN, HÜLS AND LEVERKUSEN

Hasche, R. L. and McNally, J. D.



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OFFICE OF MILITARY GOVERNMENT FOR GERMANY (US)

FIAT FINAL REPORT NO.836 18 July 1946

THE PRODUCTION OF ACRYLONITRILE IN THE I.G. FARBENINDUSTRIE PLANTS AT LUDWIGSHAFEN, HÜLS AND LEVERKUSEN

BY

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FIELD INFORMATION AGENCY, TECHNICAL

A B S T R A C T

This report is concerned with the production of acrylonitrile in the I.G. Farbenindustrie plants at Ludwigshafen, Hüls and Leverkusen and contains information on the process used, plant equipment, quality of product and rate of production.

TABLE OF CONTENTS

I N T R O D U C T I O N

Objective:

The purpose of the investigation was to obtain complete information on German production of acrylonitrile by the addition of HCN to acetylene.

Evaluation:

This method of synthesis for acrylonitrile was operated successfully and, in the opinion of the German technical people interviewed, was the cheapest method so far developed.

Guide to the Reader:

This report gives detailed information on the practice followed in the I.G. Farbenindustrie plants at Hüls, Ludwigshafen and Leverkusen. The production from ethylene oxide and HCN is described in CIOS 22 - XXX - 4.

MANUFACTURE OF ACRYLONITRILE AT I.G.FARBENINDUSTRIE, LUDWIGSHAFEN

This report is based on information obtained by the interrogation of Dr. Keller at the I.G. Ludwigshafen plant on June 7 1946. We were informed that the early development work on the addition of HCN to acetylene was carried out in the Ludwigshafen plant but large scale manufacture was not carried out there. The main plant for this operation was located at I.G. Leverkusen, and the Ludwigshafen plant produced 12 metric tons a month when in full operation. This plant was completely destroyed by bombing and hence was not available for inspection.

Process Operation:

The acrylonitrile synthesis was carried out by passing a mixture of acetylene, nitrogen and HCN through a catalyst tower where the acetylene and HCN reacted to form acrylonitrile. The gaseous reaction products were led off the top of the reactor to a counter current water scrubber where the acrylonitrile was carried out the bottom in the water layer and unreacted acetylene was recycled from the top of the scrubber back to the reactor. The aqueous layer containing about 1.5% acrylonitrile was fed with the middle of a still, and the water acrylonitrile azeotrope was condensed and the two phases separated in the decanter. The product out of the top of the decanter was about 80% acrylonitrile and was shipped from Ludwigshafen without further purification. A flow sheet of the process is included in this report.

The following section dealing with a more detailed description of some features of the process is divided into three sections describing the reactor, the scrubber and the distillation system.

Reactor:

The reactor was a rubber lined steel cylindrical vessel having an operating capacity of two cubic meters. The dimensions were approximately 12 meters high and 50 cm diameter. The reaction vessel contained no plates or packing.

Reactants:

The acetylene was generated from calcium carbide and purified in the usual way by washing with 0.5% chlorine water and 10% sodium hydroxide. The nitrogen came from the adjoining I.G. Oppau plant and the HCN was made at Ludwigshafen by reacting NaCN with H_2SO_4. The HCN usually contained 20% water and no stabilizer was used. It was fed into the recirculation leg as a liquid. The nitrogen and acetylene feed lines ran into a mixing valve and at the start of a run the valves were adjusted to feed 50% N_2 and 50% C_2H_2 by volume. As the run continued, the composition of the recycle gas was periodically checked by analysis and the nitrogen feed was set to maintain a 50-50 ratio of N_2 and C_2H_2.

Reaction Conditions:

The aqueous catalyst solution was run into the reaction vessel and the acetylene-nitrogen-HCN reactants introduced as indicated above. The initial feed contained C_2H_2 and HCN in the ratio of 10/1 and the acetylene and HCN feeds were adjusted throughout the operation to maintain this ratio in the feed gas into the bottom of the reactor.

The reaction temperature was not very critical and temperatures ranging between 70-90° C were used with no appreciable change in the conversion. The pressure at the top of the reactor was nearly atmospheric and the pressure drop through the reactor was about 1.5 atmospheres. The throughput of gas was given as 100 liters of gas for each liter of catalyst per hour.

Catalyst:

The catalyst used at Ludwigshafen had the following composition by weight:

Cu Cl	134
K Cl	60
NaCl	11
H_2O	105

The composition by analysis is:

Cu	24%
K	12%
Na	1.7%
Cl	27%
H_2O	35%

This catalyst crystallizes between 40 and 50°C. The catalyst life was about six months but varied depending on the purity of the acetylene feed. The copper in the spent catalyst was precipitated as copper hydroxide, washed and redissolved in HCl for re-use.

Dr. Keller was aware that at Leverkusen ammonium chloride was substituted for potassium or sodium chlorides but he stated that substantially the same operating results were obtained with both catayst. He preferred the above catalyst because it had a crystallization point about 10 below the Leverkusen catalyst and also the ammonium chloride catalyst was thought to be responsible for the chloroprene by-product which was obtained at Leverkusen but not at Ludwigshafen.

Water Scrubber:

The gaseous reaction product went from the top of the reactor to the bottom of a cylindrical steel scrubber which was about 10 meters high and 50 cm. diameter. It was packed with ceramic Raschig rings. Water was sprayed in the top of the column at such a rate that a concentration of 1.5% acrylonitrile was maintained in the solution leaving the bottom of the scrubber. The gas coming from the top contained only acetylene, nitrogen and water vapor, and was recycled to the reactor without any processing.

Distillation and Decanter:

The 1.5% aqueous acrylonitrile solution from the scrubber was fed into the middle of a column packed with Raschig rings, the still being 15 meters high and 30 cm. in diameter. The condenser at the top condensed a product comprising water and acrylonitrile in a 50-50 ratio, the boiling point of the mixture being 92 to 96° C.

The condensate went to a simple decanter, the bottom layer being water which went to waste and the top layer being the product which had the following composition:

acrylonitrile	80%
water	6%
acetaldehyde	7%
butadiene	2%
2 cyanobutadiene	1%
lactonitrile	2%
hydrocyanic acid	2%

Yield:

During good operation, the conversion to acrylonitrile was 90-95% on the HCN used and 80-85% on the acetylene.

Cost:

The best cost obtained on acrylonitrile was 120 marks/ 100 Kgs. of product. The costs of chemicals used were given as follows:

NaCN	39 Marks/100 Kgs.
HCN	65 " " "
$C_2 H_2$	50 " " "

MANUFACTURE OF ACRYLONITRILE AT I.G.FARBENINDUSTRIE, HÜLS

The following description of the work at Hüls on Acrylonitrile production was obtained from Dr. Zobel and Dr.H.Reich at Hüls on June 18, 1946.

A pilot plant was erected at Hüls in 1942 to follow the general practice at Leverkusen, but the pilot plant was destroyed by bombing in 1943 and was not rebuilt. The maximum production rate at Hüls was one ton a month. At the time of our visit, a glass laboratory size apparatus was in operation and experimental work was in progress which was being directed mainly to obtaining a higher purity product than had hitherto been made.

Process Operation:

The flow sheet included in this report (see Figure 1) indicates the way the acrylonitrile synthesis was carried out at Hüls. As the process was only on a pilot plant scale there were no drawings available showing sizes and details on the apparatus so the sketch should be regarded only as symbolic. The reaction used was a glass tube about 1 meter long and 6 cm. in diameter.

Referring to the drawing, the reactor was filled with the catalyst solution and heated to 80° C. Acetylene was blown into the bottom of the reactor and HCN was introduced through the recirculation leg on the side of the reactor. The gaseous reaction products passed from the top of the reactor through a condenser kept at 30° C, the condensate going to a jacketed vessel kept at 70° C which separated high boilers from products volatile at 70° C. The condensate was returned to the reactor as indicated and the volatile products went to a water scrubber into which water was fed at such a rate as to produce a 2% solution of acrylonitrile at the outlet. This dilute solution was fed into a packed column which distilled the water acrylonitrile azeotrope out of the top of the still. The water drawn off the base heater

was recycled through the scrubber. The water-acrylonitrile azeotrope was passed into a still fitted with a 30°C. condensing coil which was used to degas the azeotrope. The degassed azeotrope mixture was separated into a water layer, which was returned to the reactor and the product which was 96% acrylonitrile. The gases from the top of the gas stripping column were scrubbed with water, producing an aqueous solution of 20% HCN 20% acetaldehyde. These were mostly combined as lactonitrile.

About 10% of the gas recirculated was bled off for purification. It was taken off mostly from the top of the first scrubber.

Reactants:

The HCN used at Hüls was made from NaCn and sulfuric acid. It was used in aqueous solutions containing from 40 to 80% HCN with no apparent effect on the reaction.

In the plant process planned for Hüls, HCN would have been made by increasing to 6% the nitrogen content of the hydrocarbon gas fed to the electric arc cracking units. The concentration of HCN in the product would be 3%, which would provide about 200 tons of HCN per month.

The acetylene used came from the arc cracking of hydrocarbon gases and contained considerable quantities of diacetylene. Whether or not the diacetylene present resulted in low catalyst life was not fully studied but it was part of their practice to remove diacetylene either by condensing it out at -80° C or by scrubbing the gas with oil on sulfuric acid. After purification the acetylene used still contained 2% of diacetylene.

Reaction Conditions:

The acrylonitrile synthesis was run at Hüls with the reaction temperature kept at 80° C. The ratio of acetylene to HCN in the feed gas was maintained at 10:1 and HCN conversion was nearly 100% per pass. The rate of gas input was 80 liters per hour per liter of catalyst. During operation the inert gas content of the recycle gas was allowed to build up to about 35% and this was controlled by bleeding off about 10% of the recycle gas, separating the acetylene by absorption and returning it to the reactor. The composition of the bleed gas was given as 60% acetylene, 5% diacetylene and 35% inert gas, mostly nitrogen and methane.

Catalyst:

The catalyst used at Hüls had the following composition:

	Kgs.	Moles	Wt. %
CuCl	5000	50	40
KCl	1190	16	15.9
KCN	260	4	3.5
NaCl	585	10	7.8
HCl	75	-	1
H_2O	2375	-	31.8
	7485		

If the reaction was started without KCN in the catalyst, the system took several hours to arrive at the above equilibrium composition and during this initial start up period there was obtained a high concentration of diacetylene in the product. As it was thought that diacetylene shortened the life of the catalyst, the practice was to start off with KCN in the catalyst as indicated above.

The initial rate of production with new catalyst was 14 grams per hour of acrylonitrile per liter of catalyst. This rate fell off to 7 grams per hour after eight weeks of continuous operation. The catalyst was regenerated by precipitating copper hydroxide, filtering and redissolving the copper in HCl. The filtrate was discarded.

The copper chloride - ammonium chloride catalyst was used in some experimental work, but no improvement in yield or rate of conversion was obtained and it was considered more inconvenient to work with.

Recovery and Purification of Acrylonitrile:

As indicated on the flow sheet, the reaction product was recovered by scrubbing the gas with water, distilling over the 77% acrylonitrile azeotrope, degassing this product and drawing off the acrylonitrile layer in a separator. The composition of this product was given as:

$CH_2 = CH - CN$	94%
HCN	1%
$CH_3 - CHO$	1%
H_2O	4%

This was not sufficiently pure for use in polymer manufacture and laboratory work was in progress at the time of our visit to obtain a higher purity product. The test used for polymerization grade acrylonitrile was to dissolve 5 grams of acrylonitrile in 50 c.c. of methyl alcohol and add 200 mg. of benzoyl peroxide. The solution was heated for one hour at 76° C and then filtered. A good sample produced 900 mg. of solid polymer and samples showing less than 600 mg. were not acceptable.

The vapor pressure over a temperature range had been determined for dry acrylonitrile and the partial pressure of

acrylonitrile in the water - acrylonitrile azeotrope was also measured. These data are given in the table below:

Vapor Pressure of Acrylonitrile and Partial Pressure of Acrylonitrile in the Water Azeotrope.

Temperature °C	Vapor Pressure $CH_2=CH-CN$ mm.Hg.	Partial Pressure $CH_2=CH-CN$ in water azeotrope mm.Hg.
0	32	31
5	41	34
10	54	51
15	68	64
20	86	80
25	109	100
30	135	124
35	165	150
40	205	183
45	250	225
50	300	265
55	360	320
60	440	380
65	520	450
70	620	565
77	760	660

Yield:

The yield of acrylonitrile was 85% in the HCN consumed and 80% on acetylene. No manufacturing cost data were kept.

MANUFACTURE OF ACRYLONITRILE FROM ACETYLENE AND HCN AT I.G. FARBENINDUSTRIE, LEVERKUSEN.

The acrylonitrile plant at Leverkusen was the largest plant in Germany for the manufacture of acrylonitrile from acetylene and HCN, employing the Nieuland catalyst. The unit had a capacity of 70 metric tons per month. Operation was stopped late in 1944, due to bomb damage to the HCN generation unit. The method of operation was essentially the same as that employed at Ludwigshafen and Hüls. The main difference was in the use of NH_4Cl in the catalyst in place of the mixture of NaCl and KCl employed at the other two plants.

At the end of the war a larger unit was under construction with a rated capacity of about 200 metric tons per month.

Reactants:

Acetylene was generated from calcium carbide obtained from the Knapsack plant. It was purified by passing through three washing towers, the first 0.1% chloride water, the second 10-15% NaOCl and the third a water solution containing 10% each of NaOCl and $Na_2S_2O_4$.

Hydrocyanic acid was generated by the interaction of sulfuric acid and sodium cyanide. It was fed to the system as a 90% water solution.

Catalyst:

The catalyst had the following composition:

	Parts by Weight
H_2O	560
CuCl	650
NH_4Cl	350
Conc.Hcl	20
Mol.ratio $CuCl/NH_4Cl$	1:1
Sp. Gr. of solution	1.6

The solidification point of the catalyst was 50°C.

Description of Operation:

The operation of the process will be described by reference to the accompanying drawings (Figures 1, 2 and 3). Acetylene was generated from calcium carbide and purified by passage through three scrubbers in series. In the first column 0.1% chlorine water was employed, followed by scrubbing with 10-15% NaOH solution and finally with a solution containing 10% each of NaOH and $Na_2S_2O_4$. The scrubbing solutions were recirculated through the columns. Fresh acetylene added to the system was 70 cubic meters per hour. From the washers the purified acetylene entered the suction side of a water ring Elmp pump where it was mixed with recirculating acetylene amounting to 800-900 cubic meters per hour.

The acetylene entered the catalyst vessel through three pipes provided with nozzles and located at the bottom which in turn served as injectors in three stand pipes 300 mm. I.D. Approximately 400 cubic meters of steam per hour was introduced with the acetylene to maintain the temperature of the catalyst at 80°C and to make up for loss of water from the solution. The ratio of total acetylene to HCN was 10:1 and of fresh gas 1:1.

The acetylene was introduced into the catalyst solution at 17 psi. Hydrocyanic acid containing 10% water, which was produced from sodium cyanide and sulfuric acid, was introduced into the side of the catalyst vessel at a point about one third from the bottom. Several additional HCN inlets were installed to give greater

flexibility to the unit. The catalyst filled about two-thirds of the catalyst vessel and amounted to 11 cubic meters. In starting up the apparatus a large excess of HCN was fed for the first two hours.

It was claimed by Leverkusen that the regular Nieuland catalyst containing NH_4Cl was more active than when a mixture of NaCl and KCl was used. However, the life of the catalyst was shorter. The drop in catalyst activity is indicated by the capacity of the plant, starting with fresh catalyst.

	Daily Capacity Metric Tons
1st Day	3.0
2nd "	3.0
3rd "	2.9
5th "	2.85
6th - 21st Days	2.4

At the end of three weeks the catalyst was removed and the copper recovered by a method described later in the report.

The acetylene recirculation gas carrying with it vapors of acrylonitrile, by-products and a small amount of HCN passed from the catalyst vessel to a water scrubber. The amount of wash water was 8-10 cubic meters per hour and leaving, it contained 1.5-2.0% of acrylonitrile. It then passed to a stripper operating with live steam and the vapors leaving the tower passed to a condenser and decanter. From the latter, the lower water layer was returned to the tower and the crude nitrile had the following composition:

	Wt. %
Acetylene	0.5
Monovinyl Acetylene	3.0
Hydrocyanic Acid	1.0 - 2.0
Chloroprene	1.0
Water Azeotrope with Acrylonitrile	3.5
Acrylonitrile	80.0
Divinyl Acetylene	0.2 - 0.4
Cyanobutadiene	4.0
Lactonitrile	2.0

The acetylene leaving the top of the scrubbing column contained about 10-15% of vinylacetylene. It was maintained at that figure by purging 5 cubic meters per hour.

Recovery and Purification of Acrylonitrile:

Three columns were required for the separation of acrylonitrile from by-products and final purification. All of the

columns were packed with Raschig rings and the last two were operated at 140 mm. Hg. absolute pressure.

The first column was operated with a base heater temperature of 80°C and 22°C at the top. It served as a degassing column, acetylene and vinyl acetylene passing overhead as gas together with acetaldehyde, HCN, and chloroprene as liquid condensate.

The second distillation column was operated with a base heater temperature of 50°C and top at 28°C. Overhead pure acrylonitrile (99.5%) was obtained.

The third distillation column was operated with a base heater temperature of 90°C and 28°C at the top. Overhead crude acrylonitrile containing HCN (derived from lactonitrile decomposition) was obtained and the bottoms consisted of cyanobutadiene and lactonitrile. The latter were wasted although it was planned to attempt to recover these at a later date.

Chemicals and Yields:

Charge	Kgs.per Hr.	Kgs.per Day	Kgs.per Mo. (600 Hrs.)
Calcium Carbide	344.0	8,250	206,000
Acetylene	79.0	1,985	47,400
Hydrocyanic Acid	78.5	1,885	47,400
Sodium Cyanide	142.0	3,410	85,200
Production:			
Acrylonitrile	120.0	2,880	72,000

Yields: (Monthly operation)

Based on Acetylene	74.5%
" " HCN	78.0%
" " NaCN	78.0%

100 Parts of Acrylonitrile required:

Acetylene	65.8 pts.	(49.1% of theor.)
HCN	65.4 "	(51.0% " ")
NaCN	118.5 "	(92.4% " ")

Regeneration of Spent Catalyst:

8,000 liters of spent catalyst solution containing about 3,200 kilograms of copper in the form of cuprous chloride was diluted with 4,000 liters of water. To this solution 1,650 kilograms of zinc dust was added in portions during a period of 16 hours. The reaction was in accordance with the following equation:

$$2\ CuCl + Zn = 2\ Cu + ZnCl_2$$

Heat was developed and the solution was cooled by direct addition of water. The reaction temperatures were held between 60°-80°C by the addition of about 4,000 liters of water, whereupon the total volume of catalyst solution was increased to about 16,000 liters.

During the addition of zinc dust the solution was kept acid to Congo Red and towards the end of the reaction it was tested for copper content (Knife test or reaction with ammonia after oxidation with nitric acid).

If the test showed absence of copper in the solution the hot zinc chloride solution was then filtered and the precipitated copper was washed 3 or 4 times with large quantities of water (Total volume 16 cubic meters) until it was free from zinc chloride. After the washing there was obtained about 6 cubic meters of moist cement copper which was converted directly into copper chloride by chlorination in accordance with the following equation:

$$2\ Cu + Cl_2 = 2\ CuCl$$

The chlorination was carried out in the presence of ammonium chloride. To the moist cement copper, 2,700 kilograms of ammonium chloride was added, and the solution was made acid with nitric acid (Specific gravity 1.19). Water was added to a volume of 7,500 liters, and gaseous chlorine was passed through the solution during which there was a strong evolution of heat. The copper passed into solution in the form of cuprous chloride and the catalyst was then ready for use.

Equipment:

1. Catalyst Vessel.

The catalyst vessel was rubber lined with a ceramic tile inner lining. The inside diameter was 1680 mm. and the height 3 meters. The top of the vessel was steam jacketed to prevent solidification of the catalyst solution.

2. Scrubber and Stripper.

The scrubbing column was cast iron 800 mm. in diameter and 8 meters high. It was made of cast iron.

The stripper was the same size as the scrubbing column and was of welded steel construction.

3. Distillation columns.

The first distillation column was 400 mm. in diameter and 10 meters high. The second column was 400 mm. in diameter and 8 meters in height. The last column was 200 mm. in diameter and 6 meters high. All three columns were packed with Raschig rings.

A P P E N D I X 1

LIST OF GERMAN SCIENTIFIC AND TECHNICAL PERSONNEL INTERVIEWED

Name	Position	Location
Dr. Zobel	Production Manager	I.G. Farbenindustrie, Hüls
Dr. H. Reich	Chemist	" " " "
Dr. Bulow	Department Manager	" " " Ludwigshafen
Dr. Keller	Chemist	" " " "
Dr. Ludwig	Department Manager	" " " Leverkusen

A P P E N D I X 2

LIST OF GERMAN TARGETS VISITED

Name	Location
I.G.Farbenindustrie, Ludwigshafen	Ludwigshafen
I.G.Farbenindustrie, Hüls	Hüls
I.G.Farbenindustrie, Leverkusen	Leverkusen

A P P E N D I X 2

LIST OF GERMAN TARGETS VISITED

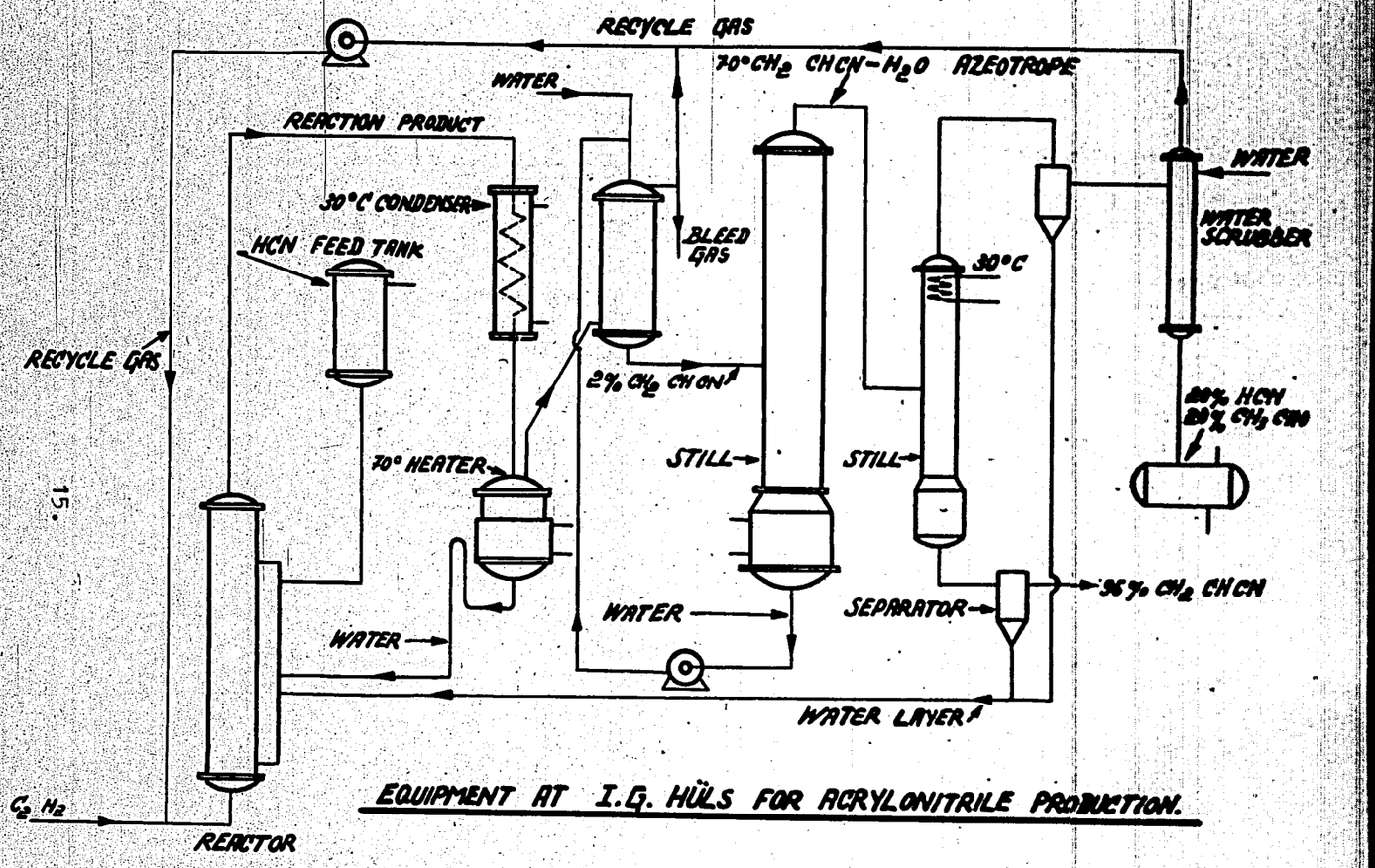
Name	Location
I.G.Farbenindustrie, Ludwigshafen	Ludwigshafen
I.G.Farbenindustrie, Hüls	Hüls
I.G.Farbenindustrie, Leverkusen	Leverkusen

A P P E N D I X 3

BIBLIOGRAPHY ON RELATED REPORTS

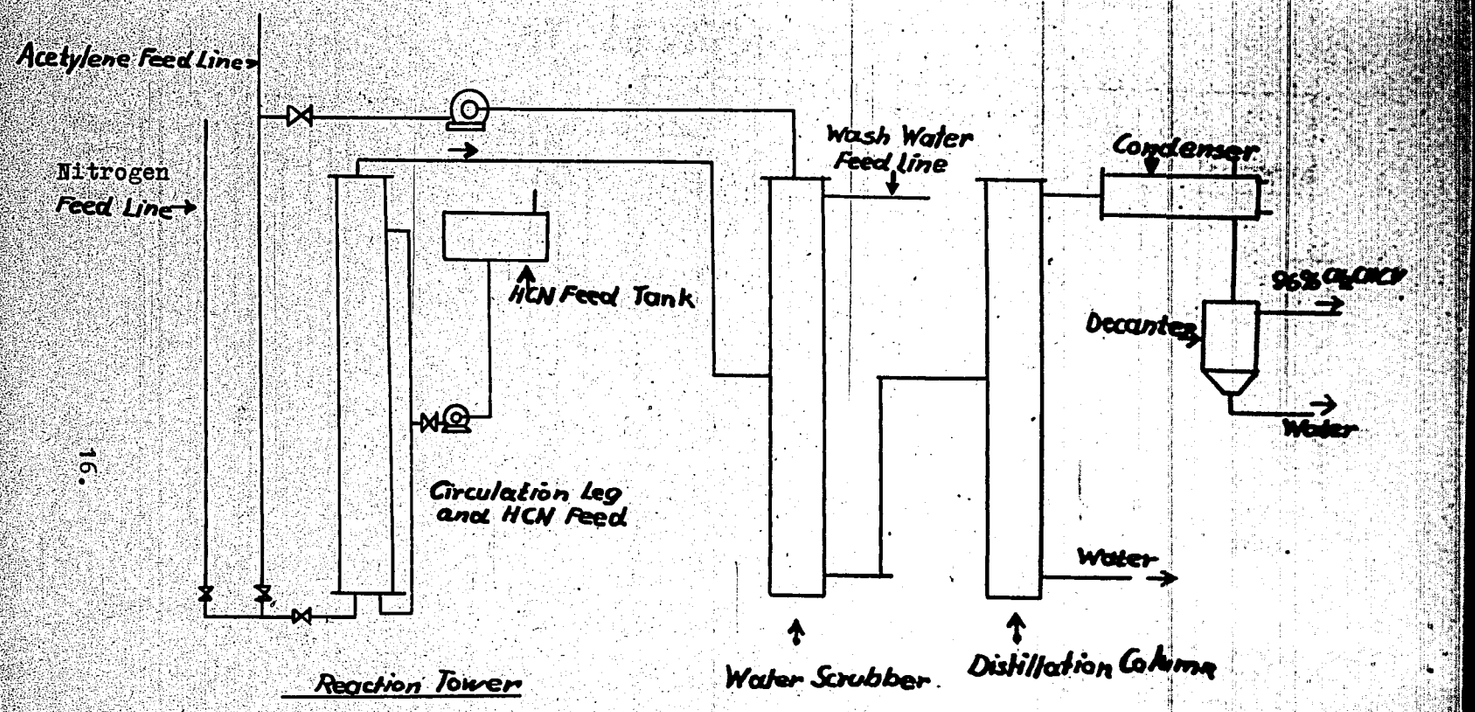
FIAT Final Report No. 14 — Acrylonitrile: Preparation by One Step Pilot Plant Method

CIOS 22 - XXX - 4. — Acrylonitrile: Production at Leverkusen



EQUIPMENT AT I.G. HÜLS FOR ACRYLONITRILE PRODUCTION.

FIAT FINAL REPORT Nº 636 FIG. 1



FIAT FINAL REPORT No 836

EQUIPMENT AT I.G. LUDWIGSHAFEN
FOR ACRYLONITRILE PRODUCTION

FIG. 2

REACTION UNIT - ACRYLONITRILE MANUFACTURE AT LEVERKUSEN.

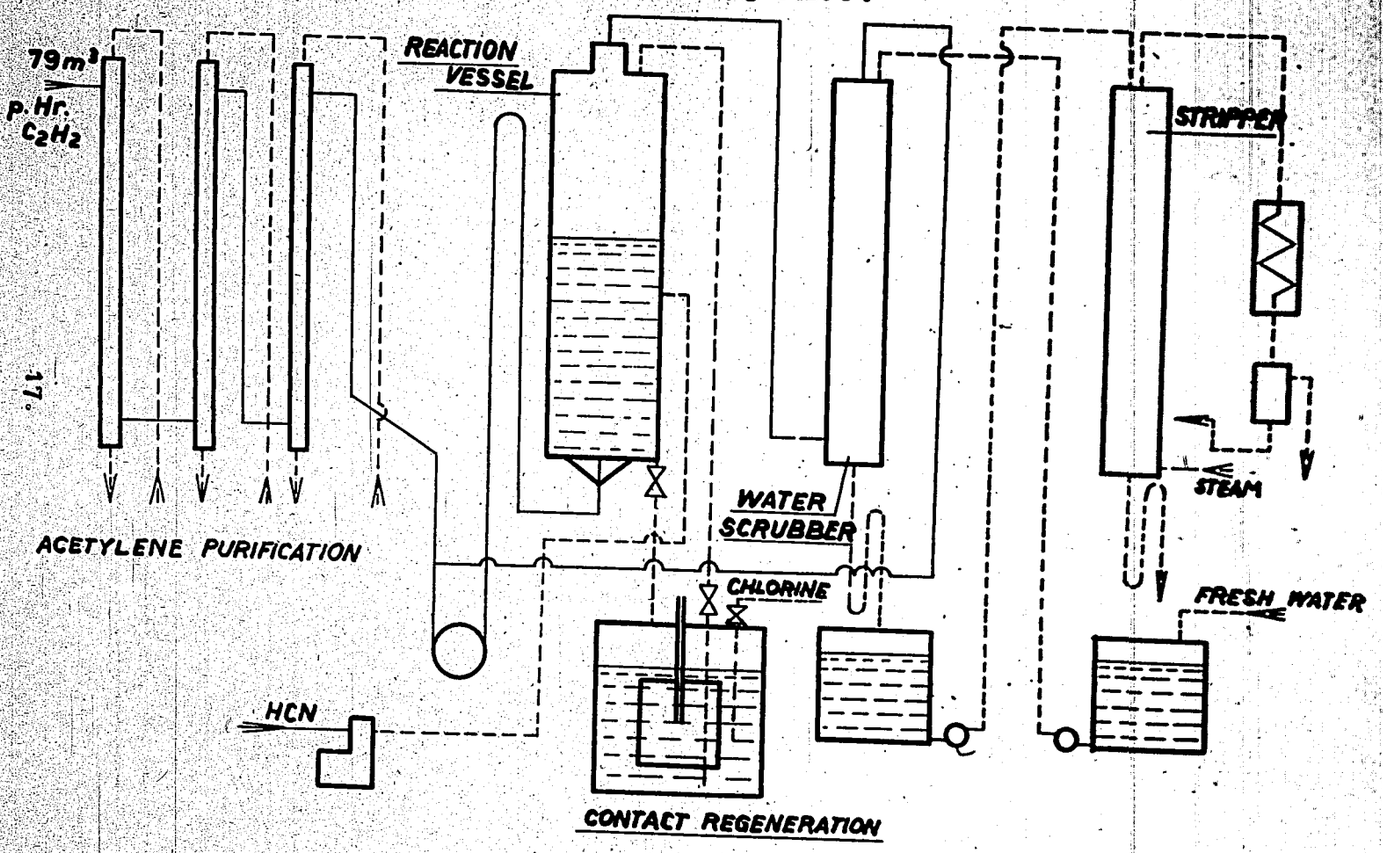
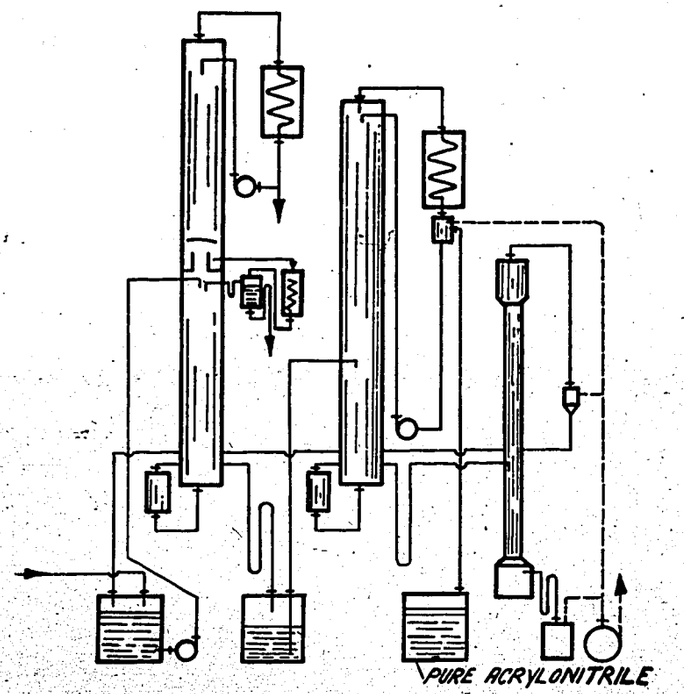


FIG. 3

FIAT FINAL REPORT No. 836

DISTILLATION UNIT - ACRYLONITRILE MANUFACTURE AT LEVERKUSEN.



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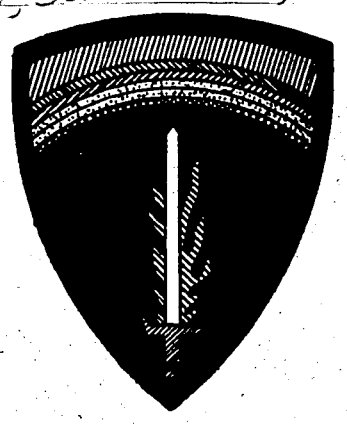
FIAT FINAL REPORT No. 854

ENGLISH TRANSLATION
OF
PREPARATION OF MIXED POLYMERIZATION PRODUCTS OF VINYLSULFONES

(Heyna (Dr.), Schumacher, W. V., [illegible])



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FIAT FINAL REPORT NO. 854 5 August 1946

ENGLISH TRANSLATION
OF
PREPARATION OF MIXED POLYMERIZATION PRODUCTS OF VINYLSULFONES

BY

GERMAN STAFF MEMBERS

I.G. FARBENINDUSTRIE

FIELD INFORMATION AGENCY, TECHNICAL

A B S T R A C T

This is a report made at a meeting of the Kunststoff Commission in 1943, on work done at I.G. Farbenindustrie, Höchst. New methods for the preparation of a number of vinyl-sulphones, as well as the mixed polymerisation products of these vinyl sulphones with other monomers are described. Vinyl-phenyl-sulphone was more closely investigated with a view to its aptitude for polymerisation with other vinyl-compounds.

FOREWORD

This is a translation prepared in London from German documents evacuated in the early stages of Technical Industrial Intelligence operations. The selection of reports for translation was made by Sherlock Swann and N. N. Elias. The abstract was prepared in the office of the Miscellaneous Chemicals Sub-Committee, Industry Branch, Field Information Agency, Technical.

AUTHORS

Co-authors: Dr. Heyne, Dr. U.V. Schumacher, Dr. Overbeck, all of I.G. Farbenindustrie, Frankfurt am Main (Höchst). Paper prepared for the 26th meeting of the Kunststoff Commission.

PREPARATION OF MIXED POLYMERISATION PRODUCTS OF VINYLSULFONES

I. Preparation of Vinylsulfones

In D.R.P. 635396 a method is described for the preparation of both vinylsulfoxides and vinylsulphones. The method consists in the treatment, under mild conditions, of vinylsulfides of the formula:

$$CH_2 = CH - S - R$$

- where R can be an aliphatic, cyclo-alphatic, aromatic or mixed residue of a saturated or unsaturated character - with oxidizing agents. The vinylsulfides used for this preparation are obtained by the addition of mercaptans on acetylene, as described in D.R.P 617543. Generally speaking then, the preparation of vinylsulphones is effected by the oxidation of vinylsulfides or vinylsulfoxides.

It is the purpose of our investigations to prepare vinylsulphones without oxidation. We first choose splitting off of hydrogen-halide from chlorethyl-sulphones:

$R\text{-}SO_2\text{-}CH_2\text{-}CH_2\text{-}Cl$ ---------- $R\text{-}SO_2\text{-}CH = CH_2$; R represents an aliphatic or aromatic residue.

Since the investigations carried out during the last few years into sulpho-chlorinations, aliphatic sulphochlorides are as easily accessible as aromatic ones, and by now are sometimes produced on a technical scale. Up to date, the cheapest and most uniform of the sulphochlorides, ethane and benzol-sulphochloride, were put to use for the preparation of vinylsulphonates. From these sulphochlorides, sulfinic acids were prepared by reduction, and these brought to reaction with ethylenechlorhydrin. This reaction was carried out by heating the sulfinic-acid-salts with ethylenechlorhydrin in the prescence of small amounts of water to 110 - 120°, with subsequent vacuum distillation. The hydroxyethyl-sulphones of the formulae:

$CH_3\text{-}CH_2\text{-}SO_2\text{-}CH_2\text{-}CH_2\text{-}OH$ and $C_6H_5\text{-}SO_2\text{-}CH_2\text{-}CH_2\text{-}OH$

are in that way obtained in a very pure state and can be distilled in vacuum without decomposition. The ethyl-W- hydroxyethyl-sulphone melts at 41 - 42° and boils at 210 - 212°, 18 mm. This compound was already prepared by Otto/J.pr./2/36,443/, who describes it as a thick oil. The phenyl-W-hydroxyethyl-sulphone boils at 182-184°, 2-3 mm.

Both the W-hydroxyethyl-sulphones can, with the help of thionyl-chloride, be converted into the corresponding W-chlorethyl-sulphones, which can also be distilled in vacuum without decomposition. The yield is almost quantitative. The ethyl-W-chlorethylsulphone is liquid and boils at 110 - 112°, 1-2 mm, the phenyl-W-chlorethylsulphone at 169 - 171°, 7 mm. Its melting point is 56 - 57°.

From these W-chlorethylsulphones the hydrogen choride can easily be split off. Even in aqueous suspension the vinyl compounds are obtained in almost quantitative yield with dilute sodium-hydroxide. When the splitting-off of the hydrogen-chloride by alkali is effected in alcoholic solution, some caution is advisable, as even a small excess of alkali leads to a conversion of the intermediate vinyl compounds into the corresponding ethers. The preparation of vinylsulphones through the splitting-off of hydrogen-halide from W-halogen-ethylsulphones has been protected by the patent application 1.71960 IVd/120.

A second new method was found by which the vinylsulphones can also be prepared in a simple fashion and with almost quantitative yields. This consists of converting the W-hydroxyethylsulphones into their sulphuric acid esters and the subsequent treatment of these with dilute alkalies, according to the following equation:

$R-SO_2-CH_2-CH_2-OH$ ------ $R-SO_2-CH_2-CH_2-O-SO_3-H$ ----- $R-SO_2-CH = CH_2$

The sulphuric acid esters are easily obtained by the action of sulphuric acid in different concentrations or by the action of chlorsulphonic acid etc. on the W-hydroxyethyl-sulphones in the presence or absence of organic solvents or organic diluents. The sulphuric acid esters are easily soluble in water and relatively stable both in acid and neutral solution. In alkaline solution they are, even in the cold, decomposed into the corresponding vinyl-sulphones. The preparation of vinyl-sulphones by way of the sulphuric acid esters has been registered as patent I.71294 IVd/120/.

The W-hydroxyethyl-sulphones can also be converted into the corresponding vinylsulphones by heating them with the alkali salts of the fatty acids, e.g. sodium acetate, with subsequent distillation in vacuum. This is analogous to the research carried out by the Committee of the Electro-Chemical Industry, who converted the esters of α methyl-W-hydroxy-propionic-acid into the corresponding methacrylic-acid esters by means of small quantities of an alkali salt of an organic carboxylic acid, e.g. sodium acetate. (F.P.868465).

Further it was found that nitration of the sulphuric acid esters of the hydroxyethyl-aryl-sulphones can easily be effected in the nucleus in sulphuric acid solution. The sulphuric acid esters of the nitro-aryl-hydroxyethyl-sulphones are also easily soluble in water, and with dilute alkalies can be split into the corresponding nitro-aryl-vinyl-sulphones. In this way it is easily possible to obtain the previously unknown vinyl-nitro-aryl-sulphones from the hydroxy-ethyl-aryl-sulphones in a single operation. These discoveries were also safeguarded by a patent application (1.71447 IVd/120).

In contrast to the sulphuric acid esters of the hydroxy-ethyl-aryl-sulphones, the nitric acid esters of these sulphones are only with difficulty soluble in water and their resistance to alkalies is relatively great.

The nitro-aryl-vinyl-sulphones can also be prepared with very good yields through nitration of aryl-vinyl-sulphones. The m-nitro-phenyl-vinyl-sulphones is a faintly yellowish substance. For the nitration of the aryl-vinyl-sulphones patent protection was requested by the application I.71448 IVd/120.

The previously unknown Aminoaryl-vinyl-sulphones were prepared in the following ways!

a) Acetylated amino aryl-sulfinic-acid-salt was converted into the corresponding hydroxyethyl-compound with chlorethanol, by the method described above. The hydroxy-ethyl-compound was then converted into the amino-aryl-vinyl-sulphone by way of the sulphuric-acid-ester and the splitting-off of the acetyl group.

b) Through reduction of the nitro-aryl-vinyl-sulphones.

c) Through the replacement of active halogen-atom by the NH_2-group.

Vinyl-sulphones substituted with halogen in the vinyl group were prepared by adding bromine to vinyl-sulphones in aqueous suspension, and subsequent splitting-off of the hydrogen-bromide by the method already mentioned. The following hydroxyethyl-sulphones and vinyl-sulphones were prepared:

$CH_3-CH_2-SO_2-CH_2-CH_2-OH$	F.P. 41-42°
$C_6H_5-SO_2-CH_2-CH_2-OH$	B.P. 182-184°
$p-CH_3-C_6H_4-SO_2-CH_2-CH_2-OH$	F.P. 54-55°
$p-Cl-C_6H_4-SO_2-CH_2-CH_2-OH$	F.P. 52-53°
$p-NH_2-C_6H_4-SO_2-CH_2-CH_2-OH$	F.P. 109-110°
$p-CH_3-CO-NH-C_6H_4-SO_2-CH_2-CH_2-OH$	F.P. 196-197°
$C_{10}H_7-SO_2-CH_2-CH_2-OH$	F.P. 113°
$CH_3-CH_2-SO_2-CH-CH = CH_2$	B.P.$_1$ 84-85°
$C_6H_5-SO_2-CH = CH_2$	F.P. 72°
$p-CH_3-C_6H_4-SO_2-CH = CH_2$	F.P. 66-67°
$p-Cl-C_6H_4-SO_2-CH = CH_2$	B.P.$_2$ 128-129°

From these W-chlorethylsulphones the hydrogen choride can easily be split off. Even in aqueous suspension the vinyl compounds are obtained in almost quantitative yield with dilute sodium-hydroxide. When the splitting-off of the hydrogen-chloride by alkali is effected in alcoholic solution, some caution is advisable, as even a small excess of alkali leads to a conversion of the intermediate vinyl compounds into the corresponding ethers. The preparation of vinylsulphones through the splitting-off of hydrogen-halide from W-halogen-ethylsulphones has been protected by the patent application 1.71960 IVd/120.

A second new method was found by which the vinylsulphones can also be prepared in a simple fashion and with almost quantitative yields. This consists of converting the W-hydroxyethylsulphones into their sulphuric acid esters and the subsequent treatment of these with dilute alkalies, according to the following equation:

$$R\text{-}SO_2\text{-}CH_2\text{-}CH_2\text{-}OH \text{ ------ } R\text{-}SO_2\text{-}CH_2\text{-}CH_2\text{-}O\text{-}SO_3\text{-}H \text{ ----- } R\text{-}SO_2\text{-}CH = CH_2$$

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$p\text{-}CH_3\text{-}C_6H_4\text{-}SO_2\text{-}CH_2\text{-}CH_2\text{-}OH$	F.P. 54-55°
$p\text{-}Cl\text{-}C_6H_4\text{-}SO_2\text{-}CH_2\text{-}CH_2\text{-}OH$	F.P. 52-53°
$p\text{-}NH_2\text{-}C_6H_4\text{-}SO_2\text{-}CH_2\text{-}CH_2\text{-}OH$	F.P. 109-110°
$p\text{-}CH_3\text{-}CO\text{-}NH\text{-}C_6H_4\text{-}SO_2\text{-}CH_2\text{-}CH_2\text{-}OH$	F.P. 196-197°
$C_{10}H_7\text{-}SO_2\text{-}CH_2\text{-}CH_2\text{-}OH$	F.P. 113°
$CH_3\text{-}CH_2\text{-}SO_2\text{-}CH\text{-}CH = CH_2$	$B.P._1$ 84-85°
$C_6H_5\text{-}SO_2\text{-}CH = CH_2$	F.P. 72°
$p\text{-}CH_3\text{-}C_6H_4\text{-}SO_2\text{-}CH = CH_2$	F.P. 66-67°
$p\text{-}Cl\text{-}C_6H_4\text{-}SO_2\text{-}CH = CH_2$	$B.P_2$ 128-129°

$m\text{-}NO_2\text{-}C_6H_4\text{-}SO_2\text{-}CH = CH_2$	F.P.	108-109°
$m\text{-}NO_2\text{-}p\text{-}CH_3\text{-}C_6H_3\text{-}SO_2\text{-}CH = CH_2$	F.P.	61°
$m\text{-}NO_2\text{-}p\text{-}Cl\text{-}C_6H_3\text{-}SO_2\text{-}CH = CH_2$	F.P.	74-75°
$p\text{-}NH_2\text{-}C_6H_4\text{-}SO_2\text{-}CH = CH_2$	F.P.	75°
$m\text{-}NH_2\text{-}C_6H_4\text{-}SO_2\text{-}CH = CH_2$	F.P.	57-58°
$m\text{-}NH_2\text{-}p\text{-}CH_3\text{-}C_6H_3\text{-}SO_2\text{-}CH = CH_2$	F.P.	78-79°
$p\text{-}CH_3\text{-}CO\text{-}NH\text{-}C_6H_4\text{-}SO_2\text{-}CH = CH_2$	F.P.	123-124°
$C_{10}H_7\text{-}SO_2\text{-}CH = CH_2$	F.P.	101-102°
$C_6H_5\text{-}SO_2\text{-}CBr = CH_2$	F.P.	45-46°
$m\text{-}NO_2\text{-}C_6H_4\text{-}SO_2\text{-}CBr = CH_2$	F.P.	91-92°
$CH_2\text{-}CH\text{-}SO_2\text{-}CH = CH_2$	$B.P._{13}$	109-110°

The vinyl-ethyl-sulphone is a colorless oil, easily soluble in water. In the D.R.P. 635396 vinyl-ethyl-sulphone is described as a yellow oil sparingly soluble in water. The majority of the other vinyl-sulphones prepared are not known.

All sulphones show a great addition-tendency towards compounds with available hydrogen-atoms, as for instance alcohols and amines. This has already been described in the memorandum by Lu. about "The addition-reactions of vinylsulfoxides and vinylsulphones".

The esters obtained from various vinyl-sulphones and alcohols were examined for their possible use as plasticizers.

II. Mixed polymerisation of vinyl-sulphones.

From the vinyl-sulphones quoted, vinyl-ethyl-sulphones and vinyl-phenyl-sulphones were closely investigated in our Laboratory for Synthetic Materials /Dr. Overbeck/, with a view to their aptitude for polymerisation. The vinyl-ethyl-sulphone is a component that tends to polymerise relatively readily,but offers only low molecular weight polymerisation-products.

As a component in mixtures it was investigated both in bulk and emulsion-polymerisation. The results of the individual experiments are summed up in the following table:

Mixing-ratio:	Polymerisation-component vinyl ethylsulphone plus	degree temperature	Yield	K-value	Properties:
50:50	Styrol	50	50	approx. 35	Brittle mass, Softening Point (M.P.) 80°
20:80	vinyl-chloride /emulsion-polymerisation/	50	30	36	Softening Point 80° Igelit PCU S.P. 75°
20:80	vinyl-chloride /with sodium-hydrosulphite-addition/	25	50	57	S.P.84° Igelit PCU S.P. approx 80°

It can be seen from this, that the vinyl-ethyl-sulfone has a delaying action and is a component reducing the degree of polymerisation; it does, however, slightly increase the softening-point of the polymerisation product.

In conjunction with vinyl-acetate and vinyl-chloride, or on its own, vinyl-phenylsulphone does not polymerize.

With styrol, acrylic-acid-methyl-esters, methacrylic-acid-methyl-esters, acrylic-acid-di-iso-butylamide and acryl-nitrile, however, mixed polymerisation products could be obtained. It was found, that with an increasing proportion of vinyl-phenyl-sulphone the polymerisation is gradually slowed down, so that with a ratio of 50 parts vinyl-phenyl-sulphone and 50 parts of the other monomeric component almost no polymerisation takes place.

The mixed polymerisation of vinyl-phenyl-sulphone with styrol in the ratios 10:90 and 40:60 was more closely investigated, and the conditions determined under which polymerisation-products with a K-value of over 75 are obtained. Of these mixed polymerisation products, the one containing 20% vinylsulphone is particularly interesting. It shows rather similar properties in appearance, in the "Vikatzahl" approx. 135° and in the "Schlagbiegefestigkeit" as the mixed polymerisation-product from 80% styrole and 20% acrylic-acid-di-phenyl-amide, which has been registered as artificial resin 28840 for manufacture, and is now in the pilot plant stage. Because of these good properties the new vinyl-phenyl-sulphone-styrol mixed polymerisation product is being further investigated, for instance with a view of establishing by sinter-experiments, whether the mechanical properties of the product can be improved by such treatment.

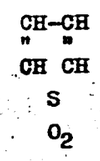
The mixed polymerisation-products of vinyl-sulphones with methacrylic.acid-esters also are of some interest and therefore are further investigated.

A similar behavior was noted in the mixed polymerisation of styrol and vinyl-p-tolylsulphone and vinyl-B-naphthyl sulphone. Vinyl-B-naphthyl sulphone polymerised markedly more slowly with styrene than did vinyl-p-tolyl sulphone.

The mixed polymerisation-products from vinyl-p-acetylamino-phenyl-sulphone with styrol show K-values of over 100; their heat resistance, however, is poor and they have no satisfactory mechanical properties, so that they cannot be used for extrusion casting.

The vinyl-amino-phenyl-sulphones, the vinyl-nitro-phenyl-sulphones and brom-vinyl-phenyl-sulphones polymerize neither alone nor in conjunction with other monomers.

Because of its similarity to butadiene-sulphone



the di-vinyl-sulphone

$$CH_2 = CH - SO_2 - CH = CH_2$$

was prepared. The preparation was carried out by the well-known method from B - B'-dichlor-diethyl-sulfide, oxidation to the sulphone, and splitting-off of the hydrogen-halide with triethylamine in benzol solution.

The divinyl-sulphone polymerizes both on its own and in conjunction with other monomers, as for instance styrol or acrylic acid ester. The products, however, are completely insoluble and brittle and unusable for synthetic materials. The polymerisation with butadiene is still being investigated.

SUMMARY

New methods for the preparation of a number of vinyl-sulphones, as well as the mixed polymerisation products of these vinyl-sulphones with other monomers are described. Vinyl-phenyl-sulphone was more closely investigated with a view to its aptitude for polymerisation with other vinyl-compounds.

The mixed polymerisation product styrol-vinyl-phenyl-sulphone 80:20 is of interest because of its good mechanical properties, its high "Vikatzahl" approx. 135°/ and its light color, and is therefore further investigated. The investigation of the whole field is being continued.

(Sgd) Dr. Heyna
Dr. W.V. Schumacher
Dr. Overbeck

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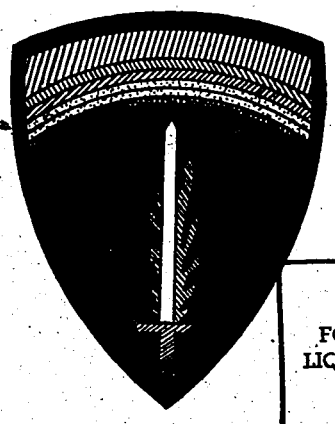
FIAT FINAL REPORT No. 846

PRODUCTS FOR THE LEATHER INDUSTRY FROM ETHYLENECHLORIDE AND XYLOL AND THROUGH THE SULFURIZATION OF XYLOL

(I. G. Farbenindustrie A. G. Höchst)



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FIAT FINAL REPORT NO. 846. 9 July 1946

ENGLISH TRANSLATION OF PRODUCTS FOR THE LEATHER INDUSTRY FROM ETHYLENECHLORIDE AND XYLOL AND THROUGH THE SULFURIZATION OF XYLOL

BY

A GERMAN STAFF MEMBER
I.G. FARBENINDUSTRIE, A. G.

FIELD INFORMATION AGENCY, TECHNICAL

ABSTRACT

Manufacturing processes used in I. G. Farbenindustrie (Höchst) are described for type Derminoil, Hö 1/142, Derminoloil Hö 1/143 and Derminoloil Hö 1/146, condensation products of xylol and ethylenechloride. By varying the proportion of xylol, ethylenechloride, the viscosity of the products can be altered. Sulfurization of the xylol, from xylol and sulfur chloride, are simpler to manufacture. From these, Derminoloil Hö 1/151 and Derminolfat Hö 1/153 are made. Condensates from xylol and xylochloride are also described.

FOREWORD

This is a translation prepared in London from German documents evacuated in the early stages of Technical Industrial Intelligence operations. The selection of reports for translation was made by Sherlock Swann and N.M. Elias. The abstract was prepared in the office of the Miscellaneous Chemicals Subcommittee, Industry Branch, Field Information Agency.

AUTHOR

The author is a staff member of I.G.Farbenindustrie, A.G.Frankfurt (Main) Höchst.

I.G. FARBENINDUSTRIE AKTIENGESELLSCHAFT
FRANKFURT (MAIN) HOCHST

Hö 43/9/ 10.2.43. Dr. Ba/K

PRODUCTS FOR THE LEATHER INDUSTRY FROM ETHYLENECHLORIDE AND XYLOL AND THROUGH THE SULFURIZATION OF XYLOL

In our report Hö 42/2 of 28.11.1942, "SYNTHETIC OILS ON THE BASIS OF AROMATIC HYDROCARBONS", the uses in various applications have already been indicated of the condensation products of xylol and ethylenechloride. In the meantime, a large quantity of the Type Derminoloil Hö 1/142 has been produced for the carrying out of ——— tests in practice. The manufacturing process is as follows:-

2120 kgs. xylol - 20 mol. were used and 128 kgs. Al Cl_3 mixed at room temperature and the mixture heated to 85 - 90 degrees. During the course of two hours 990 Kgs. ethylenechloride = 10 mol. were added. A constant flow of hydrogen chloride escaped. After final adding of initial ethylenechloride the reaction mass was stirred for an additional hour at 85 - 90 degrees. The temperature was then raised within one hour to 100 degrees and kept at this level for three hours. The condensation product was obtained by separating the viscous by-product Al Cl_3 residue, thoroughly stirred with 0.5% Fuller's earth (bleaching earth) at a temperature of 60-70 degrees for two to three hours and finally filtered.

Through distillation of the light oil obtained, the unreacted starting materials and light volatile constituents are removed in vacuum at 16 mm. and 55 - 60 degrees. The distillation residue constitutes the Derminoloil Hö 1/142. The yield amounts to 1,446 kgs. 103 kgs. ethylenechloride and 511 kgs. xylol are recovered and can be used for the next batch. The Derminoloil Hö 1/142 has a viscosity of about 60 seconds, measured in Fordbeaker at 20 degrees, its volatility is about 5% at 7 hours' heating at 100 degrees.

A combination of 80 parts Hö 1/142 and 20 parts Igevin I 30 has in the meantime been submitted to the C.K. as Derminoloil Hö 1/143. The new product is superior to Hö 1/142 because of its excellent water-resisting quality.

A substitute product for tallow for the greasing of leather has been announced by the C.K. It is the Derminolfat Hö 1/146. It consists of a mixture of 70 parts of Derminoloil Hö 1/142 and 30 parts of a solid chlorinated paraffin containing 6% chlorine. It is a light tallow-like product. It is easily absorbed into the leather and makes it water-resisting and gives it a tanned finish similar to that of tallow.

In the above mentioned report Hö 42/3 it has already been indicated that the viscosity of the condensation products of xylol

and ethylenechloride can be very much altered by varying the proportion of xylol: ethylenechloride. Thus a product, which is very much like the Igevin I 30, is obtained. When in the above mentioned process for Hö 1/142 the mol. ratio of 2 xylol : 1 ethylenechloride is changed to 1 mol. xylol : 1 mol. ethylenechloride, the condensation products comes out as a dark, highly, viscous oil, which is suitable for the impregnating and the preserving of the leather. The usual solvents can be used and it can be mixed with mineral oils in any proportion. The product is named by the C.K. as the "DENSODRIN HO 1/148"

As present circumstances do not permit a quite simple technical manufacturing process of the xylol-ethylenechloride condensates it was necessary for us to find a product of the same quality as the xylol-ethylenechloride condensate, but which on the other hand should be more simple to manufacture, and which has in some degree a more available raw material basis. We then came to the sulfurization products of the xylol, which are easily accessible from xylol and sulfur chloride. The substitute which has been submitted to the C.K. in this class of substances, the Derminoloil Hö 1/151 is a reddish-brown oil, viscosity measured in Fordbeaker at 20 degrees at 40 seconds and evaporation of 1-2% at 100 degrees, and in every respect is equal to the well-known Derminoloils. The product is, for the time being, being manufactured in the following way:

106 kgs. pure xylol = 1 mol. are put into a lead-linde stirring kettle at room temperature and 57 g. tin tetrachloride added, and during one hour 33,75 kgs. sulfur chloride = 0,25 mol. are added. During the evolution of hydrogen chloride the temperature is slowly raised to 50 - 60 degrees and is kept at this level.

During the course of about 2 hours the reaction is in the main finished and the evolution of hydrogen chloride is negligible. Then the temperature is slowly raised to 80 degrees, the mass stirred for about one to two hours at 80 degrees, and then cooled off. The crude oil is washed neutral with warm water, the neutral product dried with sulfate, thoroughly stirred for two hours at room temperature with about 2% Fuller's earth and filtered. The filtrate is distilled in vacuum. At 4 mm. vacuum and at about 140 degrees bath temperature about 50 kilos of unreacted xylol is distilled off. The distillation residue is the Derminoloil Hö 1/151. The yield is about 60 kgs.

Work is still in progress which is aiming at the utilization of other catalysts as for instance: zinc dust, zinc chloride, silicon tetrachloride, surface contacts, etc.

The new Derminoloil with a combination of solid chlorinated paraffin containing 6% chlorine, has been named Derminolfat Hö 1/153:

70 parts Leatheroil Hö 1/151
30 parts chlorinated paraffin
100 parts Leatherfat Hö 1/152

It is also possible by altering the proportions of xylol-sulfur-chloride in the Hö 1/151 of 4 mol. xylol - 1 mol. sulfur chloride to arrive at xylol-sulfur-chloride condensations products with other viscosity qualities. A type of oil, for instance, completely analogous in qualities with the Densodrin Hö 1/148 can be produced, when in the above mentioned way 2 mol. xylol with 1 mol. sulfur chloride are condensed. A very sticky soft resin is obtained through the condensation of 1 mol. xylol with 1 mol. sulfur chloride. The latest products are still in the experimental stage and will be submitted to the C.K. as Densodrin substitutes and as constituents of Degras standard.

An additional class of products which was described in our report Hö 42/2 is likewise being investigated. They are the condensation products of W-halogen methylated xylols.

From the thus obtained oily condensates it seems so far that the one especially which has been produced by condensation of xylylchloride with xylol is very useful. It is a light colored oil of extremely low volatility and a very low Fordbeaker viscosity of 20-30 seconds at 20 degrees.

It is also possible with these condensations to obtain products with rising viscosity by lowering the xylol portions in relation to the xylylchloride and finally a light brown soft resin-like condensate is obtained through the self-condensing of xylylchloride. By the use of xylylchloride, a great variety of products with various physical properties can be produced, the systematic investigation of which is in progress.

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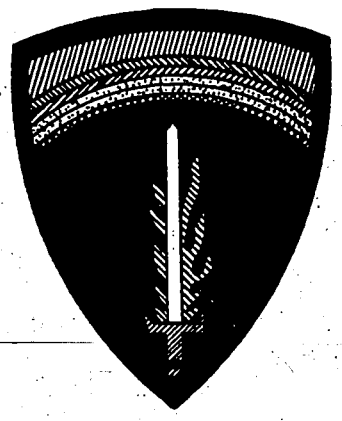
FIAT FINAL REPORT No. 848

THE INFLUENCE OF OXYGEN ON THE CHLORINATION OF METHANE



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FIAT FINAL REPORT NO. 848. 10 July 1946

ENGLISH TRANSLATION

of

THE INFLUENCE OF OXYGEN ~~ON~~ THE CHLORINATION OF METHANE

BY

A GERMAN

FIELD INFORMATION AGENCY, TECHNICAL.

ABSTRACT

The report describes experiments showing the inhibitory effect of oxygen on the chlorination of methane. Tests for carbon deposition in chlorination ovens are also described. Addition of oxygen causes no carbon deposition.

FOREWORD

This is a translation prepared in London from German documents evacuated in the early stages of Technical Industrial Intelligence operations. The selection of reports for translation was made by Sherlock Swann and N.M. Elias. The abstract was prepared in the office of the Miscellaneous Chemicals Subcommittee, Industry Branch, Field Information Agency, Technical.

THE INFLUENCE OF OXYGEN ON THE CHLORINATION OF METHANE

The influence of oxygen on the chlorination of methane was of interest in connection with the Deacon chlorination of methane in which a small amount of oxygen is left in the gas. According to Pease and Wals. J. Am. chem. Soc. 53, 3728 (1931) the oxygen strongly inhibits the chlorination; however, only temperatures up to 285°C were considered. (e.g. methane : chlorine ratio 2 : 1 at 250°C and a reaction time of 255 seconds; without O_2 the yield was 63.9 to 66.6%; with 2.5% O_2, the yield was 5.8%).

Measurements have now been taken at higher temperatures. The results, however, can only be taken as an indication of what happens, especially as catalytic influences (wall catalysis) were not eliminated.

Apparatus: Supremax-tube with 100 ccm. heated content (capacity) in Cu block, hourly (per hour).

Note: Apparatur: Supremax-Rohr mit 100 ccm beheiztem Inhalt in Cu-Block stündl.

a) 25 liters CH_4 + 6 liters Cl_2 no O_2

b) 25 liters CH_4 + 6 liters Cl_2 + 0.5 liters O_2(1.6%)

c) 25 liters " " + 2.0 liters O_2(6.85%)

The results were plotted graphically i.e. the ratio

$$\frac{\text{CONVERTED CHLORINE}}{\text{CHLORINE STILL FREE}}$$

IN RELATION TO THE TEMPERATURE

was graphically represented. Since, during the reaction, the concentration of H atoms replaceable by chlorine is only reduced by less than 6%, the above ratio is, for all practical purposes, a measure of the speed of the reaction. If the reaction speed of the oxygen-free gases at 400°C is taken to be 100, the reaction speeds for the investigated mixtures are:

Temperature, in °C.	with 0.00% O_2	Speed of reaction, with 1.60% O_2	with 6.85% O_2
400	100	68	42
375	48	21	12
350	24	8.5	2.5

The inhibitory effect of the oxygen can clearly be seen. It decreases with rising temperature. Under production conditions it must be still noticeable unless it is cancelled by subsequent catalysis.

According to previous investigations, oxygen has no effect at 450°C on the catalytic chlorination of methane. (Dr. Dachlauer, Dr. Schmitzler) At temperatures up to 400°C values (which can not now be reproduced) were obtained with a filter stone contact catalyst. No conclusions can be drawn from these tests, however.

The decrease in the inhibitory effect of oxygen with rising temperature is explained by the fact that the chain reaction is gradually replaced by a normal thermal bi-molecular reaction. It has been proved kinetically that the pure chain reaction below 270°C is a thermal bi-molecular reaction.

Whereas the previous note deal only with the influence of oxygen on the chlorine substitution, tests were recommenced in October 1942 for investigation the carbon deposition in the oven. The chlorination ovens often had considerable carbon deposition after prolonged effect of forced air draughts on the sodium hypochlorite. The laboratory circulating oven of Jena glass with porcelain rings as secondary contact catalyst was heated in a slat bath of 390°C to avoid any overheating. Chlorination was carried out with the following gas mixture:

a) 8 liters Cl_2 per hour + 40 liters methane

b) " " " " " + " " "
+ 10 liters CH_3Cl

c) " " " " " + 40 liters CH_3Cl

d) " " " " " " " purified by intensive washing with 98% H_2SO_4 and passing over an "A" carbon filter.

After 8 hours the oven was purged with pure nitrogen and investigated for carbon deposition or graphite formation. In a). and b). there was a slight incrustation of carbon, especially in the

diffuser tube and slight graphite formation on the secondary contact. In c). there was considerable carbon deposition and graphite formation in the oven and on the secondary contact. In d). there was more carbon deposition than in a). but noticeably less than c). No noteworthy temperature changes were observed on addition of 0.5 liters, 1.0 liters, or 3.0 liters of O_2 per hour. Surprisingly, however, the oven remained completely clean, during lengthy tests with all the gas mixtures a). to d). Addition of oxygen caused no carbon deposition.

This observation directly contradicts works experience. It can, however, be reproduced as often as desired.

The foregoing may provide a new way of protecting the contact mass in the methane chlorination process, from being ruined by gradual accumulation of carbon.

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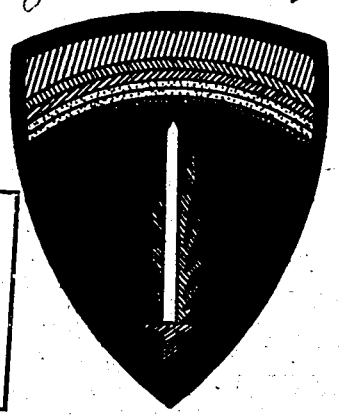
FIAT FINAL REPORT No. 852

ENGLISH TRANSLATION OF N - CHLORO - AMIDES OF HIGHER MOLECULAR FATTY ACIDS AND THEIR CONVERSION PRODUCTS

(Jacobs (Ver.))



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FIAT FINAL REPORT NO. 852 5 August 1946

ENGLISH TRANSLATION

of

N-CHLORO-AMIDES OF HIGHER MOLECULAR FATTY ACIDS AND THEIR CONVERSION PRODUCTS

by

DR. JACOBS (GERMAN)
I.G. FARBENINDUSTRIE

FIELD INFORMATION AGENCY, TECHNICAL

A B S T R A C T

Chlorination of the C_{15} - C_{17} compounds at I.G.Farbenindustrie, Höchst, is described. The N-chloro-compound is capable of the same conversion as the chloro-amides of the saturated fatty acids. With the reaction of ethylene imine on N-chloro-amides, emulsion for softening can be prepared, for use with textiles. Taurine and methyl taurine can be used in the conversion.

FOREWORD

This is a translation prepared in London from German documents evacuated in the early stages of Technical Industrial Intelligence operations. The selection of reports for translation was made by Sherlock Swann and N.N. Elias. The abstract was prepared in the office of the Miscellaneous Chemicals Subcommittee, Industry Branch, Field Information Agency, Technical.

AUTHOR

Dr. Jacobs of Central Laboratory, I.G. Farbenindustrie, Höchst.

This Report is dated 17 March 1939

N-CHLORO-AMIDES OF HIGHER MOLECULAR FATTY ACIDS AND THEIR CONVERSION PRODUCTS

The investigations in Höchst concerning the softening of cellulose wool substitutes and rayon had led to some success when the N-octadecyl-N'N'-ethylene-urea $C_{18}H_{17}NH.CO.N\begin{matrix}CH_2\\CH_2\end{matrix}$ was discovered and prepared technically from the isocyanate of octodecylamine and ethylene imine. It occurred to us to synthesize such compounds in a different way, in which the use of organic solvents and more difficultly available raw materials could be avoided. According to earlier investigations, as performed years ago in the Science Laboratory in Le., the investigators started from the carboxylic acid amides, using the Hoffmann degradation process and its modification according to JEFFREYS (B.30,898) to obtain the intermediates, to proceed through their N-mono-Cl- or Br- products to the urethanes, and further to the amines, as outlined in the following equations:

$$R.CO.NH_2 \longrightarrow R.CO.NH.Br \longrightarrow +R.CO.N. \longrightarrow +R.N.CO \longrightarrow R.NH.C\begin{matrix}O\\OX\end{matrix} \longrightarrow R.NH_2$$

Details are to be found in the report of the Science Laboratory Le. of 30/6/1933 "Experiments for the preparation of high molecular amines ."

The essential part of this series of reactions is the intermediary formation of isocyanates, e.g. of such compounds as might be used for the preparation of ethylene ureas as starting substances. The preparation of the N-chloro-compounds is, however, a preliminary condition to carrying through such a reaction and these could not yet be obtained by using higher fatty acid amides.

E. Jeffreys has worked on the problem of obtaining such chlorination products in his paper (B.30,899). Only by extremely complicated and difficult methods was he able to isolate the chloramide of palmitic acid from various mixtures. Because of the unsuitability of this method the present workers did not attempt the preparation of the pure N-chloro-compound.

Later on, Le. re-started experiments in this direction. They were successful in chlorinating the lauric acid amide in dilute acetic acid to its chloro-amide. ($C_{11}H_{23}.CO.NH_2$). All further efforts, however, to transfer this method to higher fatty acids - palmitic and stearic acid - were unsuccessful, even in the chlorination in acetic acid, where these amides are completely soluble. Alcoholic solutions were excluded owing to the danger of explosions.

In spite of these discouraging preliminary investigations, the experiments for the preparation of the N-chloro derivatives of higher fatty acid amides were resumed once more in Höchst and the results of previous reports confirmed.

It was, therefore, very surprising to ascertain that it was possible to chlorinate the C_{15}-C_{17} compounds quantitatively and without difficulties to the chloro-amides, by forming a fine dispersion of the amide with Igepon T or similar product and introducing the calculated amount of Cl_2 into the aqueous suspension without using organic solvents. The desired chloro-amides thus separated as beautifully crystalline substances from the emulsion, and could be washed and filtered easily showing a constant melting point. The N-chloro-amides thus obtained are relatively stable, even when dried carefully under vacuum. Only after standing for several weeks do they lose perceptible of chlorine, which can be ascertained by the increasing insolubility of the decomposition products in ether and the increase in the melting point. The method of production of these chloro-amides is protected by the Patent Application of Höchst I 67108 IVd / 12 o (7513).

Unsaturated amides, like oleic acid amide are chlorinated to oleic acid chloro-amide, surprisingly without addition of chlorine to the double link. The working conditions, however, are somewhat different and are not to be determined as accurately owing to the low m.p. of the N-chloro-compound. It is, however, capable of the same conversions as the chloro-amides of the saturated fatty acids. Details will be given later.

With the preparation of pure N-chloro-amides the way was open for the various conversion products. We find already in the above mentioned report of Le. the conversion at the chloro-amide of lauric acid, dissolved in alcohol, into urethane by addition of NaOH.

The reaction proceeds with strong evolution of heat in hot alcoholic solution and an undesirable by-product, lauryl-undecylic-urea, is formed.

$$C_{11}H_{13}.CO.NH.C(=O)NH.C_{11}H_{13}$$

In the same way taurine and methyl taurine and similar amines were reacted with lauric acid chloro-amide to form analogous water soluble ureas. All these operations were performed warming in unreactive organic solvents.

Reaction Products of Ethylene Imine on N-chloro-amides:

Höchst was first interested in the reaction with ethylene imine. The simple translation of the experiments made at Le. was not feasible because of the inclination of the ethylene ureas to polymerize when warm, as only its monomeric form was of interest. Besides, for reasons of cost and technical considerations only a preparation in aqueous suspension was feasible.

The danger existed that on warming in water the intermediate isocyanate would undergo extensive decomposition and other reaction.

The heating which was necessary for the reactions - degradation, rearrangement, condensation - had to be held to temperatures below 60°C. The fact that these theoretical objections were contradicted by the practical preparation may be due to the high reactivity of the N-chloro-amides on the one hand and the strongly basic character of the ethylene imine on the other. When the two components were allowed to react at initial temperature of 5-10°C. in aqueous suspension with the NaOH addition solution of a definite concentration, up to 20°C. the water soluble sodium salt of the stearic acid chloro-amide was formed. On slowly raising the temperature the compound gradually reacted with ethylene imine. At 30°C. the original fluid mixture became a thick mush, which at 40-45°C. turned into an almost rigid paste and was so finely divided that it had become unfilterable. By adding suitable emulsifiers, a finely dispersed emulsion could be prepared of the desirable strength for use directly as a textile aid - especially as a softener.

The N-heptadecyl-N^1.N^1-ethylene urea prepared in this manner had the advantage of cheapness as compared to the C18 product which must be prepared from octadecyl-isocyanate.

It is possible that it will find application as softener for cellulose fibers and rayon, as soon as the investigations for additional suitable emulsifiers have been concluded. The conversion occurs to 90% of theory. All detailed information about the course of such reactions, including the low molecular and aromatic N-chloro-amides are specified in Patent Application I 67531 IV c / 12 p (7554).

Conversion of N-chloro-amides to Isocyanates:

The high molecular N-chloro-amides can also be converted into the corresponding isocyanates via the urethanes. When these are treated with PCl_5 and distilled in vacuum to remove $POCl_3$ the isocyanate is obtained in a good yield according to the equation:

$$C_{17}H_{35}.NH.CO.O.CH_3 + PCl_5 = C_{17}H_{35}.N.CO + HCl + POCl_3 + CH_3.Cl.$$

Reaction Products from N-chloro-amides and Water Soluble Amines:

The object of further investigations was then the capacity of reaction of the N-chloro-amides of higher fatty acids with water soluble amines, like taurine, methyl taurine, sarcosine, glycocoll, etc. to form the corresponding ureas. It is well known that ureas are obtained from isocyanates and taurines, which show satisfactory qualities as textile aids resembling Igepon T. The technical advantage is evident, if it were possible to use the easily available chloro-amides, as described. The investigations concerning this are so varied and the products of reaction insufficiently tested to enable one to give a final valuation of their suitability and the technical possibilities of the performance of the reactions. The general points

of view have already been specified in Patent Application I 68673 IVc/ 12 o (7554 a). It can be stated even now that a greater heat of reaction is required, and that the velocity of reaction, too, is not the same in all cases depending on whether primary or secondary amines are employed. It has not been determined whether it is possible to work in water or in organic solvents. Insofar as the results of the technical tests for textiles of the available products are concerned, the following generalities can be stated.

The conversion, for example, of stearic acid-N-chloro-amide with taurine proceeds considerably slower than with methyl taurine, probably by reason of its reduced basicity. The detergent qualities of both products are also considerably at variance. Whereas the substituted urea from taurine possesses a low

$$C_{17}H_{35}.NH.CO.NH.CH_2.CH_2.SO_3Na$$

lathering effect and a considerably lesser detergency, compared with Igepon T, the corresponding urea from methyl taurine, although of inferior lathering power is superior to Igepon T in its detergency. The analogous oleic acid product does not reach quite the detergency of Igepon T, but its lathering effect in well water is far above that of Igepon T, about 28:44. It should, therefore, be possible to use a suitable mixture of stearic acid chloro-amide and oleic acid chloro-amide with methyl taurine to compensate for these advantages and disadvantages. Such mixture are at present under investigation.

The ureas from stearic acid-N-chloro-amide and glycocoll, alanine, or sarcosine should be too insoluble in water to be considered for detergents. The corresponding compounds from oleic acid-N-chloro-amide are more easily soluble, but have not yet been sufficiently tested to furnish a final conclusion as to their merits.

So far the products were prepared by stirring equivalent quantities of, for instance, solid or a concentrated solution of methyl taurine with concentrated NaOH in acetone, heated to boiling and a hot acetone solution of stearic acid-N-chloro-amide added in a fine stream. After completion of the very active reaction, heating was continued for some time, the acetone was distilled off, water added and evaporated to a concentration of 25-30%. The products from palmitic, stearic, and oleic acid-N-chloro-amides with taurine give practically clear solutions.

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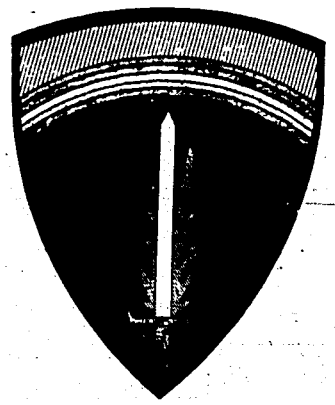
FIAT FINAL REPORT 823

UTILIZATION OF BLAST FURNACE SLAG IN GERMANY

Josephson, George W.



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FIAT FINAL REPORT NO. 823 17 May 1946

UTILIZATION OF BLAST FURNACE SLAG IN GERMANY

BY

GEORGE W. JOSEPHSON

TECHNICAL INDUSTRIAL INTELLIGENCE BRANCH

U.S. DEPARTMENT OF COMMERCE

FIELD INFORMATION AGENCY, TECHNICAL

A B S T R A C T

Briefly describes the utilization of blast furnace slag in Germany.

TABLE OF CONTENTS

INTRODUCTION

Objective:

The purpose of this investigation was to reveal the ways in which Germany utilized its blast furnace slags.

Evaluation:

In general, the uses of slags in Germany are similar to those in the United States. However, there is some difference in emphasis owing to variation in domestic needs, and the energy with which one product or another has been promoted through research and education. Producers have been very successful in the promotion of the blast furnace cements which contain a high percentage of slag ground with portland cement clinker. The review of various methods of processing foamed slag also may be useful to prospective producers.

Guide to Reader:

The general utilization of slag is outlined under the following section titled "General Discussion", and the more interesting methods of processing for special uses are discussed in the following sections on lump slag, cast slag, etc. Twenty-two figures and graphs are scattered throughout the text for the convenience of the reader.

GENERAL DISCUSSION

Germany, like any country with a large iron and steel industry, has produced great quantities of slag that have been looked upon as anything from an annoying expense item to a valuable by-product. Ordinarily the blast furnace operator is primarily concerned with the production of metal and is often reluctant to make necessary expenditures or even make much effort toward control of slag quality.

On the other hand, for many years Germany has made a great effort to utilize her domestic resources as fully as possible, and in many companies the profitable disposition of slag is a prime element of policy. That they enjoyed considerable success is shown by the fact that in recent years between one-half and two-thirds of the total blast furnace slag produced has been utilized.

Figure 1, page 2, shows the sources and uses to which slag was put in 1942; and Figure 2, page 3, is a simplified outline of the production methods, products and uses of slag in Germany.

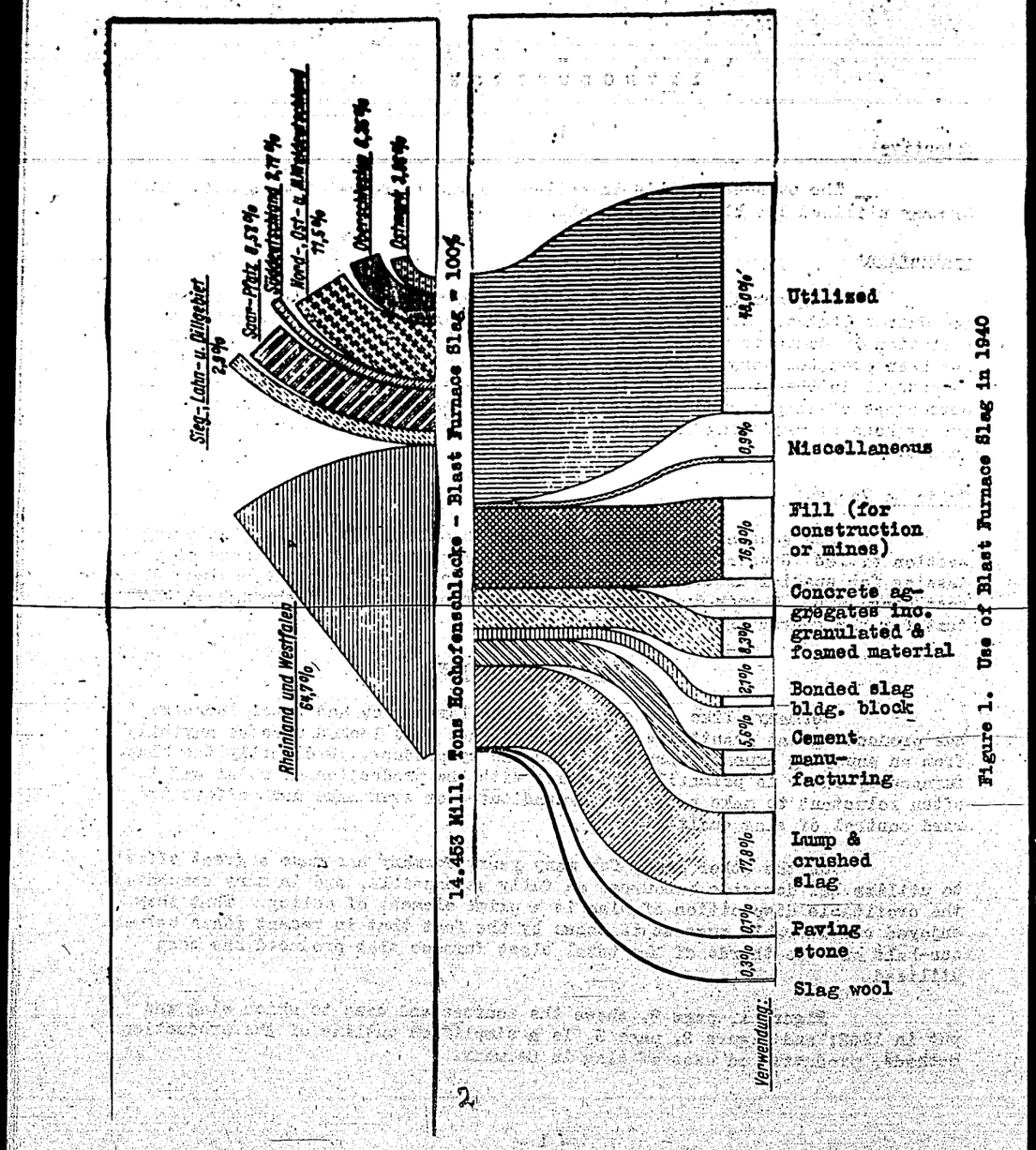

Figure 1. Use of Blast Furnace Slag in 1940

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Figure 2. WORKING METHOD AND USE OF BLAST FURNACE SLAG

Type of Production	Product	Use
Solidified in ladles	Crude slag	In road building as lump and broken slag and tar macadam
Poured into pits		
Poured on dumps	Lump slag	Railroad ballast
Poured into molding bed	Crushed slag(1)	Concrete aggregates construction and mine fill
Casting in forms	Paving stones	As paving on streets
Granulation in water	Slag sand(1)	Various uses in building, for Hüttenportland and Hochofenzement production, in slag building bricks
Foaming with water	Foamed slag	In light weight construction, in light weight slag building brick, in light weight concrete, heat and sound insulation
Blowing with steam	Slag wool	In the building industry and in other fields for insulation and as a substitute material; loose, in mats, ropes and formed pieces

(1) Also ground for lime fertilizer

As might be expected, the major uses for slag were found in road construction, filling (for construction, mines, etc.), and as concrete aggregates. Cement manufacturing also consumes a substantial quantity. The tonnage of bonded building brick and block is increasing and these products will play an important role in the reconstruction. Slag wool and paving stones are profitable products locally but their demands on the slag resources of the country are minor.

From information supplied by various German authorities, supplemented by direct investigation of operations at selected plants, the following conclusions are drawn:

1. Slag cooled in the ladle, in pits, or on the dump is widely used in lump and crushed form for fill, aggregates, ballast, general road and building construction, and for breakwaters.

2. Slag (principally from a copper blast furnace) cast in paving block form is used in Germany, and the technology of production has received considerable attention. However, owing to the popularity of smooth surfaced roads in the United States it is doubtful that cast slag block production offers an attractive field of development for American companies. Cast slag bricks have not found a market in building construction in Germany.

3. Considerable research has been done on the fertilizing properties of slag. These indicate that slag is of real value. However, its quality and cost advantages have not been sufficient to achieve commercial success. The amount of slag used for fertilizer in Germany is negligible.

4. Granulated and foamed slags are made in a number of ways and are used widely in light weight construction and cement manufacture.

5. A great deal of research has been done on the use of blast furnace slag as a cement constituent. Through this program of study and advertising the slag cements have captured about one-third of the total cement market. This material is claimed to develop strengths equivalent to those of portland cement over a period of time, and have other advantageous properties. Its cost of production is considerably lower than that of portland cement. Any American company contemplating entrance into this field will find it profitable to review the German experience.

6. Slag wool is produced in modest quantities but technically the industry is considerably behind American practice.

LUMP SLAG

Slag lumps, ranging up to several hundred pounds in weight (but usually less than 50 pounds) are made by pouring molten slag from a ladle into a shallow pit about 3 x 10 meters in area. The thickness of the sheet of slag is usually from 15 to 35 cm in order to allow easy breakage by pick and bar

into the desired size blocks. These lumps, called "packlage", are loaded by hand into railroad cars and used in breakwaters, roads, or as crusher feed. One of the principal requirements is slow cooling to avoid brittleness. Very large pieces may require as much as a 2 week cooling period, but ordinarily packlage is cooled in only about 4 days.

The more siliceous basic slags (with a p value of 1.0-1.2)($p = \frac{CaO}{SiO_2}$) are preferable for lump production because of their relative stability. For example, an analysis of slag at Mannesmannrohren Werke showed 39.5% CaO and 34.5% SiO_2. However, other slags with somewhat higher p values also give good service. Low gas content is desirable and consequently the low temperature slag is favored.

At some plants fine ore, blast furnace flue dust, or sand are added by shovel to the molten slag to improve its density, strength, and to give it a color similar to natural stone. This practice requires careful control, because errors result in trouble from temperature drop, uneven quality, and iron disintegration. The ultraviolet lamp test for lime disintegration is used as a production test to control quality.

CAST SLAG

Owing to the widespread use of cobblestone paving in Germany there is an active market for cast slag paving brick. Roads made from this material are very durable, but it must be conceded that they lack smoothness and anti-skid qualities. They are most useful where a pavement must be occasionally removed to facilitate repair of a public utility. For example, along a street car line. Cast slag bricks are also used for yard paving on farms, in workshops, etc. and for retaining walls. At one plant a 700 mm cube is being produced experimentally for breakwaters.

On the other hand, slag bricks are not used in buildings. High heat conductivity, and lack of attractive appearance are given as the reasons.

Slag bricks are cast in a form made of metal strips and plates as shown in Figures 3 and 4. Usually the brick is 16 x 16 x 14 or 16 cm in size.

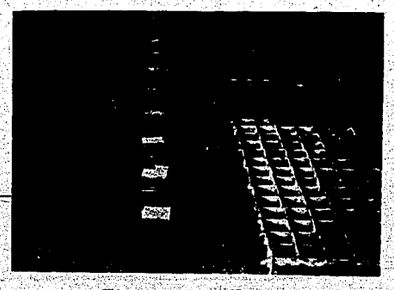

Figure 3. Forms

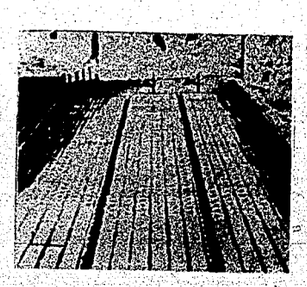

Figure 4. Parting Plates Over Forms

The form rests on a bed of fine coke 1 cm thick. A 5 mm layer of crushed slag (3-5 mm fragments) is spread on the bottom of each box. This material will be embedded in the surface of the brick and will act as a top wearing surface to provide better anti-skid properties. Parting plates are then laid on the top of the box forms as shown in Figure 4, and slag is run over the whole bed from a ladle. The slag runs through and around the top parting plates until the form is filled and pouring is continued until hot slag 15-25 cm deep covers the entire top of the casting bed. This slag cover reduces the rate of cooling and allows the formation of a tougher paving block. After a cooling period of 6 days the form is broken apart with bars, the paving blocks are removed and are then ready for shipment.

Chemical composition of the slag is important in maintaining the quality of the product. No slags that are subject to lime disintegration are adaptable to this market. The high silica basic slags are preferred. As in the case of packlage, iron oxide and silica are sometimes added to slag in the runner to improve color and strength.

An analysis of one casting slag is as follows:

SiO_2	33-36%	MnO	1.2-1.6%
CaO	39-43%	FeO	0.8-1.2%
Al_2O_3	12-14%	S	0.9-1.1%
MgO	4-5 %	CaS	-

For proper perspective it must be made clear that copper blast furnace slag paving blocks are preferred to those made from iron blast furnace slag. A maximum of only 4 iron blast furnace plants has been made in commercial production. The output of slag paving blocks started in the copper plant about 60 years ago and today copper slags furnish probably 90% of the total production. The copper slag is said to make a brick that is better crystallized and has better friction properties. The analyses of the copper is as follows:

SiO_2	45-50%	$K_2O + Na_2O$	3-5 %
CaO	16-22%	FeO	3-5 %
Al_2O_3	16-19%	S	0.2-0.3%
MgO	6-9 %	MnO	0.2-0.3%

CRUSHED SLAG

Slag for crushing may be solidified in the ladle, or poured into a deep pit from which it is recovered with a power shovel, but in Germany it is usually cooled in shallow pits, up to 35 cm deep, after which it is broken up with picks and bars and sent to the crushing plant.

Crushing slag is cooled slowly to allow crystallization to progress as far as possible and develop strength. Not more than 5% of glassy constituent is desirable.

Dense slag is preferred to excessively porous material. The average weight per cubic meter for slag sized from 30 to 60 mm is said to be about 1250 kilograms.

The p value of crushing slag preferably is from 1.0-1.3% for maximum stability. Actually other basic slags are also used and the principle concern is to avoid using slags that will give trouble from lime decomposition. To predict a slag's performance freshly broken pieces are put under an ultraviolet light. Under this light the bad slags show various single or nested, large or small fluorescent spots of yellow, bronze, or cinnamon color. Good slags have violet tints or show only a few or small fluorescent points and those evenly distributed.

Iron decomposition is estimated by observation of the decomposition of 10 pieces of freshly broken slag immersed in water for a few days. Breakdown usually will be apparent in 4 hours. It is said that slags having over 3% FeO and 1.5% S often will disintegrate. Immersion in water is required for proof. Under 1.5% FeO and 0.5% S no iron disintegration is found.

For determination of the degree of crystallization the sample should be examined under a petrographic microscope. Figures 5, 6, and 7 show the appearance of slags in thin sections under the microscope. Figure 5 is fully crystallized by slow cooling, Figure 6 is glassy from quick cooling, and Figure 7 is the partial crystallization of chilling the surface of a molten slag.

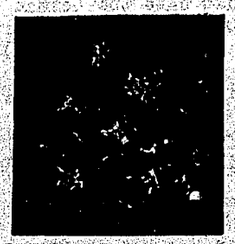

Figure 5

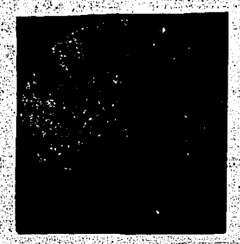

Figure 6

Figure 7

In addition to selling crushed slag in a variety of sizes some companies have plants to make tar mixes. These units are mechanized along lines common in the United States.

FERTILIZER SLAG

As in the United States, blast furnace slag has made comparatively little progress in the fertilizer market.

About 15 years ago there was a considerable interest in ground slag as a substitute for lime. Research, particularly by Dr. Hubert Kappen at Bonn University, showed that slag has many beneficial properties. In addition to lime value, slags have varying amounts of minor elements that are necessary for plant growth.

These points have been widely publicized but in the face of competition from lime and other fertilizers promotion of sales has been unsuccessful. Although advocates point to the virtues of blast furnace slag, there has not yet been accumulated a sufficient body of evidence to convince the consumer that he should buy for quality reasons. Nor can slag be offered at a sufficiently low price to undersell its competition. Grinding costs are relatively high.

An outline of recommended practice follows:

1. Fertilizer slag must be sold only under the name "Huttenkalk" (blast furnace lime).

2. The chemical analysis must have a total of 42% of basic elements expressed as CaO. In calculating this lime figure the MgO must be considered as molecularly equivalent to CaO and so the MgO content is added to the CaO content. Slags that contain less than 42% of basic elements (CaO plus MgO) should not be sold as fertilizer according to the standard specifications of the German Farming Control Committee, which established a minimum of 75% for the $CaCO_3$ content of ordinary lime.

3. The particle size of the slag should correspond to that of ground limestone used for fertilizer. That is, 80% must pass the German Industry Standard Sieve No. 20 (0.3 mm opening, and 400 meshes per sq.cm.), and all should pass the No. 6 screen (1 mm opening and 36 mesh per sq.cm.).

4. Content of calcium sulfide in the fertilizer should not exceed 5%.

5. Mixture of ground slag with other fertilizer materials is not permitted.

GRANULATED AND FOAMED SLAG

Substantial quantities of slag are expanded for use in light weight construction and for the manufacture of cement.

Raw Materials: For cement production the hydraulic high calcium slags are best. For use in light weight concrete insulation, or bonded brick and block the "long" slags from p = 1.0-1.3 are preferable, but in practice others are also used. Most commercial slags can be foamed if the temperature is high enough, but a slag with over 50% CaO is likely to be too "short". The following table shows some compositions of foamed slag:

SiO_2	38.4	29.9	33.8	30.7
CaO	43.1	44.8	43.0	38.7
MgO	4.6	6.7	7.1	10.4
Al_2O_3	9.6	14.4	11.8	11.8
FeO	0.4	0.3	0.3	0.5
MnO	0.3	1.0	0.5	2.8
CaS	2.7	3.5	3.2	5.6

The foaming properties of a slag depend principally on its temperature and chemical composition. The temperature should be high. Condition of a slag is judged by the furnaceman by the length of a string that will form from the slag test ladle - a long string indicates that it will foam well. The high silica slags are easiest to foam.

Three ways of testing the foamability of a slag are as follows:

a) Bucket test: A common bucket is filled with water to a depth of 8-10 cm, and on this water is poured slowly half the contents of a slag test ladle. If, when the slag strikes the water, it immediately forms a great deal of light foam it can be classified as easily foamable. On the other hand, even though it sinks immediately it probably still can be foamed and should be tested by methods "b" and "c".

b) Ladle test: A slag ladle (25-30 cm diameter, 10-12 cm deep) is filled with 5 cm of water or wet sand. If sand and water are used, 2 mm of water should be covering the sand. Slag is then poured from another ladle into the water. This method is more sensitive than "a" and indicates the slags that give a heavy foam.

c) A semi-commercial test of performance can be obtained with a small version (about 1½ meters long) of the chute shown in Figure 8. This method permits the expansion of slags that are not easy to foam.

Production: Granulated and foamed slag are produced in several ways.

Most slag is granulated by running it through a chute to which a small amount of water is fed, into a pond in which the slag is immersed. From this pond the granulated material is recovered with a clamshell and is then ready for use.

The same type of simple chute (see Figure 8) may be used to make foamed slag by carefully controlling the amount of water released into the chute and catching the foamed product in a receptacle or on the ground. An improved version of this chute has a curved end that conducts the excess water running along the bottom away from the line of fall of the slag. The water can then be caught and carried away from the pile of slag product. (see Figure 9).

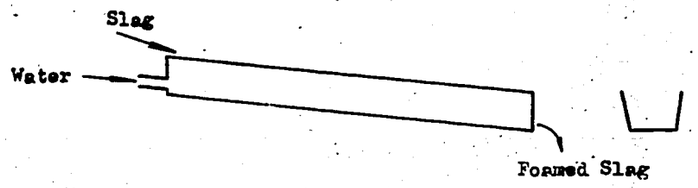

Figure 8. Slag Foaming Chute

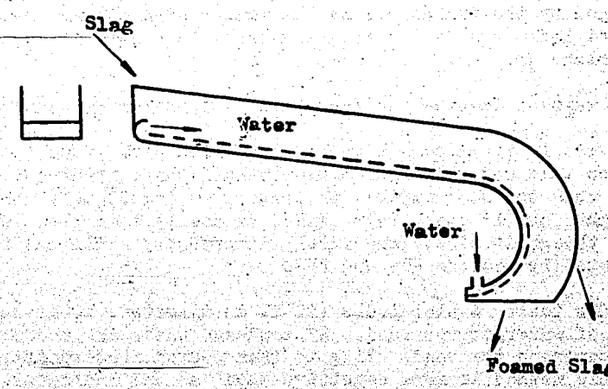

Figure 9. Slag Foaming Chute - designed to carry excess water away from product.

A commonly used method of foaming is with the slag wheel, which is essentially a rotating trough. As shown in Figure 10 it is designed to make a separation of product and excess water. A variation of the slag wheel is one having cups into which the slag and water are fed. As the wheel revolves the foam forms and is dumped out (Figure 11).

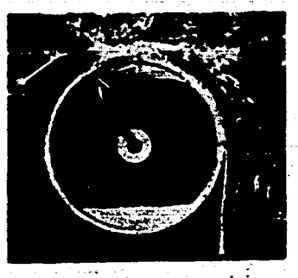

Figure 10. Slag Wheel

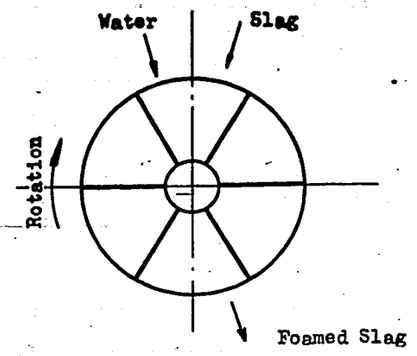

Figure 11. Slag Wheel With Deep Cups

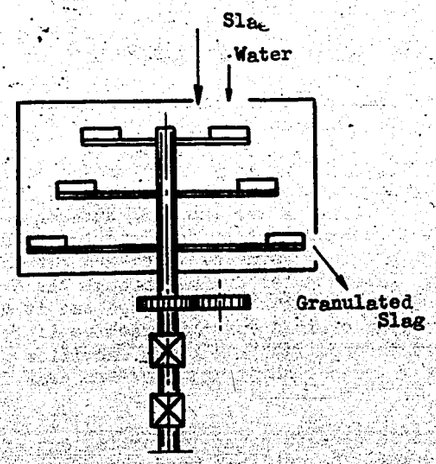

Figure 12. Opterbeck Granulating Mill

The Opterbeck mill is used at the Schalke plant of Deutsche Eisenwerke. It has circular plates, carrying radial bars, mounted on a central rotating shaft as shown in Figure 11. The slag and water enter the top of the mill, and as it passes through the mill to the discharge the slag is granulated.

The Buderus trommel is used at Wetzlar. This machine is unique in that it granulates with a blast of air and moisture somewhat in the same way slag wool is produced. Comparatively little wool is formed because the air and water blast cools the drops rapidly. However, the slag is still sticky when it falls in the trommel and lumps form. These lumps break up by falling from lifters and the product passes through the holes (about 6 cm in diameter) of a punched plate screen mounted on the discharge end of the trommel. A water spray plays on the outside of the shell. Figure 13 shows this machine. It is about 2½ meters in diameter and 14 meters long.

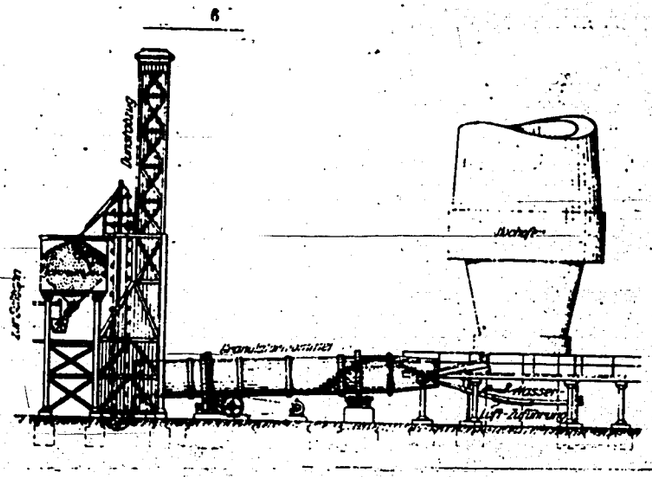

Figure 13. Buderus Trommel

Another unique type of foaming machine is shown in Figure 14. This is said to be used at Trzynietz, Poland. After the slag strikes a bed of water and sand at the feed end it foams and is carried along to the discharge by the screw conveyor. A high pressure spray of water and air cools the product as it is conveyed along. Excess water drains through the 5 mm holes in the perforated bottom of the trough. At the discharge end is a crusher made of bars. The main advantage claimed for this machine is that it will produce a relatively dry crushed product with a minimum sacrifice of space. The product is discharged only 1 meter lower and 4 meters away from the point the slag enters.

It is said to be difficult to operate owing to burning out of the feed end of the screw conveyor. However, the unit has been used for several years so apparently the difficulties are not insurmountable.

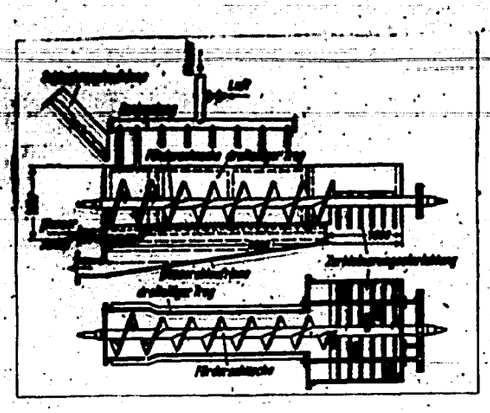

Figure 14. Foaming Machine used at Trzynietz

Products: In addition to its use in cement production granulated slag may be mixed with ground slag, lime or cement and formed into "Huttensteine" building brick or block.

In Germany, granulated slag is bonded by ground slag in a few plants but usually it is bonded by 6-8% of burned lime. The slag is mixed with the lime in a paddle flight mixer, aged for a day, conditioned in a mixer with 12-15% water, and formed into bricks with an hydraulic press. The green brick is hardened simply by storing in the open air for 3 to 6 weeks.

Foamed slag may be crushed in a roll set at 20 mm opening and screened to the desired sizes. A typical separation is as follows:

(a) 12-20 mm
(b) 3-12 mm
(c) 0- 3 mm

(c) is sometimes rescreened as follows:

(1) 0-¼ mm (proposed for use as fertilizer slag)
(2) ¼-1½ mm (for plaster sand)
(3) 1½-3 mm (for loose wall fill)

If good strong foamed slag is used the brickmaker adds only about 10% of cement as a bond but if the slag is relatively weak it may be necessar to add 16% of cement. This foamed slag brick and block is also formed in an hydraulic press but at somewhat lower pressures.

In addition to its use in bonded building brick, crushed foam slag is used as a concrete aggregate, plaster sand, in loose form as a heat and sound insulator, and for fertilizer.

BLAST FURNACE CEMENTS

General: In the past 20 years probably more research and promotion has gone into the use of slags in cement manufacture than into any other slag product. This work continued through the war and is active on a reduced scale today.

Two laboratories, Forschunginstitut der Hüttenzement Industrie and Forschunginstitut des Vereins Deutscher Eisenportlandzement Werke have been particularly active in this work. They were both located in Düsseldorf. During the war their laboratories were so badly damaged that they have been consolidated into a single institution named Forshunginstitut der Hüttenzement Industrie.

A measure of success is shown in the production figures of the German cement industry. In the past 20 years slag cement has gained an increasing proportion of the total cement market. In that period the slag cements have increased from 10% to approximately a third of the total cement output. Improvement in quality is shown by the compressive strength average; in 1916 it was about 280 kg per cm^2 after 28 days, whereas in 1935 it had increased to 500 kg per cm^2.

Slags are used today in the manufacture of cements in two ways: They can serve as one of the constituents that are burned in the manufacture of portland cement clinker and they are ground with portland cement clinker in varying proportions to produce Eisenportlandzement and Hochofenzement, which are grouped under the term "Hüttenzement". In the production of Hüttenzement the manufacturer takes advantage of the cementing properties of slag itself. These hydraulic properties are not impressive when slag is used as a cement alone but if it reacts with other compounds, such as lime or cement clinker, great strengths are attained. A surprisingly high percentage of slag can be added in the production of such a product. In exceptional cases, where a very hydraulic slag is used, as much as 85% of the final cement product can be slag.

Eisenportlandzement may have up to 30% of slag admixed and usually is close to that figure. On the other hand, Hochofenzement has a much more variable formula owing to differences in the hydraulic properties of the various slags. The following table outlines the makeup of these cements:

Constitution of Slag Cements

	Eisenportlandzement	Hochofenzement
Portland cement clinker	67-70%	31-85%
Slag	27-30%	15-69%
Gypsum	3-5%	3-5%

Probably on the average, 50 to 60% of slag is ground with clinker in making Hochofenzement.

A typical cement plant using slag as a principal constituent could be described somewhat as follows: Hot slag from the blast furnace is granulated by immersion in water, being run through an Opterbeck granulating mill, or through a Buderus trommel. This treatment is for the purpose of freezing the slag so quickly that it remains glassy and retains maximum hydraulic properties. The granulated slag is then taken to the feed end of the portland cement plant. Here slag and limestone are dried and ground in ball mills and fed into a rotary kiln. Ordinarily, to one part of blast furnace slag is added about 1.4 parts of limestone in the production of the portland cement. The final product is then made by adding the proper proportion of slag to portland cement clinker and gypsum and grinding them together to the desired particle size in a ball mill. The Hüttenzements are ground to pass at least 95% through a 4900 mesh per cm^2 screen, whereas portlands may have 12% retained on the 4900. A flow sheet of a German cement plant is shown in Figure 15, page 16.

Properties: The properties of the slag cements are somewhat different from those of portland cement. As shown in Figure 16, page 17, portland cement develops strength more quickly but over a period of time blast furnace cement attains equal strength. The blast furnace slag cements are accepted now on an equal basis with portland cement in the construction industry of Germany.

One advantage of the slag cements is that they release their heat more slowly than does portland cement, therefore they are of particular value in the construction of mass concrete structures. The CaO content of blast furnace cement should be kept under 55% to assure retention of this heat release advantage. Figure 17, page 18, shows heat characteristics of slag cements.

Another advantage of blast furnace cements is their resistance to salt water. As is shown in Figure 18, page 19, resistance to $MgSO_4$ increases directly with the percentage of slag contained in the cement.

However, the principal advantage of the slag cements is their low fuel consumption. It has been estimated that the slag cements require only about 45% as much coal as does portland cement and that the heat savings were even greater than this figure indicates if slag is credited with waste energy recovered in its processing. It is this advantage that has made the production of blast furnace cements financially attractive to the manufacturer. The cost advantages have enabled producers to undersell portland consistently. After November 1, 1936, the comparable prices of the three types of cement were as follows:

Portland cement	34.6	marks per ton
Eisenportland cement	33.3	" " "
Hochofen cement	32.0	" " "

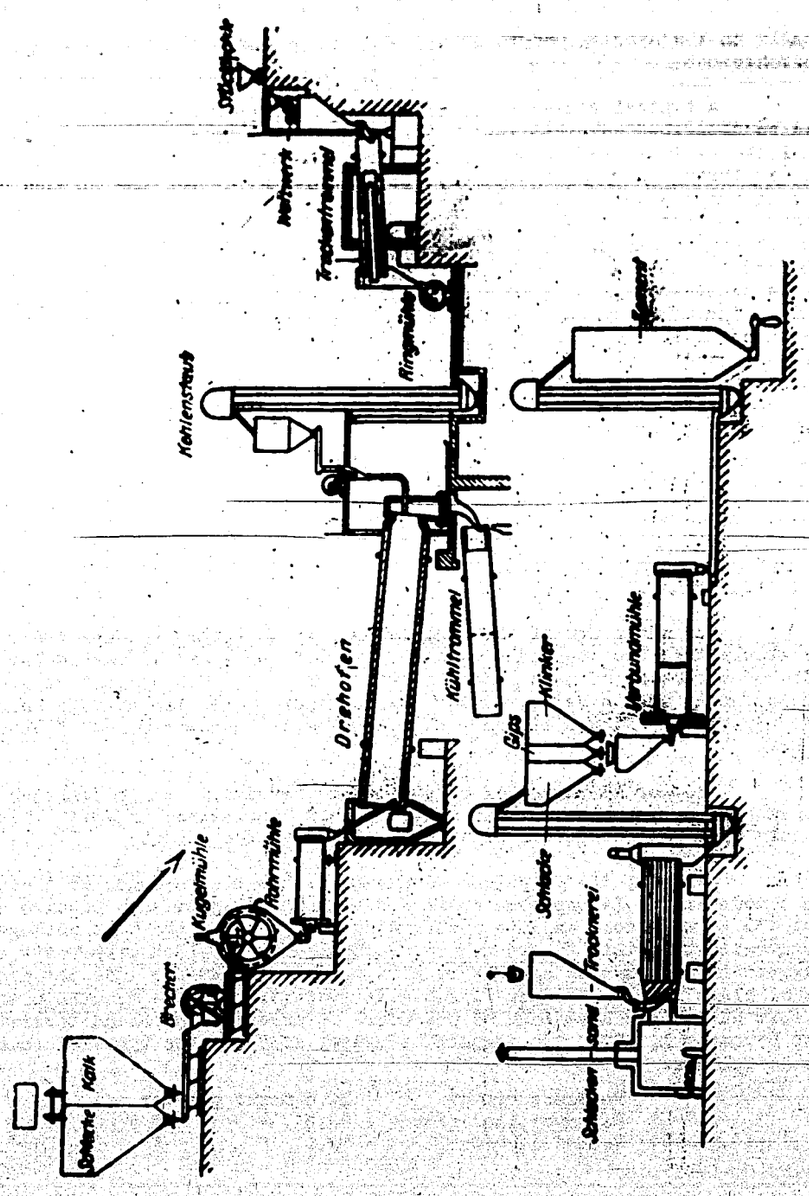

Figure 15. Production of Blast Furnace Cement

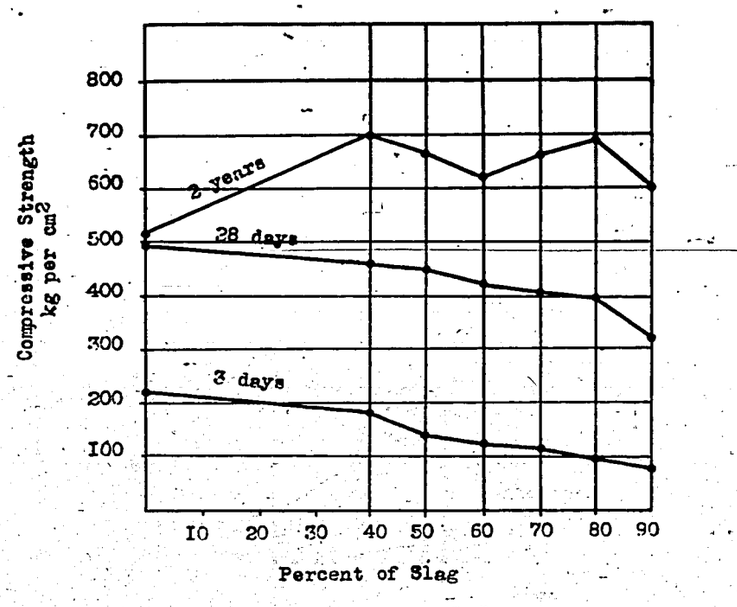

Figure 16. Development of strength of portland cement and blast furnace cements containing various percentages of slag.

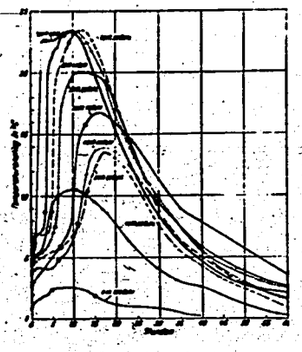

Figure 17. Release of heat by various mixtures of portland cement clinker and slag.

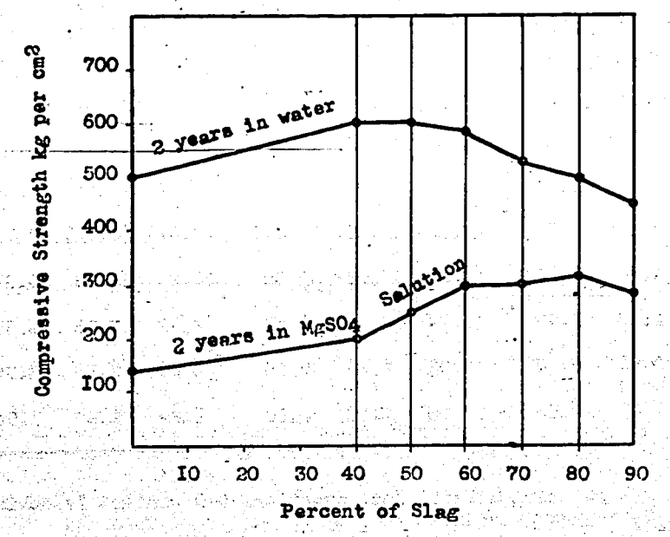

Figure 18. Strength of portland cement and various blast furnace cements exposed to $MgSO_4$ solution for 2 years compared with normal exposure in water.

As a means of revealing the properties required of a slag that is to be used in cement a review of German experience is of some interest.

The first consideration is chemical constitution. The following table shows the average analyses of the constituents and of blast furnace cement during recent years:

Chemical Analyses of Clinker, Slag and Blast Furnace Cement

	Portland Cement Clinker			Blast Furnace Slag			Blast Furnace Cement		
	1942	1943	10 Yr. Avg.	1942	1943	10 Yr. Avg.	1942	1943	10 Yr. Avg.
SiO_2	21.17	20.78	20.81	34.54	33.82	33.95	28.04	27.31	27.95
Al_2O_3	7.72	7.74	7.01	13.56	13.85	13.42	10.29	11.25	10.60
Fe_2O_3	2.57	2.48	2.84	0.86	1.02	0.84	1.54	1.64	1.66
Mn_2O_3(MnO)	0.50	0.38	0.49	(0.51)	(0.58)	(0.80)	(0.67)	(0.71)	(0.71)
CaO	63.93	64.79	65.05	42.31	43.06	42.65	50.61	50.06	50.27
MgO	3.08	2.86	2.79	4.74	4.25	4.59	3.92	3.96	3.89
$CaSO_4$	0.96	0.90	0.93	0.23	0.16	0.25	3.04	3.18	2.96
CaS	0.07	0.07	0.08	3.25	3.26	3.50	1.89	1.89	1.96

As a general principle the highest practical CaO content is desirable. Also high Al_2O_3 is very good.

In 1942 a review of methods recommended for the evaluation of cement slags was published. The following is abstracted from it.

Commercial slags have some differences in properties that are due not so much to the techniques of handling the slag as they are to the type of iron that is being produced and the ores available. Even assuming the same or similar chemical composition these properties will vary according to the following.

Raw Iron

	Hot Blown (produces water granulated cement slags with the following properties)	Cold Blown
1.	light color	dark color
2.	foamy	grainy
3.	low weight per liter	higher weight per liter
4.	water rich	water poor
5.	easy grinding	hard grinding
6.	more hydraulic	less hydraulic

Unfortunately it is impossible for a single slag to have all the properties desired by the cement industry. If it is low in water content then it is hard to grind and less hydraulic than it should be, whereas if it has good hydraulic properties and is easily ground, it is difficult to dry because of the high water content. However, as a general principle if a slag with the best chemical properties is desired one should be chosen that is easily grindable, high in water and highly hydraulic, and make proper provisions for drying it.

For evaluation of the more or less moist cement slags of the trade the following three properties must be considered:

(a) content of water
(b) grindability
(c) hydraulic properties

Drying costs are widely variable depending upon the equipment and heat sources available. In well equipped cement plants where drying equipment is part of a well integrated operation and waste gases are available the cost is very low, but if the slag must be brought to a special drying plant and handled two or three times drying costs rise considerably. As evaluation of the water content depends as much on other considerations as it does on the amount of water to be evaporated, the limiting percentage tolerable is an economic problem peculiar to the individual plant.

According to Mussgnug, grinding resistance usually rises with the weight per liter of granulated slag. Experiments have shown that this test is relatively accurate particularly if the liter weight is determined after vibrating the sample. He divides the slag sands into three groups as follows:

Grindability	Liter weight (run in)
easy	less than 0.6 kg per liter
medium	0.6-1.2 kg per liter
difficult	greater than 1.3 kg per liter

Easy grindable slags are rare and most of the presently used cement slags belong to the middle group. The easily grindable slags have the advantage of low grinding cost. However, they retain much more water and this somewhat counterbalances their cost advantage.

It is believed that it is now possible to fairly well evaluate the hydraulic properties of slag. It has been known for some time that hydraulic properties depend largely on chemical composition. Based on past experiences the following formula is a useful indicator:

$$F = \frac{CaO + CaS + \frac{1}{3} MgO + Al_2O_3}{SiO_2 + MnO} \quad \text{or}$$

$$= \frac{CaO + \frac{1}{3} S + \frac{1}{3} MgO + Al_2O_3}{SiO_2 + MnO}$$

The final determination of hydraulic value entails the use of laboratory experiments but, as will be shown, there seems to be good correlation between the F value and strength developed. F values of 1.5 or over are preferred for cement.

Unfortunately there are so many variables that it is very difficult to develop a laboratory technique that will enable the experimentor to obtain characteristic or perfectly reproducible values. The order of magnitude of the figures obtained depends on such factors as the type of activating compound (chalk, gypsum, or clinker) that is used. Fineness of grinding and the procedure and time of storing and treating the test bodies has a strong effect on the figures obtained.

There follows a description of a test method that has been proposed as a means of physically determining hydraulic value. First, it is necessary to grind to the same fineness (25% residue on the 10,000-mesh sieve, corresponding to 7 to 9% on the 4900-mesh sieve) properly chosen samples of portland cement, clinker, slag, gypsum and silica sand. Then the strength of a mixture of about 25% portland cement and 75% slag is determined. (The proper quantity of gypsum to add is controversial. In these tests from 2 to 4% was used to allow each sample to develop its greatest strength). Next, the strength of a mixture of the same proportion of portland cement and silica sand is determined, and finally the strength of pure portland cement. These values reveal the hydraulic properties of the slag owing to the fact that strengths of the silica sand mixtures decline at an almost linear rate with increasing quantity of sand. For each mixture three values are obtained:

- k strength of the pure clinker without slag (value 100)
- h strength of a mixture of clinker and slag
- s strength of a mixture of same parts of clinker and standard sand (value 0).

Then: $\left[\frac{h - s}{k - s}\right] \times 100$ = a value (or valence number) indicating the degree of reaction of the slag greater than that between the portland cement and the standard silica sand. It must be conceded that such a method is not perfectly exact. However, despite the lack of precision useful figures are obtainable.

Figure 19, page 23, shows the chemical composition of certain tested cement slags.

Figure 19: Chemical analysis of various slags and pumice used in the experiment

	Basic granulated blast furnace slag					Acid granulated blast furnace slag		Stuck-schlacke	Rann-schlacke	Pumice	
	a	aa	f	k	b	kx	b	m	p	A	
SiO_2	33.54	31.49	30.42	34.89	35.84	41.36	41.03	39.29	57.38	55.97	
Al_2O_3	14.41	16.65	15.68	7.89	8.98	13.31	24.73	12.09	14.75	16.08	
TiO_2	0.28	0.44	0.88	0.46	0.33	0.70	2.24	2.31	1.11	1.10	
FeO	0.23	0.56	1.33	0.81	0.40	3.07	3.93	7.89	7.68	-	
MnO	0.56	0.37	4.57	0.73	0.52	0.93	1.39	0.90	0.32	0.26	
CaO	46.03	43.64	40.64	48.69	48.51	34.56	16.64	22.87	8.91	2.46	
MgO	4.35	4.15	4.72	2.51	2.58	3.44	5.93	9.77	4.04	1.53	
BaO	0.26	0.24	0.21	0.24	0.21	0.18	Trace	Trace	Trace	Trace	
Na_2O	0.23	0.29	0.76	0.98	0.61	0.57	2.19	2.33	0.67	5.10	
K_2O	0.45	0.84	0.27	0.78	0.81	0.88	1.24	1.24	3.01	3.97	
SO_3	0.00	0.02	0.02	0.07	0.05	0.09	0.00	0.00	0.00	0.00	
S	2.02	1.10	0.73	1.75	2.36	0.60	0.60	0.46	0.08	0.00	
H_2O	0.26	0.51	0.23	0.95	0.39	0.31	0.22	1.14	0.00	0.24	
CO_2	-	-	-	-	-	0.20	0.00	0.00	0.00	0.25	
C	-	-	-	-	-	-	-	-		-	
F-Value	1.9	2.0	1.7	1.6	1.6	1.2	1.1	1.0	0.45	0.34	

Figure 20 shows how the valence numbers of three different cement slags decline in the 28 day test, with the increase in slag content. However, slag cements increase in strength as time goes on. Figure 20 also shows this increase over the brief interval of 7 and 28 days.

Figure 20. Changes in valence numbers with increase in slag content.

	Valence numbers corresponding to:											
	Compressive Strength						Bending Strength					
	7 days			28 days			7 days			28 days		
Slag content	45	60	75	45	60	75	45	60	75	45	60	75
Slag hh	56	46	48	81	69	56	53	40	44	60	66	58
Slag k	51	43	36	49	39	32	53	44	47	67	56	56
Slag g	34	27	22	49	37	29	37	32	25	33	37	31

Figure 21 shows figures for basic slags, two very strong acid slags, a crystallized slag, a slag from a low iron ore process and pumicite. The figures are for a proportion of clinker to cement of 25 to 75. These show that the strength of slag cements increases greatly between the 28th and 90th day and that basic slag sands have considerably better hydraulic properties than acid ones. The acid crystallized slag acts almost in the same way as standard silica sand. It is interesting to note that even some of the SiO_2 rich substances such as the acid slags and the Rennschlacke show great increases in strength with the passage of time.

Figure 21. Valence figures for various slags and pumice (avg. value of compressive and bending strength) (Ratio of portland cement clinker to slag = 25:75)

	F Number	7 days		28 days		90 days	
Basic slag							
hh	2.0	46		57		94	
e	1.9	57	(72)	66	(86)	92	(97)
g	1.7	24		30		82	
k	1.6	42		44		71	
t	1.6	33	(40)	32	(68)	49	(88)
Acid slag							
te	1.2	-	(14)	11	(36)	30	(52)
mx	1.0	-	(13)	5	(23)	22	(33)
Stückschlacke	-	-	(2)	-	(2)	-	(7)
Rennschlacke	-	-	(5)	-	(15)	16	(52)
Pumice	-	5)	(25)	19)	(25)	24)	(24)

Figure 23 shows the performance of the various tests graphically. Valence numbers for the bending tests are higher than those of compressive strength. The curves of those materials that were selected for regrinding show that the bending strength has increased greatly as compared with clinker ground to the same fineness. As shown in Figure 21 there is a good correlation between hydraulic values and F figures.

This test also showed that the blast furnace cements made from the slags that had good hydraulic properties developed strength more slowly than portland cement but that they reach strengths comparable to portland cement as time goes on. In this case for example, the blast furnace cement had approximately 50% as much strength as portland cement after 7 days, about two-thirds as much after 28 days, and after 90 days was virtually as strong.

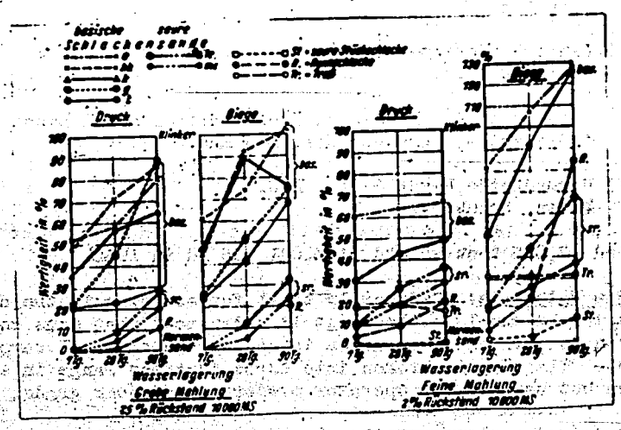

Figure 22. Valence figures for mixtures of portland cement with slags and pumice at 7, 28, and 90 days for two grinding specifications. Ratio of mixtures same as for Figure 20.

It is important to remember that all the above value figures were obtained with samples that had been ground to equal fineness. In commercial practice blast furnace cement is commonly ground slightly finer than is portland cement.

The author, Dr. Keil, warns that the test method he presents is admittedly based on a comparatively small amount of experimental data, and suggests that it should be substantiated by further investigation.

SLAG WOOL

Slag wool production in Germany is well established but has not reached the state of development that it has in the United States. Wool is produced by the following companies:

1) Deutsche Eisenwerke A.G., Schalker Verein, Gelsenkirchen

2) Concordiahütte G.m.b.H., Engers (Rhein), Postfach 15

3) Isola-Mineralwolle-Werke Wilhelm-Zimmermann, Kasslinghausen

4) Isola-Mineralwolle-Werke, Gleiwitz

5) Deutsche Patent-Warmeschutz A.G., Haigerer Hütte, Haiger/Dillkr.

6) Emser Mineralwollwerk u. Isoliermittelfabrik Linde & Dreisbach, Fachbach über Bad Ems

7) Hermannhütte Heyde & Co., K.G. Essen, Schubertstr. 1

Output totaled 80,035 tons valued at 5,041,906 RM in 1942.

Raw Materials: Ordinarily blast furnace slag is the only raw material fed to the cupola although it is understood that some companies have added limestone or silica on occasion to adjust the chemical composition of their product. The slag is broken into lumps that may range in size as widely as 3 to 20 cm but usually the operator prefers a narrower grade.

Chemical analyses of the slag used at two plants is as follows:

SiO_2	32.05	35-38
CaO	43.32	up to 42
Al_2O_3	12.15	8 up to 16
FeO	0.91	under 1
MgO	6.09	4 to 6
MnO	1.63	-
S	1.21	1-2
Alkalies	1.66	-
Other	1.06	

In one plant it was observed that they were salvaging their high shot waste wool by feeding it back into the cupola for remelting.

Production: Sized lump slag and coke are fed into a small cupola (for example, 1½ meters diameter by 4 meters high). The slag is melted at about 1400°C, flows out of one or more tap-holes and is blown by steam pressure through a pipe, about 60 cm in diameter by 3 meters long into the wool room.

Waste heat is recovered by preheating the combustion air with a heat exchanger through which the cupola flue gases pass. Even so, fuel efficiencies are not high - from 1 to 1½ tons of slag melted per ton of coke.

Steam pressures of 5 to 9 atmospheres are used in blowing the wool. Both V and U shaped nozzles are used.

Each cupola has two wool rooms. A typical room is 3½ meters wide, 10 meters long, 3 meters high, and has one wall of 6 mesh wire screen. While one room is being filled the other is being emptied by hand labor. Ordinarily wool is blown into a room for about 4 hours until a maximum depth of 1 meter has been accumulated. The best grade of product is recovered from the end most distant from the cupola, and the poorest is nearest. Some rooms have a fluted sheet metal box designed to trap the shot and let only the saleable wool through the flutes.

Three grades of wool are taken from the room. Specifications vary somewhat but ordinarily first quality will have less than 5 or 10% of shot. Second quality may have a shot content as high as 20%, and third quality usually has more than 20%. About 50% of the saleable product will meet first quality specifications, 20% is second quality and 30% is third.

The wool is gathered and sacked or baled as loose wool. Although some special products, such as wire-bound insulating rope and granulated wool are known, the list does not compare with that of American plants. Granulation is used as a means of recovering some value from the highest shot wool that is wasted in some plants. This product is used as an inferior grade of house fill.

APPENDIX I

LIST OF GERMAN PERSONNEL INTERVIEWED

Name	Position	Location
Dr. H. Hoelbe	Commercial Manager, Deutsche Eisenwerke, Werk Schaker Verein	Gelsenkirchen
Dip. Ing. E. Hensgen	Manager of Cement and Slag Wool Departments, Deutsche Eisenwerke, Werk Schaker Verein	"
Dr. Ing. A. Weyel	Director, Mannesmannrohren Werke, abt. Heinrich Bierwes Hutte	Drusburg-Huckingen
Dip. Ing. Kahlhöfer	Plant Superintendent, Mannesmannrohren Werke, abt. Heinrich Bierwes Hutte	" "
Dr. G. Bulle	Director, Gutehoffnungshutte Oberhausen A.G.	Oberhausen
Dr. Ing. W. Harnickell	Gutehoffnungshutte Oberhausen A.G.	"
Mr. Fred Krefting	Plant Manager, Isola Mineralwollwerke	Hasslinghausen, Westf.
Mr. K. P. Harten	Assistant Director, Verein Deutsche Eisenhuttenleute	Dusseldorf-Breitestrasse 27
Dr. K. Thomas	Verein Deutsche Eisenhuttenleute	" "
Dip. Ing. E. Loh	Manager, Blast Furnace, Slag, Foundry or Mining, Coke Oven Departments, Verein Deutsche Eisenhuttenleute	" "
Prof. Dr. R. Grün	Director, Forschunginstitut der Huttenzement Industrie	Eckstrasse 17, Dusseldorf

Name	Position	Location
Dr. F. Keil	Director, Forschunginstitut des Vereins Deutsche Eisenportlandzement Werke	Eckstrasse 17, Dusseldorf
Mr. Carl H. Schol	Carl H. Schol	Allendorf (Dillkreis)
Mr. Emil Hein	Deutsche Patent Warmschutz	Haiger
Dr. Voo:	Buderus'sche Eisenwerke	Wetzlar
Mr. Ketter	Buderus'sche Eisenwerke	"

APPENDIX 8

LIST OF PERSONS VISITED

Name	Location
Deutsche Eisenwerke, Werke Schaker Verein	Gelsenkirchen
Mannesmannrohren Werke, abt. Heinrich Bierwes Hutte	Drusburg-Huckingen
Gutehoffnungshutte Oberhausen A.G.	Oberhausen
Isola Mineralwollwerke	Hasslinghausen, Westf.
Verein Deutsche Eisenhuttenleute	Dusseldorf - Breitestrasse 27
Forschunginstitut der Huttenzement Industrie	Eckstrasse 17, Dusseldorf
Forschunginstitut des Vereins Deutsche Eisenportlandzement Werke	Eckstrasse 17, Dusseldorf
Carl H. Schol	Allendorf (Dillkreis)
Deutsche Patent Warmschutz	Haiger
Budsrus'sche Eisenwerke	Wetzlar

APPENDIX 8

SLAG PROCESSORS

(B indicates blast furnace operation)

B	August Thyssen-Hutte A.G., Duisburg-Hamborn
B	Reichswerke A.G. "Hermann Göring", Luitpoldhütte, Amberg (Opf.)
B	Birlenbacher-Hütte Schleifenbaum & Co. K.G., Geisweid (Kr. Siegen)
B	Bochumer Verein für GuBstahlfabrikation A.G., Bochum
B	Buderus'sche Eisenwerke, Wetzlar, (Leichtbaustoffwerk Oberscheld)
B	Ver.Hüttenwerke Burbach-Eich-Düdelingen A.G., Abt. Burbach, Burbacherhütte, Saarbrucken 5
B	Deutsche Eisenwerke A.G., Mülheim (Ruhr)
B	Deutsche Eisenwerke A.G., Gelsenkirchen
B	AG der Dillinger Hüttenwerke, Dillingen (Saar)
B	Dortmund-Hoerder-Hüttenverein A.G., Dortmund
B	Duisburger Kupferhütte, Duisburg
B	Eisenwerk-Gesellschaft Maximilianshutte m.b.H., Sulzbach-Rosenberg-Hütte (Opf.)
B	Eisenwerk-Gesellschaft Maximilianshütte m.b.H., Unterwellenborn (Thür.)
B	Gontermann-Peipers, AG. für Walzenguss und Hüttenbetrieb, Siegen
B	Halbergerhütte G.m.b.H., Brebach (Saar)
B	Hoesch Aktiengesellschaft, Dortmund
B	Hüttenwerke Siegerland A.G., Siegen
-	Isola-Mineralwolle-Werke Wilhelm Zimmermann, Hasslinghausen i.W.
B	Ilseder Hütte, Peine
-	Ilseder Schlackenverwertung Dr. Schmidt & Co., GroB-Bülten (Kr. Peine)
-	Klöckner-Werke A.G., Duisburg
B	Klöckner-Werke A.G., Osnabrück
-	Fried. Krupp, GuBstahlfabrik, Essen
B	Fried. Krupp, Friedrich-Alfred-Hütte, Rheinhausen
-	Lehnert & Co. G.m.b.H., Schotterwerk, Neunkirchen (Saar)
-	Mannesmannröhren-Werke, Düsseldorf
B	Mansfeldscher Kupferschieferbergbau A.G., Eisleben
B	Neunkircher Eisenwerk A.G., vorm. Gebr. Stumm, Neunkirchen (Saar)
B	Niederdreisbacherhütte G.m.b.H., Niederdreisbach u. Betzdorf (Sieg)
-	Hub. Optelaak & Sohn, Essen-Bergeborbeck, Hafenstr. 32
-	Raab Karcher G.m.b.H., München 2, Wittelsbacherplatz 4
-	Carl Risch G.m.b.H., Essen, Hügenbergstr. 33, Postfach 430
B	Röchling'sche Eisen- und Stahlwerke G.m.b.H., Völklingen (Saar)
B	Ruhrstahl A.G., (Witten)
-	L. Scheidl & Co., Eschweiler, Jülicherstr. 22
B	Staatl. Muldner Hüttenwerke, Muldenhütten i.Sa
-	Theodor Stephan, Essen, Brahmsstr. 3
-	Wilh. Weber & Co., Dortmund, Albert-Vögler-Str. 5
-	Max Brandus G.m.b.H., Magdeburg-Neustadt, Gröperstr. 2
-	Schlackensteinfabrik L. Trockle, Völklingen (Saar) Wehrden
-	Schlackenstein- u. Kreidswerk, Hoffmann G.m.b.H., Völklingen (Saar)
-	Deutsche Patent-Wärmeschutz A.G., Haigerer Hütte, Haiger (Dillkreis)

-	Norddeutsche Affinerie, Hamburg 36, Alsterstr. 2.
-	Litwinschuh & Bonk O.H.G. Baumaterialien, Gersweiler (Saar)
-	O.f.Z Vereinigte Ost- u. Mitteldeutsche Zement A.G., Oppeln
-	Friedr. Göttel, Mülheim (Ruhr), Holzstr. 17
-	I.G. Farbenindustrie A.G., Z.A.-Büro, Frankfurt (Main) 20, Grünsburgplatz
B	Eisenwerk Sulzau-Werfen, R.u.M. Weinberger, Wien IV/50, Schwindgasse 20
-	Isolo-Mineralwolle-Werke, Gleiwitz O.-S
B	Reichswerke A.G. Alpine Montanbetriebe "Hermann Göring", Wien 15 Friedrichstr. 4
-	Korksteinfabrik A.G., Wien-Mödling 1
-	Ernst Stähler, Siegen, Nordstr. 9, Postfach 243
-	Emser Mineralwollwerk u. Isoliermittelfabrik Linde & Dreisbach, Fachbach über Bad Ems
B	Geisweider Eisenwerke A.G., Geisweid (Kr. Siegen)
B	"Oberhütten" Ver.Oberschl.Hüttenwerke A.G., Gleiwitz O.-S
B	Berg- und Hüttenwerks-Gesellschaft Karwin-Trzynietz A.G. Teschen O.S., Hotzendorf Platz 6
-	"Montadom" Vereinigte Baustoff- und Montagehauswerke G.m.b.H., Kattowitz O.S., Friedrichsplatz 12
B	Konigs- und Bismarckhütte A.G., Werk Bankhütte, Dombrowa, Kr. Bendsburg O.-S
-	A. Jokiel, Kattowitz O.S., August-Schneiderstr. 21
-	Saarländische Teerschotterwerke G.m.b.H., Völklingen (Saar)
-	Steine und Erden G.m.b.H. der Reichswerke "Hermann Göring", Gosler am Harz, Oberer Triftweg 24
B	Eisen- und Stahlwerke Carlshütte G.m.b.H., Diedenhofen (Westmark)
B	Neunkircher Eisenwerk A.G., vorm. Gebr. Stumm, Treuhandschaft Uckingen, Diedenhofen-Uckingen (Westmark)
B	Rombacher Hüttenwerke G.m.b.H., Rombach (Westmark)
B	Klockner-Werke A.G., Eisen- und Stahlwerke Kneuttingen, Kneuttingen (Westmark)
B	Hüttenverwaltung Westmark G.m.b.H. der Reichswerke "Hermann Göring", Hayingen (Westmark)
-	Hermannhütte Heyde & Co. A.G., Essen, Schubertstr. 1, Postfach 341
-	Unternehmung Vaglio, Montingen-am-Berg (Westmark)
-	K. Reisch, Beuthen O.-S., Wilhelmplatz 5
B	Eisenhüttenwerke Rodingen G.m.b.H., Rodingen (Moselland)
B	Differdinger Stahlwerke A.G., Differdingen (Moselland)
B	Arbed Vereinigte Huttenwerke Burbach-Eich-Dudelingen A.G., Zentralverwaltung, Luxemburg
-	Schotteranlagen Felix Cloos, Esch-Alzig, Dicks-Str. 32
-	Angelo Moretti, Baumaterialien, Rodingen (Moselland), Michel Rodange Str. 8
-	Luxemburger Zementwerke A.G., Luxemburg, Königsring 22
-	Obersitzer Schlackenindustrie, Dipl.-Ing. Max Hoge, Obersitz (Kr. Samter), Wronkestr. 1
-	Deutsche Erd- u. Steinwerke G.m.b.H., Hochofenschlackenwerk Linz (Donau)
-	Gesellschaft für TeerstraBenbau m.b.H., Essen, Dreilindenstr. 91
B	Bergbau- und Hütten A.G., Friedrichshütte, Herdorf (Sieg), Kreis Altenkirchen

-	Oberschlesische Kompagesellschaft m.b.H., Kattowitz O.S., Ringstr. 4
B	Hochofenwerk Lübeck A.G., Lübeck-Herrenwyk
B	Stahlwerke Warthenau A.G., Warthenau O.-S., Grenzstr. 88
B	Norddeutsche Hütte A.G., Bremen-Oslebshausen
-	"Termak" Unternehmen für Teerstraßenbau, Kattowitz, Dürerstr. 9

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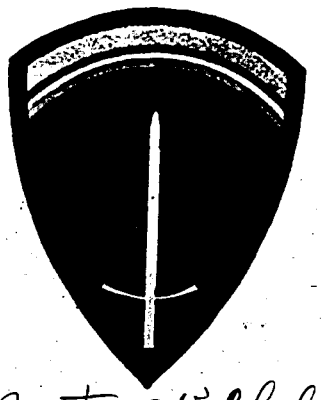
FIAT REPORT NO. 673

THE SELF-IGNITION OF MIXTURES OF HYDROCARBONS AND AIR SUBJECTED TO VERY SUDDEN ADIABATIC COMPRESSION



Joost, Wilhelm

FIELD INFORMATION AGENCY, TECHNICAL (US)

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FIAT REPORT NO. 873 20 SEPTEMBER 1946

THE SELF-IGNITION OF MIXTURES OF HYDROCARBONS AND AIR SUBJECTED TO VERY SUDDEN ADIABATIC COMPRESSION

BY -
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ABSTRACT

The present report describes investigations on the kinetics of oxidation and combustion of hydrocarbons carried on to explain the reactions causing "engine knock". The experiments consisted of the very sudden adiabatic compression of mixtures of heptane and air and disclose the occurrence of a chain reaction followed by a not clearly defined secondary reaction.

BIOGRAPHICAL NOTE

Professor Wilhelm Jost studied physical chemistry at Halle and Munich, was assistant to Professor Bodenstein at Berlin University, Rockefeller Research Fellow at Massachusetts Institute of Technology, and taught at Hannover and Leipzig. He has been Professor of Physical Chemistry at Marburg since the winter of 1943. He has worked on the kinetics of explosion and combustion processes on which he published "Explosions- und Verbrennungsvorgänge in Gasen", Springer-Verlag, Berlin 1939.

Die Selbstzündungsreaktion von Kohlenwasserstoffen bei kurzen Induktionszeiten

Von W. Jost

In einer Apparatur, in welcher gasförmige Gemische von verschiedenen Anfangsdrucken und Anfangstemperaturen aus schnell adiabatisch komprimiert werden konnten, und an deren Entwicklung besonders die Herren v. Müffling, Rögener, Rohrmann, Teichmann, v. Weber beteiligt waren, wurde von den Herren Rögener und Braesch die Selbstzündungsreaktion von n-Heptan-Luftmischungen untersucht, durch Aufnahme des Druck-Zeitverlaufs mittels Piezo-Quarz und Elektronenstrahl-Oszillograph. [1])

Diese Versuche meiner früheren Mitarbeiter lassen einen charakteristischen zweistufigen Verlauf der Zündung erkennen, wie er an sich bei niederen Drucken und längeren Induktionszeiten bekannt ist, und wie er für kurze Induktionszeiten zuerst von Rögener und v. Weber aus Ionisationsmessungen erschlossen wurde. [2])

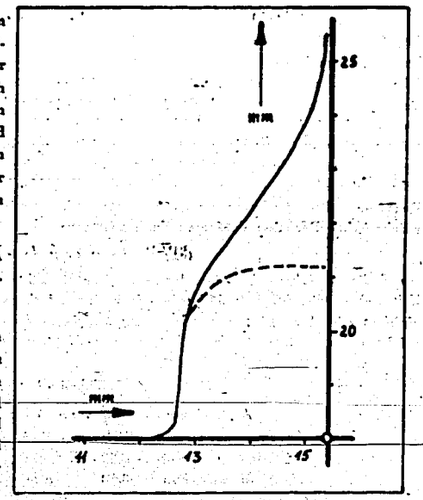

Abb. 1

Es wurden die Aufnahmen A bis I von Rögener-Braesch von Januar 1944 ausgewertet.

Die Aufnahmen A bis E zeigen einen typischen Druckverlauf, wie im Masstab 10:1 in der Abb. 1 nach Aufnahme C 1 für den letzten Teil wiedergegeben ist (der erste Teil verläuft gradlinig). Es folgen zwei Induktionsperioden einander, der Druck-Zeitverlauf weist zwei Wendepunkte auf, die daraus als dp/dt entnommene Reaktionsgeschwindigkeit würde zwei Extrema, erst ein Maximum und dann ein Minimum zeigen.

[1]) Die Apparatur, bei der es hauptsächlich darauf ankam, gleichzeitig grosse Kompressionsgeschwindigkeiten zu erreichen und störende Erschütterungen zu vermeiden, wird an anderer Stelle zu beschreiben sein.

[2]) z. B. E. A. Andreew, Acta Physicochimica URSS 6 (1937) 57; B. V. Aivazow und M. B. Neumann, Acta Physicochimica URSS 6 (1937) 278.

Die zweite Induktionsperiode, von dem ersten Wendepunkt bis zum Schluss (d. h. dem Zeitpunkt unmessbar schnellen Druckanstiegs) gerechnet, macht etwa 1/6 (C 1), 1/5 (A 2), 1/4 (B 1), bis fast 1/3 (E 1) der gesamten Induktionszeit aus, was in allen Fällen für die zweite Induktionszeit Werte von $\tau_2 = 0{,}0006$ sec ergibt.

In den Versuchen F—H ist die zweite Induktionsperiode vielleicht noch eben angedeutet, aber nicht mehr mit Sicherheit zu erkennen, und auf alle Fälle wesentlich kürzer als in den ersten Versuchen (Versuch I 2 zeigt nur die erste Induktionsperiode und keine Zündung). Neben $\log \tau$ wurde in einer nicht mehr in meinem Besitz befindlichen Figur auch $\log \tau_1$ ($\tau_1 + \tau_2 = \tau$) für die Versuche A—E eingetragen; τ_2 beträgt im Mittel etwa $3{,}9 \cdot 10^{-4}$ sec, mit den äussersten Schwankungen 4,55 und 3,35, ein eindeutiger Gang mit der Temperatur ist nicht zu erkennen. Für τ_1 erhält man näherungsweise

$$\text{(A—E)} \qquad \tau_1 \sim 5{,}37 \cdot 10^{-13} \exp\,(33\,600/RT);$$

die Versuchsschwankungen sind nicht unbeträchtlich. Für die Induktionsperiode τ der Versuche F—I (welche bei niedrigerer Anfangstemperatur und dafür höherem Druck ausgeführt sind) erhält man ebenso

$$\text{(F—I)} \qquad \tau \sim 4 \cdot 10^{-17} \exp\,(45\,700/RT).$$

Um festzustellen, ob die erste Induktionsperiode einer Wärmeexplosion zugeordnet werden kann (was nach den Zahlenwerten der Interpolationsformel unwahrscheinlich ist), wurde folgendermassen verfahren. Bis zum Maximum der Reaktionsgeschwindigkeit steigt die Temperatur um weniger als 100° an (insgesamt ist der Temperaturanstieg während der ersten Induktionsperiode vergleichbar mit dem bei kalten Flammen, wo er 100 bis 200° beträgt); bei rund 2000° Temperaturanstieg für vollkommenen Umsatz wäre der Umsatz also nur zu grössenordnungsmässig 10% erfolgt (auf eine zu irgend einer Aldehyd- o. ä. Stufe führende Reaktion bezogen natürlich u. U. mehr). Man wird daher näherungsweise mit einer Reaktion nullter Ordnung zu rechnen versuchen. Für die Erhitzungsgeschwindigkeit bei adiabatischer Reaktion darf man dann ansetzen:

$$dT/dt \sim c \exp\,(-E/RT),$$

wo E die scheinbare Aktivierungsenergie der Reaktion ist. Man kann nun zu verschiedenen Zeitpunkten die Steigung dT/dt aus der Registrierkurve entnehmen und kann diese vergleichen mit den Werten, welche man mit einem vernünftigen Werte von E erhält, beispielsweise etwa 30 000. Man erhält dann z. B. folgendes, Tab. 1:

Tabelle 1

Auswertung von Versuch A 2

t = Zeit vom Ende der Kompression an

Abszisse 1 mm = $2{.}82 \cdot 10^{-4}$ sec
Ordinate 1 mm = 0.90 atm

t (sec)	p (atm)	Steigung α (Grad)	tg α	T(° abs, berechnet a. d. Druckanstieg)
0	15.8	< 2	< 0.035	759° abs
$2.54 \cdot 10^{-3}$	15.8	< 2	< 0.035	759
$2.82 \cdot 10^{-3}$	15.8(+)	7	0.123	759(+)
$3.1 \cdot 10^{-3}$	16.3	18	0.325	783
$3.3 \cdot 10^{-3}$	17.8	85	11.4	855

Bei rein thermischer Reaktion sollten sich die Tangenswerte wie die entsprechenden Exponentialfunktionen der Temperatur verhalten, also:

gefunden < 1 : < 1 : 3.5 : 9.3 : 326
berechnet 1 : 1 : 1 : 1.77 : 9.15

berechnete Werte = exp. (15000/T)

Die gefundenen Werte sind mit keiner vernünftigen Wahl einer Aktivierungsenergie wiederzugeben, selbst bei Annahme einer beträchtlichen Unsicherheit in der Ablesung der Winkel. Nimmt man z. B. an, bei dem dritten Messpunkt habe die Temperatur 10° über der des ersten gelegen, so brauchte man immer noch eine Aktivierungsenergie von 144 kcal, um den beobachteten Geschwindigkeitsanstieg auf das 3,5fache zu erklären. Dazu würden dann ausserdem die folgenden Punkte nicht passen.

Versuch A 1 ist qualitativ analog

Versuch B 1 ergab folgendes: (Tab. 2)

Tabelle 2

Auswertung von Versuch B 1

Abszisse 1 mm = $2.5 \cdot 10^{-4}$ sec
Ordinate 1 mm = 0.9 atm

t (sec)	p (atm)	α (Grad)	tg α	T
0	20.2	< 2	0.035	788° abs
$1.36 \cdot 10^{-3}$	21.7	85	11.4	848

Geschwindigkeitsverhältnis gefunden 1 : > 326
berechnet 1 : 3.78 für
E = 30 000.

Versuch B 2 analog, desgl. Versuch C.

Versuch D ergab Tab. 3:

Tabelle 3

Auswertung von Versuch D

Abszisse 1 mm = $1.64 \cdot 10^{-4}$ sec
Ordinate 1 mm = 0.9 atm

t (sec)	p (atm)	α (Grad)	tg α	T
0	17.5	< 2	0.035	754° abs
$2.6 \cdot 10^{-3}$	19	80	5.7	819

Geschwindigkeitsverhältnis gefunden 1 : > 163
berechnet 1 : 4.93 für
E = 30 000

Tabelle 4

Auswertung von Versuch E

Abszisse 1 mm = $5.27 \cdot 10^{-4}$ sec

Ordinate 1 mm = 0.9 atm

t (sec)	p (atm)	α (Grad)	tg α	T
0	23	< 2	< 0.035	802° abs
$7 \cdot 10^{-4}$	25.3	88	28	882

Geschwindigkeitsverhältnis gefunden 1 : > 800

berechnet 1 : 5.75 für

E = 30 000.

In den Versuchen F bis I ist, wie oben erwähnt, der Druckverlauf ein anderer. Beispielsweise ergab die Auswertung von Versuch G Tab. 5:

Tabelle 5

Auswertung von Versuch G 3

Abszisse 1 mm = $1.89 \cdot 10^{-4}$ sec

Ordinate 1 mm = 0.9 atm

t (sec)	p (atm)	α (Grad)	tg α	T
0	20.6	im Mittel < 2	< 0.035	704° abs
$4.7 \cdot 10^{-3}$	20.6			
$5.31 \cdot 10^{-3}$	21.8	74	3.5	745

Geschwindigkeitsverhältnis gefunden 1 : > 100

berechnet 1 : 3.2 für

E = 30 000.

Versuch I 2 ist nicht zur vollen Zündung gekommen.

Auswertung der zweiten Induktionsperiode

Zur Untersuchung der zweiten Induktionsperiode wurde folgendermassen verfahren In der Abb. 2 wurde die Registrierkurve von Bild C 1 in 10fachem Massstab aufgetragen.

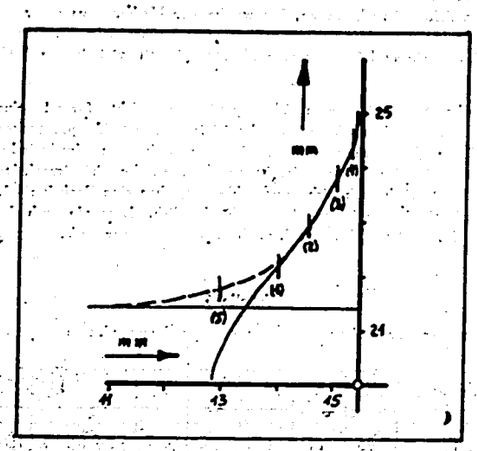

Abb. 2

Für mm 14 (1), 14.5 (2), 15 (3) und 15.3 (4) wurden die Steigungen ausgemessen, ferner wurden aus den registrierten Drucken die Temperaturen entnommen und es wurde dann log tg α gegen 1/T aufgetragen; innerhalb der Grenzen der Versuchsfehler ließ sich durch die Messpunkte eine Gerade ziehen mit der Gleichung:

$$\text{tg } \alpha = 10^{5,4} \exp (-23\,000/RT).$$

Damit wird für (5) 13 mm extrapoliert tg α = 0.33 , α = 18° bei T = 864° abs. Damit wurde graphisch die Kurve 4321 nach rückwärts ergänzt (entsprechend einer Integration), wodurch sich ein hypothetisches Ausgangsniveau ergab, von dem diese zweite Explosion ausgegangen wäre. Andererseits beträgt die tatsächliche Steigung bei (5) 75°, tg α = 3.73; für die tatsächlich beobachtete Umsetzungsgeschwindigkeit müsste daher von der primären Reaktion unter der Voraussetzung der obigen Zerlegung ein Beitrag von tg α = 3,40 entsprechend α = 73,5° übrig bleiben. Unter Benutzung dieses Wertes und des hypothetischen Endniveaus für die Primärreaktion wurde dann die gestrichelte Kurve für den zweiten Teil der Primärreaktion gezeichnet. Wenn auch die Zerlegung nicht willkürfrei ist, so überlegt man sich doch, dass für jeden Verlauf der Sekundärreaktion, welcher nicht in einem Frühstadium einen Wendepunkt des Druckanstiegs liefert, qualitativ die Zerlegung nicht merklich von der gezeichneten abweichen kann.